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Hazardous Materials Control Research Institute

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Hazardous Materials Control Research Institute

Preface

The rigorous control and management of hazardous materials and wastes is an urgent necessity for safeguarding the public health, our environment and natural resources, while at the same time, fostering the continued economic growth of the nation. Since 1980, the Hazardous Materials Control Research Institute has organized an annual conference and exhibition to review, update, and exchange information on the latest research and technical findings from the laboratory, industry, and the field concerning hazardous materials and hazardous waste management. With the cooperation of our affiliates, this annual Superfund Conference and Exhibition has become the most comprehensive gathering and information exchange available on the complex of technical and policy issues that flow from the Superfund program. These proceedings include the most up-to-date technical developments, the impact of federal and state policies as well as the legal, health and economic issues that emanate from the Superfund program.

CERCLA (The Comprehensive Environmental Response Compensation and Liability Act) or "Superfund," as it is now commonly known, was first passed in 1980. This Trust Fund, administered by the U.S. Environmental Protection Agency (EPA), was created to help pay for cleanup of hazardous waste sites that, due to its contents and its terrestrial and/or hydrogeologic setting, threaten the public health or environment.

Under CERCLA, EPA developed a strategy composed of three major elements. The first called for assessing the uncontrolled hazardous waste sites in the Agency's current inventory. Second, those sites which presented an imminent threat to public health or the environment were to be stabilized. Third, using the National Contingency Plan (NCP) for guidance, the NPL sites were ranked to receive priority attention for remedial cleanup action.

The "Superfund" extension, the Superfund Amendments and Reauthorization Act (SARA), signed into law in October 1986, was funded at a level of $9 billion. The extension represented a much increased funding level over the previous five-year period, 1980-1985. A significant portion of these resources will be devoted to remedial construction projects at existing and additionally listed NPL sites.

SARA is designed to achieve greater effectiveness by intensifying all activities under CERCLA and adding more facets to the scope of Superfund activities. Within the total program, SARA stipulates that states will be placed in the implementing role and greater responsibilities will be delegated to the EPA Regional Administrators. Through the implementation of SARA, new sites will be identified and new technologies will be developed and employed. There are now approximately 1,100 sites on the National Priorities List (NPL) plus other sites administered directly by the affected states.

In addition to EPA's program responsibilities, there is now an even larger involvement of other federal agencies concerned with hazardous materials control or cleanup at federal facilities. Chief among them are the Department of Defense and Energy. To gauge the extent of their involvement, EPA is slated to spend approximately $9 billion through 1990, while DOD and DOE have admitted to requiring $120 billion and $170 billion, respectively, over the next 30 years.

This year's *Proceedings* include 192 papers and lecture outlines that emphasize the latest developments and cumulative experiences gained from the spectrum of Superfund activities. This knowledge and experience can serve as an immediate technology transfer for solutions to your areas of concern.

Hal Bernard
Executive Director
HMCRI

Acknowledgement

Glossary of Frequently Used Acronyms

ACS	American Chemical Society
AICE	American Institute of Chemical Engineers
API	American Petroleum Institute
AQCR	Air Quality Control Region
ARAR	Applicable or Relevant and Appropriate Requirement
ATSDR	Agency for Toxic Substances and Disease Registry
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CMA	Chemical Manufacturers Association
COE	U.S. Army Corps of Engineers
CWA	Clean Water Act
DOE	U.S. Department of Energy
DOI	U.S. Department of the Interior
DOT	U.S. Department of Transportation
EDF	Environmental Defense Fund
EMSL	U.S. EPA Environmental Monitoring Systems Laboratory
EPA	U.S. Environmental Protection Agency
FEMA	U.S. Federal Emergency Management Agency
HMCRI	Hazardous Materials Control Research Institute
HMTA	Hazardous Materials Transportation Act
HRS	Hazardous Ranking System
HSWA	Hazardous and Solid Waste Amendments
HWERL	U.S. EPA Hazardous Waste Engineering Research Laboratory
HWTC	Hazardous Waste Treatment Council
LOIS	Loss of Interim Status
LUST	Leaking Underground Storage Tanks
MCL	Maximum Contamination Level
NCP	National Contingency Plan
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanographic and Atmospheric Administration
NPL	National Priorities List
NRDC	National Resources Defense Council
NSWMA	National Solid Waste Management Association
NWA	National Water Alliance
OERR	Office of Emergency and Remedial Response
ORD	Office of Research and Development
OSW	U.S. EPA Office of Solid Waste
OSWER	Office of Solid Waste and Emergency Response
OTA	Office of Technology Assessment
PCB	Polychlorinated biphenyl
PRP	Potentially Responsible Party
RCRA	Resource Conservation and Recovery Act
RI/FS	Remediation Investigation/Feasibility Study
ROD	Record of Decision
SARA	Superfund Amendments and Reauthorization Act of 1986
SITE	Superfund Innovative Technology Evaluation program
TSCA	Toxic Substances Control Act
TSDF	Treatment, Storage, Disposal Facility
TTU	Transportable Treatment Unit
UST	Underground Storage Tank
USWAG	Utility Solid Waste Activities Group

Contents

FATE AND MODELS

HEALTH AND ENDANGERMENT

RISK ASSESSMENT

COST AND ECONOMICS

SAMPLING AND MONITORING

CONTAMINATED GROUNDWATER CONTROL AND WELL TYPES

VOLATILE ORGANICS CONTROL

TREATMENT

SPILLS AND EMERGENCY RESPONSE

Massachusetts' Site Cleanup Cost Recovery Program

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ABSTRACT

This paper discusses Massachusetts' innovative approach for recovering the costs it incurs to clean up sites, including its staff and overhead costs for overseeing PRP actions. On June 9, 1989, the Massachusetts Department of Environmental Protection (DEP) promulgated new cost recovery regulations (310 CMR 40.600) as an amendment to the Massachusetts Contingency Plan (MCP). The new regulations describe how DEP will recover the costs it incurs in performing or arranging for the cleanup of releases of oil and hazardous materials under the authority of the Massachusetts Oil and Hazardous Materials Release Prevention and Response Act (Massachusetts General Laws Chapter 21E).

This paper provides background on the statutory basis for the regulations, summarizes their key provisions and describes changes that the Department has made in its existing cost recovery program to implement them. It explains to whom the regulations apply, how costs are calculated and the challenges DEP has faced in implementing this innovative program.

INTRODUCTION

In March 1983, Massachusetts enacted the Massachusetts Oil and Hazardous Material Release Prevention and Response Act (M.G.L. c.21E). This statute, although similar in many respects to the Federal Superfund law, is broader in scope, regulating not only the cleanup of hazardous wastes covered by the Federal statute, but also the cleanup of oil and other hazardous materials that are not waste products. In November 1986, Massachusetts voters overwhelmingly passed an initiative petition on the ballot commonly referred to as "Question 4." This initiative petition expanded the site cleanup program to incorporate a number of new features including cleanup deadlines, an emphasis on permanent remedies and expanded requirements for public involvement.

Partially as a result of its early enabling legislation and the overwhelming citizen support expressed through passage of Question 4, Massachusetts has one of the most extensive site cleanup programs in the country. As of July 1990, Massachusetts had identified more than 1700 confirmed sites and an additional 2300 locations to be investigated for potential contamination by oil or hazardous materials. Currently, approximately one half of the confirmed sites on the state's list involve only petroleum contamination, often as a result of leaks from underground storage tanks. Massachusetts also actively participates in cleanup activities at the 25 NPL sites located in the state. DEP is particularly proud of its record of involving PRPs in the cleanup process. At over 90⁴ of the confirmed sites, PRPs perform most cleanup activities themselves, subject to DEP's review and oversight .

In 1988, in response to a requirement in M.G.L. c.21E, Massachusetts

promulgated the Massachusetts Contingency Plan (MCP). This document, which is similar in some respects to the NCP, establishes the ground rules for the site cleanup process. Currently, most sites must proceed through a multiphase cleanup process with DEP approvals required at significant decision points.

In June 1989, the Massachusetts Department of Environmental Protection (DEP) promulgated revisions to Subpart F of the Massachusetts Contingency Plan (310 CMR 40.600—Enforcement and Cost Recovery). These revisions contain DEP's interpretation of its statutory authority to recover, pursuant to M.G.L. c.21E, 5a(i), "all costs of assessment, containment and removal that DEP incurs on behalf of the Commonwealth in performing or arranging actions in response to releases or threats of release of oil or hazardous material." The regulations accomplish this purpose by establishing a formula for calculating these costs and a procedure for recovering them through administrative action. They provide a framework for DEP to enhance recovery of "response costs from persons responsible for releases" (Acts of 1983, Ch.7).

The regulations emphasize recovery of the costs DEP incurs in planning, managing and directing (overseeing) response actions that are actually conducted by PRPs. This emphasis, which is an expansion of past DEP cost recovery practices, has resulted in both the new regulations and the program to implement them being commonly referred to as "Oversight Cost Recovery." However, the regulations define recoverable response action costs (hereinafter "costs" or "recoverable costs") as having two components: (1) the costs of direct personnel hours, including the cost of labor and expenses needed to support those hours (so-called oversight costs) and (2) payments made to the Department's agents (contractor costs). Each component is explained in more detail later in this paper. The regulations contain provisions for the recovery of both types of costs through a single action.

The cost recovery regulations promulgated in June 1989 apply to recovery of costs DEP incurs performing or overseeing remedial response actions at disposal sites; provisions for recovery of costs DEP incurs performing or overseeing emergency response actions at spills have been reserved for later promulgation at 310 CMR 40.630. PRPs who qualify for a streamlined agency review process under 310 CMR 40.537, commonly called the "waiver" program, are subject to different cost recovery provisions as long as they comply with the terms and conditions of the waiver program. Applicants for the waiver process pay a one-time charge of $1200 to cover the average costs of agency review and audit of waiver sites.

KEY PROVISIONS OF THE REGULATIONS

As discussed above, response action costs include two major components: (1) personnel costs, often referred to as oversight costs and (2) contractor costs. This portion of the paper explains how the regula-

tions define each of these components and how they are combined to calculate total response action costs.

Oversight Costs

Oversight costs for a particular site are based on DEP's actual costs of supervising response actions at that site. Oversight costs are composed of the costs of direct labor and indirect costs.

The costs of direct labor are the salary-related expenses for DEP staff who plan, manage, direct or perform activities associated with site cleanup. Direct labor hours (which are defined in 310 CMR 40.020) include, for example, time DEP staff spend reviewing reports submitted by PRPs, meeting with PRPs and their representatives and inspecting a site. The costs of these direct hours include each employee's actual hourly salary plus other salary-related costs such as fringe benefits and paid leave (see the definition of hourly rate of compensation in 310 CMR 40.020).

The regulations exclude certain site-specific activities that might otherwise be classified as direct labor from the definition of direct hours. These activities include all time spent on public participation and reviews of preliminary assessments, limited site investigations and site classification reports submitted by PRPs or their agents (except to the extent this review is part of the approval of a short-term measure, i.e., a rapid action to abate or eliminate a release that poses an imminent hazard).

Indirect costs include labor and other expenses needed to support the direct labor described above. Specifically, indirect labor costs include costs for DEP employees such as supervisory, clerical and administrative staff who support direct site-specific activities. Indirect expenses include the portion of DEP's space and equipment rentals, office supplies, telephones, field and laboratory equipment, training expenses, utilities, maintenance and repairs, printing and miscellaneous noncapital expenses that support direct site-specific activities. Only those indirect costs that are closely related to direct labor are recovered.

Indirect costs are allocated to individual sites by using an indirect rate (defined in 310 CMR 40.020). At the end of each fiscal year (which runs from July 1 through June 30), DEP totals its indirect costs (both labor and nonlabor) and its direct hours, based on actual expenses in that fiscal year. DEP then calculates the ratio of its total indirect costs to its total direct hours (310 CMR 40.621(1)). This ratio (called the indirect rate) may be used during the next calendar year to calculate indirect costs for a specific site by multiplying the number of direct hours for that site by the indirect rate (310 CMR 40.620(2)(b)).

Beginning July 1, 1989 and continuing until DEP changes the indirect rate pursuant to 310 CMR 40.621(1), the regulations (310 CMR 40.621(2)) establish an indirect rate of $18.40 per direct hour. DEP developed this rate based on budget and program planning information and on information from its existing fiscal and time tracking systems. If the actual indirect rate for a particular fiscal year is lower than the current rate established under the regulations, DEP must amend the regulations to decrease the indirect rate. If DEP's actual indirect rate for a particular fiscal year is higher than that specified in the regulations, DEP can amend the regulations to increase the rate or continue to use the lower rate already established in regulation.

Contractor Costs

The regulations (310 CMR 40.620(2)(c)) require PRPs to reimburse the Commonwealth for all payments DEP makes to contractors, grantees or agents who perform or oversee response actions at a site. PRPs are not required to reimburse the Commonwealth for any activities performed by contractors, grantees or agents that are excluded from the definition of direct hours (e.g., public participation and reviews of preliminary assessments, limited site investigations and site classifications submitted by PRPs).

Total Costs

DEP uses the following formula to calculate the total response action costs for a site: total response action costs + total costs of direct labor + total indirect costs + total contractor costs.

Total response action costs will vary significantly from site to site. In general, these costs will be higher if the site presents complex assess-

ment and cleanup problems (e.g., it is contaminated with many different substances and/or threatens to contaminate a drinking water supply or other sensitive environmental resource). They also will be higher if PRP submittals are inadequate or incomplete and therefore require substantial DEP review and/or many rounds of revision.

IMPLEMENTATION

DEP has spent considerable effort developing new computer systems and management procedures to implement its cost recovery regulations and training its staff in the use of these new systems and procedures. Much of this effort has focused on the three areas described below:

- Tracking and management of response action costs
- Recovering response action costs from PRPs
- Administrative review of costs disputed by PRPs

Tracking and Management of Response Action Costs

Although DEP has always had procedures for managing its site cleanup activities, the new cost recovery regulations make the Department accountable to the public in a way that few public agencies ever are. DEP believes that it is the only public agency in Massachusetts that effectively "bills its time by the hour" similar to the way that law, engineering and other consulting firms bill for their services. To ensure that its response action costs are fair and reasonable, DEP has revised or developed a number of time-tracking and site management procedures. These procedures include:

- Having employees fill out weekly timesheets that provide a detailed record of the activities they perform
- Having supervisors review these timesheets before the information is entered into the computerized time management system
- Making one person, usually the site manager, responsible for reviewing all recoverable activities performed at each site
- Having the supervisors of site managers review response action costs whenever oversight costs exceed a specified amount

The Department has conducted numerous training sessions and developed guidance manuals to explain these new procedures to its staff and answer any questions they might have.

Several of the new procedures are designed to improve communication among the many DEP programs involved in site cleanup and provide site managers with more information on the activities performed by DEP personnel at their sites. These procedures require site managers to sign off on all recoverable time spent on a site and to document through a work order process any recoverable activities performed by DEP staff outside the Bureau of Waste Site Cleanup.

To support the implementation of its new cost recovery regulations, DEP substantially revised its existing computerized time-tracking system, developed new computerized accounting systems to track all site-specific costs and revised its procedures for updating basic site information.

The revisions to the time-tracking system enable DEP to track time spent on site cleanup in several different ways:

- By the type of activity performed (e.g., report review, meetings with PRPs, enforcement activities, etc.)
- By the DEP Division, Office or individual employee that performed the activity
- By the time period when the activity was performed (week, month, quarter, etc.)
- By the particular site or spill for which the activity was performed
- By the phase the site was in when the activity was performed

The revisions also enable the Department to cross-reference its time-tracking data with payroll information maintained by the State's Personnel/Payroll Management Information System (PMIS). This new reporting flexibility helps insure that salary information used to calculate costs for each employee is accurate and up-to-date and that the employee costs recovered from PRPs have, in fact, been paid by the State.

The new site accounting system allows DEP to calculate total costs for a site, (i.e., to add together all direct labor costs, indirect costs and contractor costs for each site) and to distinguish between those costs

that can be recovered under the provisions of the new regulations and those that cannot.

Although the primary motivation for developing these new systems and features was to implement the oversight regulations, they also enhance DEP's ability to understand and manage its site cleanup program. For the first time, DEP can easily compare information on the time spent on various activities with data on site characteristics. The agency is just beginning to exploit the potential of this management resource to analyze questions such as how much time or money has been spent on certain types of sites (or activities), or how do patterns of site activities vary across the state's four regional offices.

Recovering Response Action Costs from PRPs

The new cost recovery regulations contain several provisions describing administrative actions DEP can take to recover response action costs from PRPs. These administrative actions include sending requests for payment of response action costs to PRPs, implementing an administrative review process to resolve PRP disputes about the accuracy or reasonableness of costs included in requests for payment and using consent orders to establish "caps" on costs that will be recovered from certain PRPs. Although DEP has the discretion to decide not to use administrative actions to recover costs, it hopes using administrative cost recovery approaches will encourage more negotiated settlements and help avoid costly and protracted litigation. This section focuses on DEP's new systems and procedures for requesting payment from PRPs while the next section discusses the administrative process DEP has established to review costs disputed by PRPs.

The new accounts receivable system developed by DEP produces computerized requests for payments for most sites. This system includes several special features needed to implement the provisions of M.G.L. c.21E and the new cost recovery regulations. Because liability under M.G.L. c.21E is joint and several, each PRP at a site will receive a request for the entire amount of DEP's response action costs at that site, unless there is some formal agreement between the Department and the PRPs to allocate costs. However, total payments from PRPs cannot exceed the total costs incurred by the Department. The new accounting system tracks costs and payments for each site and also for each PRP (or group of PRPs) at the site. It then compare costs and payments to ensure that total payments by all PRPs do not exceed total costs at the site. The system also can produce computerized requests for payment that incorporate simple payment provisions that might be contained in consent orders (e.g., a proportional allocation of costs among several PRPs).

DEP staff can bypass the computerized system and produce requests for payment manually at sites with special circumstances (e.g., complicated payment schedules or allocation provisions among PRPs). The computerized accounting system enables DEP staff to identify and track those requests for payment that are produced manually. Requests for payments show: DEP labor costs (classified into two categories: costs associated with short term measures and all other costs); contractor costs; outstanding costs from previous bills and interest accrued; and a summary of payments made for the site by PRP. Requests for payment also provide the names and addresses of all PRPs receiving the request for payment at that particular site and instructions for making payments, requesting additional information on the response action costs incurred by DEP, or requesting a review of these costs (described in more detail below).

One innovative feature of Massachusetts' program is that PRPs are sent Requests for Payment on a regular basis, typically once every four months. This approach keeps PRPs informed of costs that are accruing at their sites as well as payments that they or other PRPs have made. Much of the information contained on the request for payment—such as the names of other PRPs and their payment history—is designed to encourage joint PRP action at sites with more than one PRP.

This approach and the new computerized accounts receivable system, also makes it possible to standardize DEP's procedures for assessing interest. Under the new regulations, DEP begins assessing interest on unpaid response action costs forty-five days after it has sent a request for payment (310 CMR 40.620(5)). Interest is assessed at the rate of 1% per month and will be compounded annually until the costs are paid or otherwise resolved. M.G.L. c.21E, 13 establishes an interest rate of 12% per year.

To minimize uncertainty about future oversight costs, DEP may consider including caps on response action costs in consent orders negotiated with PRPs (310 CMR 40.620(7)). The cap amount represents the Department's best estimate of the costs it expects to incur at the site. Decisions about whether or not to include such a cap in a specific consent order are made on a case-by-case basis.

Administrative Review

DEP has established a process for answering questions raised by PRPs regarding the accuracy or reasonableness of specific costs in a request for payment. This process, which implements the regulatory provisions contained in 310 CMR 40.620(4), works as follows.

First, PRPs may request information about how costs were calculated. The new accounting systems will enable DEP to provide PRPs who request it with detailed computerized reports on the costs contained in a request for payment. These reports may include some or all of the following items, depending on the type of costs incurred at the site:

- Breakdown of DEP labor hours and costs by activity, employee, time period and phase
- Breakdown of contractor costs by invoice
- List of all payments received for the site; the report will identify which PRP made the payment, the payment amount and the payment date
- Summary of interest assessments, showing the amounts and time periods used to calculate interest

PRPs who wish to dispute a specific cost must submit a written request outlining the nature of the dispute within the time limits established by the Department and include any evidence necessary to support the request. DEP staff review the disputed costs and consult with the appropriate DEP site manager and the PRP as necessary. Once the review is completed, the reviewer may approve the request, crediting the PRP's account for some or all of the disputed costs, or may deny the request, making the disputed amount due. If the PRPs disagree with the reviewer's decision, they still have the recourse provided in M.G.L. c.21E of filing an action in Massachusetts Superior Court. DEP may elect to waive its statutory right to seek treble costs from PRPs who participate in good faith in the administrative review process (310 CMR 40.620(6)(c)).

Time spent by Department staff on this administrative review process is intended to encourage voluntary payment of costs and is not included on requests for payment sent to PRPs.

ENFORCEMENT ACTIONS

If DEP does not recover its costs using the administrative procedures described above, it will seek to recover those costs through enforcement actions against PRPs. These enforcement actions may include filing a lien pursuant to M.G.L. c.21E 13 and/or asking the State's Attorney General to bring an action in State Superior Court pursuant to M.G.L. c.21E 11. DEP retains the right to seek these, or any other nonadministrative remedies, that are available to it at any point after costs have been incurred at a particular site.

DISCLAIMER

The views expressed here are those of Ms. Baci and Ms. Bingham and not necessarily those of the Massachusetts Department of Environmental Protection.

Increasing Opportunities for State Involvement in the Superfund Program: A Review of Key Regulations, Changing Cleanup Roles and Flexible Funding Options

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ABSTRACT

In 1980, when the U.S. Congress first enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the law required States to be actively involved in Superfund response actions. Under CERCLA, States with technical and management capability to carry out a response action may be authorized to lead cleanup efforts at a site. Without elaboration from Congress, the U.S. EPA took a course of action that met with limited success due to States' lack of adequate resources, experience and legal authorities. In 1986, the Superfund Amendments and Reauthorization Act (SARA) mandated what the relationship at a minimum should be between the Federal Government and the States. These amendments provided further elaboration on the U.S. EPA/State relationship. In particular, the U.S. EPA is required now to provide an opportunity for "substantial and meaningful involvement by each State in the initiation, development, and selection of remedial actions to be undertaken in that State" by Section 121 (f) of CERCLA, as amended.

This paper reviews the U.S. EPA's short- and long-range strategy for increasing States' involvement in the Superfund program in the 1990s. Four building blocks for the new strategy include: (1) the U.S. EPA's program management goals; (2) efforts to foster increased State involvement based on the recent promulgation of two Superfund regulations—the National Contingency Plan (NCP) and 40 CFR Part 35, Subpart O; (3) increased financial support through Cooperative Agreement funding to help States move toward fully operational programs of their own; and (4) new opportunities for increased State flexibility to tailor environmental programs to meet State and local needs and benefit from a balance of U.S. EPA/State influence in the direction and implementation of program activities.

INTRODUCTION

When Congress first enacted the Comprehensive Environmental Response, Compensation, and Liability Act in 1980, it provided the U.S. EPA and the States with the authority and approach for responding to uncontrolled hazardous waste sites. Congress later amended CERCLA by passing the Superfund Amendments and Reauthorization Act in 1986. SARA was distinguished from CERCLA in its emphasis on State involvement in virtually every phase of response.

CERCLA, as amended by SARA, authorizes the Federal Government to assume lead responsibility for cleanup at a site (Federal-led) or to transfer the necessary funds and management responsibility to a State when it has the technical and administrative capabilities to lead all or part of a Superfund response (State-led). Regardless of the lead agency designation. Section 121(f) of the law mandates that the U.S. EPA provide "substantial and meaningful involvement by each State in the initiation, development and selection of remedial actions to be

undertaken in that State." The extent of involvement goes beyond remedial action. Section 121(f) lists a full range of activities to evaluate and respond to the problems at the hazardous waste sites to abate or permanently clean up waste threatening human health and the environment. The intent implicit in the law is to increase the opportunities for State involvement in all aspects of the Superfund program from listing to deletion from the National Priorities List (NPL) and during removal and enforcement as well.

In *A Management Review of the Superfund Program* (The Superfund 90-Day Study), the Agency's Administrator identified the need for the U.S. EPA and States to develop joint short- and long-term strategies to enhance State program capability, improve State performance at State-led Superfund sites and foster State remedial activities at sites not on the NPL. The U.S. EPA's short- and long-term program management goals and their implications for current efforts to encourage increased State involvement through promulgation of two Superfund regulations—the NCP[1] and 40 CFR Part 35, Subpart O[2] (hereinafter referred to as the "Assistance Regulation") - and financial support provided through Cooperative Agreements[3] are presented in this paper. This overview clarifies the Agency's overall rationale and strategy for providing a wide array of opportunities for States to assume increased responsibility and to provide input into the U.S. EPA's planning on future directions in State involvement.

BACKGROUND

The U.S. EPA's Changing Approach to Environmental Management

Since the 1970s, major environmental laws have assigned to the U.S. EPA most of the key functions involved in delivery of environmental programs, while providing for a State role in assuming day-to-day program implementation responsibilities. The U.S. EPA generally has issued regulations and standards, provided detailed guidance and financial/technical assistance and monitored State performance. As their capabilities and experience have increased, States have gradually applied for and received more operational responsibilities. Along with their greater program role and responsibilities, States have been seeking to establish an equal and balanced relationship with the U.S. EPA. An equal U.S. EPA/State relationship involves: (1) a clear and appropriate division of authority and responsibility; (2) State involvement/ participation in goal-setting, policy formulation and planning; and (3) reporting and other oversight mechanisms to provide management control and evaluative information that the U.S. EPA needs to assure management accountability. A more equitable U.S. EPA/State relationship based on increased State involvement will encourage improvements that will mutually benefit the U.S. EPA and the States by:

- Promoting delivery of more effective environmental protection by placing decision-making authority at the level of government closest

to the people most affected by the decisions
- Expanding the impact of program investments of limited resources and support by taking advantage of States' advances in staffing, expertise and experience
- Reducing duplication of effort and minimizing conflicts resulting from confusion and differing perspectives on appropriate roles and responsibilities

Thus, principles to fulfill the mission of the U.S. EPA's Office of Solid Waste and Emergency Response (OSWER) include:

- Assuring an effective and open dialogue and exchange of information with all "stakeholders in OSWER's mission" who include the general public, federal, State and local governments and other groups where the exchange of information includes the provision of technical assistance and opportunities for consensus-building
- Fostering a special relationship with States (and Indian Tribes)[4] in sharing responsibility for implementing OSWER's programs.[5]

To date, the historical evolution of the Superfund Program's approach to management of the Federal/State relationship has significantly differed from the U.S. EPA's implementation of other environmental programs due to certain characteristics of CERCLA and its legislative history. Differing U.S. EPA and State perspectives regarding State involvement in the Superfund program have also been based on certain of these characteristics. CERCLA does not clearly delineate a State role in implementation of the program. That is, CERCLA is not a "traditional delegated program" (i.e., in the same sense as the Resource Conservation and Recovery Act [RCRA] and the Clean Water Act programs, although Cooperative Agreements are being used as a mechanism for sharing responsibilities between the U.S. EPA and the States and designating States as the lead during a response action). The U.S. EPA's management approach for the Superfund program has also been influenced by a lack of clarity regarding Congressional intent to permit States to assume responsibilities originally assigned to the President (e.g., selection of the remedy and approval of major cleanup project deliverables).

Discussion of Early Regulations, CERCLA 104 (c) and Effects on Cooperative Agreement Funding

The early imbalance in the State/U.S. EPA relationship was exacerbated by a limited availability of Cooperative Agreement funding to support State involvement in remedial response coupled with demanding, yet restrictive, application requirements for such funding. Following the enactment of CERCLA in 1980, the U.S. EPA focused on site-specific cleanup activities while developing an understanding of the essential program components for effective response. In 1984, the U.S. EPA provided States with an opportunity to enter into Multi-site/Multiactivity Cooperative Agreements that enabled States to consolidate their resources under one funding mechanism covering site-specific State-led projects and/or State participation in site-specific Federal-led projects. In 1985, the U.S. EPA provided States with an opportunity to participate in the hazard ranking of sites to determine whether they could be placed on the NPL. Finally, in 1987, the U.S. EPA offered assistance for removals where a 6-month planning period exists. Over time, State involvement in the CERCLA-funded cleanup process continued to be defined primarily in terms of activities at single sites and a State's willingness to provide Section 104 (c) assurances required for cleanup. States were required to provide three types of assurances that included the following:[6]

- *Cost-sharing*: The State was required to share in the costs of the remedial action performed at a site. At privately owned sites, the State was required to pay 10% of remedial action costs. At publicly owned sites (owned by the State or a political subdivision thereof), the State was required to pay at least 50% of all response costs such as Removals, Remedial Investigation and Feasibility Study (RI/FS) and Remedial Design (RD) and Remedial Actions (RA). U.S. EPA policy permitted States to defer the cost-share for Remedial Planning until a remedy was selected. Then, if a CERCLA-funded RA was contemplated, 50% of these earlier costs plus 50% of the RA had to be assured.

- *Off-Site Treatment, Storage, or Disposal*: The State was required to assure the availability of a hazardous waste treatment, storage or disposal facility that had: (1) an applicable permit or had been granted interim status in accordance with RCRA; (2) a RCRA Part B permit or a RCRA compliance inspection within 12 months prior to its use for treatment, storage or disposal of site waste and had complied with the RCRA regulations; and (3) sufficient capacity to handle wastes from the site. In addition, the U.S. EPA had to find off-site treatment, storage or disposal to be the most cost-effective cleanup option in comparison to other proposed remedial actions to protect human health or the environment.

- *Operation and Maintenance (O and M)*: The State was required to assume responsibility for all future O and M for the expected life of each RA as determined by the U.S. EPA and the State. In accordance with prevailing policy in effect at the time, the U.S. EPA could, for a period up to 1 year after completion of remedial response activities, share in the costs of any required remedy. In these instances, U.S. EPA policies assumed that costs limited to the 1 year could be considered the first part/leg of O and M.

Versions of the NCP in effect before CERCLA was amended discussed assurances to be provided by States in a Cooperative Agreement or contract before a CERCLA-funded RA could begin. The NCP did not assign States any specific role during the course of remedial response.

Without an explanation of the State role in either CERCLA or the NCP, the Agency relied on guidance to explain Cooperative Agreements and the transfer of funds and cleanup responsibilities to States. Consequently, there were more U.S. EPA leads at the onset of the program because the U.S. EPA had access to resources, experience and expertise. The U.S. EPA had access to substantial cleanup expertise through its own contractors, the U.S. Army Corps of Engineers and Emergency Response Teams; the benefits of hazardous and solid waste cleanup and management experience gained from implementing RCRA and the Clean Water Act; and adequate legal authorities to go on any site and to conduct a response. In contrast, only a few States, such as New Jersey and New York, had a cleanup program, technical cleanup experience or legal mechanisms in place to meaningfully interact with the U.S. EPA on site matters. Most States had to rely on the U.S. EPA for funding to staff up to conduct responses. As a result of this imbalance in the U.S. EPA/State relationship, States with ready sources of funds were able to interact fully with the U.S. EPA, while States lacking such resources were limited in their ability to interact with the U.S. EPA or even to develop Superfund programs.

Congress provided a resolution for this inequity when it amended CERCLA. Section 121(f) (1) of CERCLA as amended by SARA requires the U.S. EPA to promulgate regulations that generally provide for:

- State involvement in decisions regarding performance of Preliminary Assessment/Site Investigations (PA/SIs) during pre-remedial activities
- Allocation of responsibility for Hazard Ranking System (HRS) scoring
- State concurrence on NPL deletions
- State participation in long-term planning for all remedial sites in a State
- A reasonable opportunity for States to review and comment on the RI/FS and data documents leading to its issuance, the planned remedial activities identified in the RI/FS, the RD, technical data and reports relating to remedy implementation and any applicable or relevant and appropriate provisions of other laws (ARARs) considered and/or adopted or waived during remedial activities
- Notice to the State of negotiations with Potentially Responsible Parties (PRPs) regarding the scope of any response action and an opportunity to participate in such negotiations and settlements during enforcement (for a complete list of requirements, see Section 121 (f) of CERCLA as amended)

Once the State role during response was mandated, the U.S. EPA was able to elaborate on the full array of tasks/activities that could support development of an equal U.S. EPA/State relationship because the base line (i.e., minimum requirements for "substantial and meaningful involvement") was specified in the law.

REVIEW OF CURRENT REGULATIONS

NCP and the Assistance Regulation

CERCLA, as amended, is the legislative initiative that provides for cleanup of hazardous waste. The NCP describes guidelines and procedures for implementing the law. Recently, all guidance and practical experience were taken into account when the U.S. EPA began implementing 121(f) of SARA. Consequently, there are now two regulations on Superfund guiding the U.S. EPA's strategy for increasing State involvement: the NCP (especially Subpart F on State Involvement)[7] and the Assistance Regulation. Moreover, in crafting these two regulations, the U.S. EPA assumed a complementary interaction between the two rules.

While Subpart F of the NCP specifies how the U.S. EPA will satisfy 121(F) of CERCLA as amended, the Assistance Regulation provides the mechanisms to foster the birth of State Superfund programs, support the State's development of its own program goals and sustain its effectiveness to respond at sites in a variety of ways. Most importantly, the U.S. EPA is now positioned to assist States in gaining more opportunities for substantially increased involvement in the Superfund program per se, rather than site response only. Consequently, most responsibilities regarding site cleanup and administrative management pertaining to State involvement that were in guidance are now specified in both regulations, and reliance upon voluminous amounts of program guidance to implement and administer the Superfund program is reduced.

The U.S. EPA's new approach to State involvement is based on a differentiation between: (1) the technical aspects of response that include State involvement throughout that response; (2) support intended to nurture and strengthen State involvement and (3) national consistency in the U.S. EPA/State relations with regard to environmental and public health protection. The different contributions of each regulation to the U.S. EPA's strategy for increasing State involvement in the 1990s are discussed below.

NCP's Delineation of Lead and Support Agency Roles During a Response

The NCP clarifies requirements for State involvement by specifying how the U.S. EPA will implement the 121(f) requirement for the U.S. EPA to provide "substantial and meaningful involvement by each State." The NCP delineates a structure for U.S. EPA/State interactions to assure consistency of communications and coordination when the States are assisting the U.S. EPA during the conduct of a response action. The NCP also responds to States' desires for an equal U.S. EPA/State relationship by fulfilling requirements that the U.S. EPA establish comparable processes for Federal- and State-led or support agency roles during the conduct of various response activities. The basic elements of the structure of interaction include specified decision points and communication and coordination points.

During a State-led remedial response, for example, decision points include State/U.S. EPA agreement on the acceptability of major project deliverables such as the RI/FS workplans and reports; concurrence with the Record of Decision (ROD) recommending a specific remedy for site cleanup; agreement with the RD and proposed plan for RA; and acceptance of the remedy at the conclusion of RA. Acceptance of the remedy involves acceptance of the technical report on the RA that the remedy is in place, working as designed and meets the cleanup requirements specified in the ROD. The final decision point involves the State's concurrence with the U.S. EPA's deletion of a site from the NPL. Communication and coordination points during a State-led remedial action include time frames for early joint identification of ARARs, specified time frames for review of key reports and advance notice of planned dates for important meetings, conferences and the fulfillment of State goals to address the concerns of its citizens.

Assistance Regulation's Requirements for Funding State-Led/Support Roles and Core Program Funding

The Assistance Regulation relies on the NCP for designation of a lead or support agency for response and the points of involvement during response and establishes the criteria for funding to support the State's

role in a variety of site-specific response activities. In addition, the Assistance Regulation contributes to the U.S. EPA's goal to increase opportunities for State involvement by providing the U.S. EPA's current requirements for Core Program funding — the solution to the constraints imposed by early assistance requirements which focused on site-specific activities.

Finally, the Assistance Regulation makes a substantial contribution to the U.S. EPA's efficient management of Hazardous Substance Superfund ("The Fund") dollars by providing uniform and consistent requirements for the obligation, fiscal management and expenditures to procure goods or services necessary to support cost recovery. Furthermore, the shift in emphasis from guidance to regulations provides for uniform treatment of States as the U.S. EPA's partners and national consistency in the program regardless of lead/support agency designation during site response. These different contributions are discussed in further detail below.

The Original Core Program Cooperative Agreement Concept

The concept of the Core Program Cooperative Agreement was implemented in 1987 through program guidance to fund nonsite-specific activities that could support a State's ability to assume an active role in site-specific responses. Basic Core Program functions considered essential for sustaining and/or enhancing State program abilities included:

- General program management and supervision necessary to direct a program to carry out CERCLA implementation activities
- Interagency coordination on all phases of response necessary to develop and sustain a consistent and concerted State effort
- Legal assistance associated with proper administration of the CERCLA program
- Development of fiscal and contract management procedures to ensure the financial integrity of CERCLA site-specific expenditures and CERCLA-related procurement administration
- General administration and clerical support
- Additional State-specific functions considered on a case-by-case basis once a State developed a viable Superfund program (including development of response training, base line medical monitoring programs, record-keeping guidelines to support cost recovery activities and 20-year hazardous waste capacity assurance plans)

The Core Program was initiated on a pilot basis with awards to three States in three different Regions. Each State (Illinois, Utah and Washington) provided practical insights into improvements for the Core Program concept, which facilitated nationwide implementation in 1988, when all States were eligible to receive Core Program funds.[8] In this process, the U.S. EPA learned several lessons regarding States' limited abilities to participate as "full partners" in the Superfund program. These lessons included the following:

- State programs lacked full capabilities
- States desired more integrated support
- States had difficulty justifying staff
- States have unique needs

During early implementation of the Core Program concept, financial awards fluctuated in response to the following:

- The number of sites a State had in the Comprehensive Emergency Response Compensation and Liability Information System (CERCLIS) inventory and on the NPL awaiting fund financing
- The number of State-led CERCLA-funded site cleanups underway
- The level of sophistication of the State's CERCLA implementation capability
- Whether or not State-specific additional functions were deemed appropriate

Because the public comment periods for both the NCP and Assistance Regulation overlapped, the U.S. EPA received many comments that provided practical advice on how individual requirements could be made more flexible to help States move toward fully operational programs of their own. In fact, during the public comment periods for both regulations, the Agency gained more insight into the future needs of States.

Consequently, when both became final, States were able to increase the degree of their involvement via Core Program Cooperative Agreements. As a result, all 10 U.S. EPA Regions are represented by awards to 41 States, the Territory of Puerto Rico, and the Navajo Nation.[9]

Now, the U.S. EPA is willing to fund:

- Procedures for emergency and long-term remediation of environmental and health risks at hazardous waste sites (including, but not limited to, the development of generic health and safety plans, quality assurance project plans and community relations plans)
- Provisions for satisfying all CERCLA requirements and assurances (including the development of a fund or other financing mechanism[s]) to pay for studies and remediation activities
- Legal and enforcement support associated with proper administration of the recipient's program and with efforts to compel PRPs to conduct or pay for studies and/or remediation (including, but not limited to, the development of statutory authorities; access to legal assistance in identifying ARARs; and development and maintenance of the administrative, financial and record-keeping systems necessary for cost recovery actions under CERCLA)
- Efforts necessary to hire and train staff to manage publicly funded cleanups, oversee responsible party-led cleanups and provide clerical support

Once a State has these necessary program functions in place, the U.S. EPA may provide funds to support other initiatives that support the uniqueness of each State. Program support activities have also been integrated throughout the Assistance Regulation. They include such activities as development and maintenance of central files for site-specific response to support cost recovery, interagency agreements with other State agencies and municipalities to obtain a variety of services such as consolidated reporting functions, development of long-range communication strategies and multiyear workplans and budgets to support strategic planning.

There are no Federal funding limitations imposed by the regulation; rather, awards are based on State program needs, demonstrated progress against previous scopes of work and the availability of funds.

Eligibility Requirements for State Roles in
Site-Specific and Other CERCLA Activities

In general, the Assistance Regulation provides eligibility requirements for States (as well as political subdivisions and Federally-Recognized Indian Tribes) seeking to apply for Superfund Cooperative Agreements. The regulation also identifies those entities eligible to apply for specific types of Cooperative Agreements. For example, States are eligible to apply for:

- State-led Pre-remedial Cooperative Agreements
- State-led Remedial Cooperative Agreements
- State-led Enforcement Cooperative Agreements
- State-led Removal (for 6 month planning period) Cooperative Agreements
- Core Program Cooperative Agreements
- Support Agency Cooperative Agreements where the U.S. EPA or a political subdivision is the lead for response

These eligibility requirements assure the consistent treatment of States across the range of available types of Cooperative Agreements and serve as the vehicle for their eventual attainment of true partnership with the U.S. EPA.

Consistent Application and Administrative Requirements

The comment periods for both the NCP and the Assistance Regulation were concurrent. Therefore, comments not applicable to the NCP were accommodated in the Assistance Regulation and vice versa. At the same time, the U.S. EPA gained a practical appreciation of how individual States viewed the requirements and their ability to interact with the U.S. EPA at all levels. Consequently, the requirements associated with applying for and receiving CERCLA funds increased the consistency of administrative requirements across the range of Cooperative Agreement types. By focusing on the type of entity (State,

political subdivision or Federally-Recognized Indian Tribe) in a lead or support role for a response, the U.S. EPA has increased the consistency of administrative requirements by providing:

- Consistent application and award criteria regardless of the type of response
- Flexible funding alternatives that support cost recovery yet reduce burdens of paperwork
- Reductions in the need for many special conditions for each Cooperative Agreement and thereby reducing confusion due to a substantial reliance on guidance
- Minimization of the potential for significant differences in treatment, from State to State and Region to Region
- Decrease in the potential vulnerability to misuse of Fund dollars during response and a subsequent decrease in audit problems
- Consistent criteria for evaluating requests to purchase equipment for State-involvement in site response, and enhancement of State capability to respond via the Core Program funding
- Consistent equipment disposition instructions that allow transfers of equipment from one site to another and one responder to another (e.g., State to County)
- Consistent reporting requirements and reporting schedules throughout the regulation to support cost recovery

FUTURE ACTIVITIES TO FURTHER DEVELOP STATE SUPERFUND PROGRAMS

Following promulgation of the two major Superfund program regulations, the U.S. EPA's strategy for increasing State involvement in the 1990s is being implemented through two types of activities:

- U.S. EPA's strategic plan
- Program-specific activities

The U.S. EPA's activities related to these types of activities are discussed below.

U.S. EPA's Strategic Plan

The U.S. EPA's mission is to protect human health and the environment from unacceptable risks posed by solid and hazardous wastes and by releases of oil and hazardous substances into the environment. To fulfill this mission, the U.S. EPA must meet four goals:

- Minimize the quantity and toxicity of waste created by commercial, domestic and governmental activities
- Ensure environmentally sound management of solid and hazardous wastes
- Prevent harmful releases of oil and hazardous substances into the environment
- Prepare for and respond in a timely and effective manner to releases of hazardous materials into the environment[10]

The U.S. EPA's strategic plan guides the Agency toward implementation of its principal purpose — to reduce risk to human health and the environment.

The Superfund Program's chief role lies in the fourth goal of the strategic plan—to respond to releases of hazardous materials in a timely and effective manner, which emphasizes:

- High-priority sites and releases first
- Effective remedies
- An efficient, well-managed Superfund program
- Increased role of others
- Building public confidence in Superfund
- Planning efforts to support the concept that enforcement is the preferred method of cleanup

Opportunities for State Involvement

In light of these general goals and objectives, States seeking involvement in the Superfund program may obtain:

- Increased opportunities for involvement in selected areas that are most important to them depending upon their own program needs
- Increased opportunities to become active partners in protecting the environment and public health by developing, or providing expertise

Opportunities for increased State involvement directly related to the U.S. EPA's strategic goals and objectives include the following areas.

Address the worst sites first

To meet this objective, the Superfund Program needs to develop, issue and implement operating guidance for pre-remedial, remedial, removal and enforcement activities that rely on common eligibility and performance criteria for each phase of response rather than separate and seemingly contradictory instructions. Such a consolidated initiative, wherever practicable, should increase the ability of States to work independently.

States have identified 32% of the total universe of sites in CERCLIS and 55% of the sites now on the NPL.[11] This contribution to the PA/SI and hazard ranking process has helped the U.S. EPA narrow the universe of sites that require attention.

Specifically, with States, the Superfund Program's activities include development and implementation of a site discovery policy and program. A recommendation has been made to fund State site discovery programs either under the Core Program or Preremedial Cooperative Agreements. The Assistance Regulation allows for this possibility which could mean that future problem sites will be assessed and cleaned up more rapidly.

Improve the operation and effectiveness of national preparedness and State involvement in response structure

To meet this objective, the U.S. EPA is examining ways to provide States with a larger role in emergency response efforts at sites where the U.S. EPA or Federal response contractors would respond. In addition, the U.S. EPA is exploring ways to share information on sites to help States respond where the U.S. EPA cannot. This goal can be accomplished only through a concerted effort with States to train State and local officials to respond rapidly and effectively to releases. Again, the Assistance Regulation allows for this possibility.

Control threats to human health and the environment by reducing costs and length of time from identification to response

Achieving this objective requires an improvement in all areas of Superfund response and program management, including a reliance on States to conduct the work and a reduction in the degree of oversight as States enhance their ability to respond. One must acknowledge that within the universe of sites, balancing priorities does not mean one entity does everything at a site; there is more than enough work for everyone.

Optimize U.S. EPA and State resources to secure maximal involvement by Responsible Parties

In order to meet this objective, the U.S. EPA intends to pursue a balanced, aggressive enforcement program that emphasizes participation by RPs in the design and implementation of a site's remediation. The Administration has continued to focus on enforcement in order to increase the number of sites that can be cleaned up; however, the U.S. EPA cannot carry out all these efforts alone. Specifically, the U.S. EPA will provide the support necessary to increase State involvement through the Assistance Regulation. States can now apply for Enforcement Cooperative Agreements for all CERCLIS sites and receive funding to pursue PRPs and oversee RP actions. In addition, States may receive funding through the Core program to develop the legal authorities necessary to establish an active and effective enforcement program of their own.

Establish effective State programs to respond to releases of hazardous materials

Overall, the Superfund Program intends to move towards a more delegated program by enhancing State programs and encouraging States to use local governments. The Core Program funding, training and other technical assistance from the Superfund Program and other sources within the U.S. EPA can be used to promote and support cohesive State programs that deal with all aspects of the hazardous waste cleanup and management per se from cradle to grave. States can optimize the U.S.

EPA's resources by more fully participating in areas where they have a comparative advantage, thereby enhancing the quality and quantity of response actions undertaken.

Program-Specific Activities

The Superfund Program is conducting an array of specific program activities to implement the two regulations including:

- Identifying and resolving administrative obstacles to national consistency between the regulations and existing program guidance
- Providing funding opportunities through expanded Core Program Cooperative Agreements
- Increasing State flexibility to tailor environmental activities to a States' unique needs and encouraging within the U.S. EPA a greater reliance on State expertise

Each of these activities is further discussed below.

Increasing National Consistency Between Regulations and Program Guidance

Regulatory or administrative obstacles may remain because the issuance of the NCP and Assistance Regulation did not automatically rescind operating guidance. Therefore, the U.S. EPA is evaluating State/U.S. EPA roles and the new eligibility requirements for assistance to foster consistent national implementation of the Superfund Program. This initiative includes an analysis of regulatory and program guidance requirements for Cooperative Agreement funding. Results of this analysis are being used for several purposes:

- To develop recommendations for streamlining and updating current program guidance and rescinding guidance that is no longer practicable
- To develop solutions for resolving existing administrative barriers
- To develop decision-making tools for States' use to satisfy eligibility requirements when applying for Superfund Cooperative Agreement funding. In the short-term, a review of these eligibility requirements will help identify State program capabilities that need enhancement. In the long-term, it should encourage development of a national cleanup program based on the collective contributions of many fully operational State programs - capable of responding to NPL and non-NPL sites.

Funding Opportunities and the Core Program Cooperative Agreements

In the future, the U.S. EPA will continue its existing practice of basing funding allotments on State program needs, demonstrated progress against previous scopes of work and availability of funds. In addition, the U.S. EPA plans to use the larger, more flexible Core Program offered by the Assistance Regulation to encourage States to respond creatively to their unique program needs. This procedure, in turn, should ensure that States progress toward fully operational programs of their own in the 1990s. The U.S. EPA will encourage these developments first, by allowing scopes of work and associated budget requests to cover more than one year; and second, by allowing funds to pay for "publicly-funded cleanups" to be used for oversight of cleanups funded by Superfund, State-funded cleanups and cleanups required and funded by other public entities.

Increased State Flexibility

Opportunities for increased State involvement in the 1990s will be based on the changing direction of the U.S. EPA/State roles in the Superfund program. The new direction is based on four recent developments:

- Opportunities for flexibility to tailor environmental programs to meet local and State needs are increasing
- The U.S. EPA is seeking to achieve a balance of the U.S. EPA/State influence in the direction and implementation of program activities
- States are providing innovative approaches to solving waste management problems
- The U.S. EPA is acknowledging the increasing U.S. EPA/State interdependence

FOOTNOTES

1. 40 CFR Part 300, National Oil and Hazardous Substances Pollution Contingency Plan; Final Rule. *Federal Register, 55* (46), March 8, 1990.

2. 40 CFR Part 35 Subpart O. Cooperative Agreements and Superfund State Contracts for Superfund Response Actions; Final Rule; *Federal Register, 55*(108), June 5, 1990.

3. A "Cooperative Agreement" is defined as the instrument for transferring money or services to a State (or political subdivision, or Federally-Recognized Indian Tribe) when a State assumes lead responsibility for all or part of a response activity and when substantial federal involvement is anticipated. A Cooperative Agreement under CERCLA also documents the U.S. EPA and State responsibilities and serves as an instrument for obtaining any required CERCLA 104 assurances when the State is the lead agency.

4. CERCLA Section 126 treats Federally-Recognized Indian Tribes substantially the same as States. The NCP Subpart F specifies circumstances under which substantially the same treatment is required of the U.S. EPA, and the Assistance Regulation tells these Indian Tribes how they can be supported in their role as a State. Section 104 provides political subdivisions with opportunities for participation in response activities and the Assistance Regulation specifies when and how they can be involved in response activities as a lead or support agency to the U.S. EPA and a State.

5. See the U.S. EPA, *OSWER Strategic Plan for FY 1992-1995*, November 30, 1989, pp. 5 and 6. OSWER includes (1) the Office of Emergency and Remedial Response, (2) Office of Solid Waste, (3) Office of Underground Storage Tanks and (4) Office of Waste Programs Enforcement. See also "Building an U.S. EPA/State Relationship for the Changing Management of Environmental Programs" in U.S. GAO, *Environmental Protection Agency: Protecting Human Health and the Environment Through Improved Management* August, 1988.

6. The SARA amendments added two additional assurances pertaining to siting/waste capacity (104 (a)(9)) and acquisition of property (104 (j)).

7. Although several sections of the NCP include requirements that are critical for State involvement in Superfund, e.g., Subpart E requirements on Removal Site Evaluations and Removal Actions, RI/FS and Selection of the Remedy, RD, RA and O and M; or Subpart I requirements for Establishment of an Administrative Record, Subpart F contains all regulatory requirements for State participation and involvement in CERCLA-authorized response actions.

8. Baker, J.H., *History of the Core Program Concept*. U.S. EPA, Office of Emergency and Remedial Response, Washington, DC, July 1990, p. 10.

9. *History of the Core Program Concept*, pp. 10 and 11.

10. *OSWER Strategic Plan*, p.5.

11. Statistics were extracted from the U.S. EPA's official Superfund data base: CERCLIS. See the U.S. EPA, *Status of State Involvement in the Superfund Program FY 80 to FY 89*. Office of Emergency and Remedial Response, Washington, DC, April 1990.

Coordination of Site Cleanup with Natural Area Development

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ABSTRACT

The New Lyme Landfill Superfund Site is a 40 acre site that was operated between 1968 and 1978 as a disposal facility for residential, commercial and industrial wastes. A Record of Decision (ROD) was signed by the U.S. EPA in 1985 after completion of the Remedial Investigation and Feasibility Study. The selected remedy described in the ROD included groundwater remediation and installation of a multilayer cap to prevent infiltration of water into the fill area. During the development of the Remedial Design project, the Ohio EPA developed and coordinated a unique solution to provide cover material for the site. The Ohio EPA project management staff suggested using an underdeveloped wildlife area adjacent to the site as a source for cover material. The Ohio EPA contacted the Ohio Department of Natural Resources (Ohio DNR) and jointly developed a plan to improve the habitat at the state-owned New Lyme Wildlife Area. That plan has been implemented through the U.S. EPA fund lead Remedial Design/Remedial Action with the oversite of the Army Corps of Engineers. The excavation of cover material was planned and executed to create a 60 acre lake in the 500 acre swampy forest area. The lake was designed in coordination with Ohio DNR to provide diverse habitat for waterfowl, shorebirds, furbearers and game fish. The project includes development of access roads and boat ramps to improve recreational use of the wildlife area. The lake is supplied by surface water that is not from the watershed of the landfill. Almost 900,000 cubic yards of soil were excavated from the wildlife area to provide materials for grading and development of the multimedia cap. The use of cover materials from the wildlife area has lowered the implementation cost of the remedy by at least $3,500,000. Additionally, use of soils from the adjacent wildlife area eliminated the truck traffic on local public roads that would have occurred if soils had been taken from other sources. The extra design efforts of the agencies involved has resulted in a greatly improved wildlife area and increased cost-effectiveness of the final remedial action at the New Lyme Landfill Superfund Site.

INTRODUCTION

In this paper, the authors present a brief history of activities at the New Lyme Landfill Superfund Site and a description of the implementation of the wildlife area enhancement that was integrated into the remedial project for the site. The authors also summarize the pre-remedial and remedial activities that occurred under the auspices of the U.S. EPA Superfund Program. The design and implementation of the wildlife area enhancement project is described in detail.

The case history presented here supports the importance of active and creative project management in the development and implementation of remedial projects at Superfund and state-led remedial projects. The remedial project at the New Lyme Site successfully implemented a protective remedy that was made more cost-effective by using borrow materials from an adjacent wildlife area. In addition to the expected benefit of mitigation of the long-term risk posed by the New Lyme Landfill, the community and the state has benefitted from the addition of a 60 acre lake to enhance a previously under utilized state owned wildlife area.

SITE HISTORY

The New Lyme Landfill was operated between 1968 and 1978. The facility accepted residential, commercial and industrial wastes. The facility accepted an estimated 27,500 cubic yards of waste monthly. Wastes disposed of at the site included paints, paint thinners, oils, coal tar, resins and other chemicals. The site was placed on the NPL in the fall of 1983 after initial investigation of contamination at the site.

A remedial investigation was conducted by U.S. EPA between August 1983 and August 1984. The RI concluded that site related contamination had migrated into the shallow groundwater. The area groundwater is yielded to wells from weathered fractured bedrock. The low permeability surface soils confine the groundwater and create artesian conditions. The mechanisms for groundwater discharge reported in the RI[1] are:

- Flow through fractures to the surface
- Flow through fractures to sand lenses and waste cells
- Flow directly from bedrock to waste cells excavated into bedrock
- Discharges from waste cells in the form of leachate

The discharge of contaminated groundwater and the possibility of contact with contaminated soils was evaluated in the 1985 feasibility study.

The feasibility study documented excessive cancer risks posed by exposure to contaminated on-site soils and contaminated groundwater.[2] The FS also documented an environmental threat to area wetlands and surface waters from the continued migration of contaminated leachate into area surface waters. Based on the exposure routes and risks evaluated in the FS, a source control remedy was proposed to mitigate the problems at the site. A multilayer (RCRA type) cap system was to be installed over the landfill and contaminated materials were to be consolidated onto the landfill. The landfill would then be dewatered by use of a groundwater and leachate collection and pumping system. Treatment of the extracted waters would include chemical precipitation, biological oxidation and granular activated carbon adsorption to remove contaminants prior to discharge. Groundwater treatment will continue until the landfill is dewatered and contaminated leachate is no longer being produced.

A ROD was signed on September 27, 1985 selecting the remedial alternative for the New Lyme Landfill.

REMEDIAL DESIGN

During the 10 percent design review conference on May 5, 1987, Ohio EPA project management staff discussed options for borrow sources for cover material with U.S. EPA and Army Corps of Engineers representatives. Many area soils apparently would have been available and met the performance criteria for cap material. In addition to area farmers who had been in contact with the Ohio EPA about providing borrow sources, the Ohio EPA staff had initiated investigation of using a state owned (Ohio Department of Natural Resources operated) wildlife area as a source of borrow material. Ohio DNR was contacted by Ohio EPA staff and negotiations were initiated in August 1987 to begin planning and implementation of the borrow area/lake.

U.S. EPA contractors developed the initial and final design plans for the on-site construction independently of the design of the lake. The design plans included: installation of monitoring and extraction wells, excavation and placement of contaminated perimeter soils and sediments onto the top of the landfill, construction of the wastewater treatment building and systems and construction of the multilayer cap.

The cap system required more soils than would be available on-site. The soils required for construction of the cap included an initial fill/grading layer, a clay liner and a vegetative support layer. The grading layer was placed over the existing landfill surface and would require up to 6 feet of compacted silty soils to fill in depressions and low spots and correct the existing grade to allow placement of the cap. The specifications for the clay liner required a minimum of 2 feet of recompacted clay with permeability less than or equal to 1×10^{-7} cm/sec. A synthetic membrane and drainage layer would be placed directly over the clay layer. A minimum of 2 feet of silt loam would be placed over the synthetic liner and seeded.

Although the contract documents called for 225,000 cubic yard of initial fill, 539,509 cubic yards were required to meet the grading specifications for the job. The contract required 163,000 cubic yards of clay and 163,000 cubic yards of topsoil. The requirements for these materials were considerably closer to the original estimates. The overage for clays and topsoil was less than 10,000 cubic yards.

LAKE DESIGN

Ohio DNR personnel worked in conjunction with Ohio EPA, U.S. EPA and Army Corps of Engineers representatives to develop design plans for the lake borrow area that would meet the needs of both the remedial project and the development of the wildlife area. Figure 1 shows the outline of the lake and the adjacent landfill. The lake occupies approximately 80 acres of land and has 60 acres of open water. The wildlife area contains a total of 500 acres of mixed woodland and brushland.
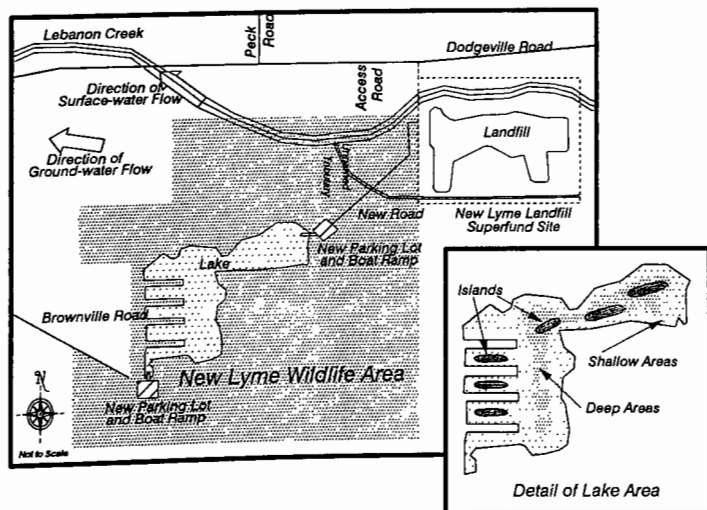
Figure 1
New Lyme Wildlife Area

The Ohio DNR has designed the lake to optimize habitat for waterfowl and fish. The deeper portions of the lake are 17 to 20 feet deep. The stumps removed during the clearing of the land have been consolidated into stump "islands" that will provide subsurface habitat for fish. Additionally, two wooded islands were left intact and surrounded by stumps. The lake will be stocked with Bluegill, Channel Catfish and Largemouth Bass. The narrow fingers along the western end of the lake were designed to provide shallow surface water intermixed with woodland to provide habitat for wood ducks and other game species.

The wildlife area has supported limited populations of wood duck, mallard, black duck and blue winged teal in the past. The addition of the lake should allow larger populations to nest in the area. Access to the area will be improved as the haul road will be converted into a public entrance road, gravel parking area and boat ramp. The area used for access during clearing of the borrow area will be converted to a second small gravel parking area and boat ramp.

The landfill area is 1/4 mile from the lake, and the access road will pass adjacent to the western edge of the site. The landfill has been completely fenced to prevent any possibility of exposure to the public. The access road does not provide unlimited access to the site so better access should not promote excessive human interference with nongame wildlife in the area.

IMPLEMENTATION OF REMEDY

With the exception of some weather-related delays and some construction problems during construction of the water treatment plant, the implementation of the remedy proceeded according to planned schedules. The excessive spring rains of 1989 caused delays soon after the borrow area had been cleared and prior to placement of site fill. During the process of clearing the land, Corps of Engineers and Ohio DNR personnel identified nesting areas that were left undisturbed until nesting was completed.

After the beginning of summer weather, the contractors worked double shifts to put the project back close to its original schedule. The continuous streams of truck traffic for 17 hour days would have created substantial public relations and traffic problems had it been necessary to move the source material along public roadways. Even the number of truck trips would have been greater because the large off-road type trucks could not have been used on public roads.

As mentioned above, that the amount of initial fill material required had been underestimated substantially. Fortunately, the plans for the lake had been designed so that the size of the lake could be fairly easily changed if demands for borrow material changed significantly. The completed lake was somewhat smaller than the maximum possible size agreed to by the Ohio DNR had agreed to. The initial fill material exceeded the permeability standards required for the soil layer. As a result, many areas of the landfill have a low permeability clay layer that is considerably thicker than the required two feet.

The problems encountered during the construction of the cap were all site-related. No implementation problems were created or in any way caused by the use of the wildlife area as a borrow source. The early season, rain delays caused construction to continue past the normal construction season and an early winter storm caused damage to the landfill cover and liner over a portion of the edge of the landfill. The addition of the fill material and cover in a year of heavy spring rains apparently increased the pressure on the artesian system and caused leachate outbreaks that had to be handled during construction. Gas generation caused some problems during the installation of the HDPE liner material.

COST BENEFITS

The most obvious benefit derived from the use of the wildlife area as a borrow source was the decreased cost of acquiring borrow material. The Army Corps of Engineers estimates that the cost of purchasing soils would have been doubled had the soils been procured from an off-site property owner. Soil excavation and placement costs totaled more than $3,800,000 for the project as completed; purchase of those soils would have cost at least another $3,500,000.

Even if the soils had been donated in exchange for construction of a lake or farm pond in another location, the cost of transporting the soils over a greater distance would have been higher. Off-site transportation of soils over public highways would have caused considerable wear and tear on the road surfaces that would have added to the cost of the project. The on-site haul road was compacted and smoothed to a great extent by the passage of many trucks.

The intangible dollar benefit resulting from the construction of an improved wildlife area cannot be determined. Ecological cost or ecological benefit can not be assessed in simple terms. The environmental assessment of the project supported the decision to exchange terrestrial wooded habitat in order to enhance aquatic habitat in the area. After a few years of operation, the Ohio DNR should be able to begin to evaluate the effectiveness of the lake system in terms of improvements in local wildlife populations and improved hunting and fishing in the area.

CONCLUSIONS

It is much easier to present this information than it was to accomplish this project. In addition to all of the difficulties involved in coordination of a Superfund Remedial Design/Remedial Action, an additional effort was expended by Ohio EPA project management staff and personnel from the other agencies to implement a creative solution to a common problem. The fortuitous location of the state-owned wildlife area is something that cannot be planned, but it is something that can be investigated at other sites. One of the most difficult aspects of managing Superfund projects at the state level is the public perception that the program is not providing any tangible benefits and is much too slow to correct apparently obvious problems. When an obvious benefit can be derived through implementation of a remedial action, project management staff should be encouraged to coordinate creative solutions to reap those benefits. The New Lyme project has been well received by the local community and the local media, and the image of all of the agencies that were involved has been enhanced by their association with this project.

ACKNOWLEDGMENTS

We would like to acknowledge all of the people who have participated in this project. Most of the agencies involved have been listed in the text and the list of individuals whose individual and group contributions to this project have contributed to its success is too long to list without inadvertently omitting someone who deserves recognition.

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Risk Assessment Versus ARARs in Wisconsin: A Case Study

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ABSTRACT

This case study illustrates conflicts between the application of state applicable or relevant and appropriate requirements (ARARs) for groundwater and the use of risk assessment for making remedial action decisions. The Algoma Landfill does not comply with state ARARs for benzene, iron and manganese in the groundwater. The state benzene standard (0.67 μ/L) is expected to be revised to the MCL (5 μ/L) and the timing of that change is critical to this site. If the ROD is signed before the revised ARAR is promulgated, the ARAR for benzene at this site will remain at 0.67 μ/L and the site will not comply. If the ARAR is promulgated before the ROD is signed, the site will not meet ARARs for iron and manganese, only. Wisconsin groundwater standards elevate federal secondary (public welfare) drinking water standards to enforceable status as groundwater protection standards. Under Superfund, these become ARARs and can then be applied as cleanup standards. In either case, risks at this site are low; but in spite of an endangerment assessment which shows risks within acceptable levels, Superfund remediation could be driven by standards that are fundamentally nonenforceable guidelines. Furthermore, such a remediation disregards results of the base line risk assessment in providing a basis for determining whether remedial action is necessary.

An RI conducted by the PRPs for the Algoma Landfill, in accordance with an agreement with U.S. EPA Region V, in 1988 and 1989. The RI Report included an Endangerment Assessment (EA) performed under the Risk Assessment Guidance for Superfund.[1] The results of that assessment included the following:

	Cancer Risk	Exposure Route	Hazard Index	Exposure Route
Current Land Use	1 x 10⁻⁶	soil ingestion	0.004	soil ingestion
Future Land Use	1 x 10⁻⁶	soil ingestion	0.02	groundwater ingestion

The risk estimates are at the 10⁻⁶ point of departure and the hazard index estimates are both below 1.0, the level of concern. Although some uncertainties exist, risk estimates for this site, based on maximum rather than reasonable maximum exposure, are within the target risk range for Superfund sites of 10⁻⁴ to 10⁻⁶.

INTRODUCTION

CERCLA Section 121 requires remedial action to meet promulgated state standards that are ARARs if they are more stringent than federal ARARs.[2] State criteria must be "promulgated" and "more stringent" to be potential ARARs. Promulgated requirements are defined as those of general applicability that are legally enforceable. When ARARs are not available or are not sufficiently protective, the 10⁻⁶ risk level is to be used as the point of departure for determining remediation goals. When the ROD is signed, ARARs become frozen for that site, unless the new ARAR is substantially more protective of human health and the environment.

The groundwater quality regulations in Wisconsin Administrative Code NR 140[3] are ARARs for Superfund sites in Wisconsin. NR 140 includes standards for substances of public health concern (e.g., aldicarb, arsenic, atrazine, etc.) that are similar to the Maximum Contaminant Levels (MCLs) under the Federal Safe Drinking Water Act. The NR 140 standard for benzene was 0.67 μ/L, but it has recently been revised to the MCL (5 μ/L). That revision, however, has not become effective; and if the ROD for the Algoma Landfill is signed before the effective date of the revision to NR 140, the ARAR for the site will be "frozen" at 0.67 μ/L. The maximum benzene concentration reported at this site was approximately 3 μ/L, which is a concentration between the old and the new ARARs.

NR 140 also includes standards for substances of public welfare concern (e.g., chloride, color, copper, etc.) that are equivalent to the Federal Secondary MCLs. Because NR 140 is an ARAR, the Federal SMCLs that are incorporated into NR 140 become ARARs, even though SMCLs are "nonenforceable limits intended as guidelines for use by states."[4] The Algoma Landfill does not comply with these standards for iron (300 μ/L) and manganese (50 μ/L). Wisconsin groundwater standards elevate Federal SMCLs to enforceable status as groundwater protection standards; and, under Superfund, these ARARs become enforceable cleanup criteria that are not related to public health risk.

The stated purpose of the base line risk assessment is to provide "a basis for determining whether remedial action is necessary and justification for performing remedial actions."[1] Because there are ARARs, risk (or its absence) is ignored and the CERCLA mandate to protect public health and the environment is superseded by the mandate to comply with state ARARs.

RISK ASSESSMENT

Site Description

The Algoma Landfill is located in Kewaunee County, approximately 2 miles west-southwest of the City of Algoma, Wisconsin. The City operated the landfill from 1969 until 1983 on seven acres of leased land. The landfill was licensed as a solid waste disposal facility and it accepted mainly municipal refuse during its operation; however, certain industrial wastes were disposed there.

The RI was conducted by the PRPs. RMT, Inc. of Madison, Wisconsin, was retained by the PRPs to provide consulting assistance for preparation of the RI/FS.

The RI was conducted to determine the nature and extent of the release or threatened release, if any, of hazardous substances at or from the Algoma Landfill.[5] Based on the findings of the RI, an FS was conducted to identify and evaluate alternatives for the appropriate extent of remedial action, if any, to prevent or mitigate the migration, release or threatened release of hazardous substances at or from the landfill.[6,7] The goal of the RI/FS is to gather information sufficient to generally characterize the site and support remedy selection.

The RI Workplan for the Algoma Landfill, which was approved by U.S. EPA Region V, identified air, surface water and groundwater as potential migration pathways for landfill-derived constituents. The air pathway was considered in the workplan to be of historical interest only, since the landfill was capped in October 1983.[8]

The RI Workplan identified surface water run-off as a potential transport mechanism of waste constituents by intermittent streams draining south and east from the landfill to wetlands and cedar bogs.[8]

A conceptual model of groundwater flow identified three potential mechanisms for transporting landfill constituents to human and environmental receptors. These mechanisms are: shallow groundwater transport discharging to surface water; groundwater movement through the shallow sand and gravel aquifer to private wells; and deep groundwater movement through the dolomite aquifer to private wells.[8]

Table 1
Summary of Risk Estimates

	CARCINOGENIC RISK ESTIMATES					
Exposure Scenario	Worst Case[a]			Reasonable[b]		
	Total Risk[c]	Route-Specific Risk[d]	Routes[e]	Total Risk[c]	Route-Specific Risk[d]	Routes[e]
Current Land Use	2×10^{-5}	2×10^{-5}	Soil ingestion	1×10^{-6}	1×10^{-6}	Soil ingestion
Future Land Use/RMEI	2×10^{-5}	2×10^{-5} 3×10^{-7} 1×10^{-7}	Soil ingestion GW ingestion VOC inhalation	1×10^{-6}	1×10^{-6} 3×10^{-7} 1×10^{-7}	Soil ingestion GW ingestion VOC inhalation
Future Land Use/MEI	2×10^{-5}	2×10^{-5} 3×10^{-6} 1×10^{-6}	Soil ingestion GW ingestion VOC inhalation	5×10^{-6}	3×10^{-6} 1×10^{-6} 1×10^{-6}	GW ingestion Soil ingestion VOC inhalation

	NONCARCINOGENIC HAZARD INDEX (HI) ESTIMATE					
Exposure Scenario	Worst Case[a]			Reasonable[b]		
	Total HI	Route-Specific HI	Routes	Total HI	Route-Specific HI	Routes
Current Land Use	0.02	0.02	Soil ingestion	0.004	0.004	Soil ingestion
Future Land Use/RMEI	0.04	0.02 0.02 0.0003	GW ingestion Soil ingestion VOC inhalation	0.02	0.02 0.0004 0.0003	GW ingestion Soil ingestion VOC inhalation
Future Land Use/MEI	0.2	0.2 0.02 0.002	GW ingestion Soil ingestion VOC inhalation	0.2	0.2 0.02 0.002	GW ingestion Soil ingestion VOC inhalation

[a] WORST-CASE estimates include some data that may not be representative of the site.

[b] REASONABLE estimates include reduction of total risk by removing contributions from questionable constituents or concentrations.

[c] TOTAL RISK is the total excess upper bound lifetime cancer risk summed across all appropriate routes for each exposure scenario.

[d] ROUTE-SPECIFIC RISK is the risk contributed by the individual exposure routes.

[e] ROUTES are the exposure routes that contribute to the risk.

GW   ground water

VOC   volatile organic compound

MEI   maximally exposed individual

RMEI   reasonable maximally exposed individual

The RI consisted of separate evaluations of soils, surface water and groundwater according to the U.S. EPA CLP. CLP analytical methods and associated QA/QC were used to analyze various samples for volatile organics, semivolatiles, pesticides/PCBs and metals.[5]

Discussion

The purpose of the risk assessment was to characterize the nature and estimate the magnitude of potential risks to public health and the environment caused by the constituents of concern identified at the Algoma Landfill. The assessment considered the risks which might exist to exposed populations under current site conditions and assessed potential future risks by evaluating assumptions of future events or land use which might increase exposure and, therefore, risk. In both the current and future land use scenarios, it was assumed that no corrective actions would occur at the site; thus, the assessment served as a base line risk assessment for the site. The risk analysis process was performed according to the Risk Assessment Guidance for Superfund: *Human Health Evaluation Manual (HHEM) Part A.*[2] The analyses were based on information collected during the Site Investigation in 1984, the RI conducted in 1988 and 1989 and the ongoing quarterly groundwater monitoring under Wisconsin solid waste authorities (NR 180).

Assessment of risks from environmental contaminants involves identification of constituents of concern, routes of migration and populations potentially exposed to the constituents of concern. This information is then integrated to estimate intake for a given population, which, in turn, can be compared to toxicological information to arrive at an estimate of health risk. Interpretation of the risk values must be made in light of the numerous uncertainties and assumptions incorporated into the risk calculation. Thus, risk values do not represent precise probabilities of the frequency of occurrence of disease. The risk values are most appropriately used to identify potential problems and to support an informed risk management decision regarding the remedy that appears to be most appropriate for a given site.

Risk assessments under Superfund are intended to "focus on providing information necessary to justify action at a site and to select the best remedy for the site."[1] The goal is to produce a streamlined assessment that facilitates determination of "what actions are necessary to reduce risks, and not to fully characterize site risks."[1] The risk assessment for the Algoma Landfill met these goals.

Results

Results of chemical analyses were used to develop a list of constituents of concern that were evaluated by the risk assessment following the guidance provided in the *Human Health Evaluation Manual (HHEM).*[1]

The risk and hazard index estimates for current and future land use exposure scenarios are summarized in Table 1. Worst-case and reasonable estimates are provided for each exposure scenario. The uncertainty in the worst-case estimates is high because some questionable data, particularly for arsenic in soils, are included in these estimates. If this questionable concentration is reduced to the next highest value, more reasonable estimates of risk result.

The reasonable estimates, while probably better estimates of total risk than the worst-case estimates, are still uncertain. The factors contributing to the uncertainty include the following:

- Using maximum concentrations to estimate average exposure concentrations

Table 2
Potential ARAR and TBCS*: Groundwater

Constituents of Potential Concern	Maximum Reported Concentration (μg/L)	WI[a] NR 140 ES (μg/L)	WI[a] NR 140 PAL (μg/L)	FED[b] DWS MCL (μg/L)	FED[c] DWS MSLG (μg/L)	DWEL[d] μg/L
Chloroethane	3	--	--	--	--	--
1,1-dichloroethane	2J	850	85*	--	--	--
Benzene	3.9	0.67	0.067*	5	0*	--
1,1,1-trichloroethane	18	200	40*	200	200*	1,000*
Butylbenzyl phthalate	22	--	--	--	--	--
Diethyl phthalate	3J	--	--	0*	--	--
Barium	166Bm	1,000	200*	1,000	5,000[g]*	--
Iron	13,100Em	300	150*	300[f]*	--	--
Manganese	400Em	50	25*	50[f]*	--	--
Potassium	26,100	--	--	--	--	--
Sodium	89,300Em	--	--	--	20,000*	--

Data Qualifier

J - Value is estimated below Contract Required Quantitation Limit (CRQL).
Bm = Reported value is below Contract Required Detection Limit (CRDL) but above instrument detection level (IDL).
Em = Value is estimated due to matrix interferences.
-- No standard, requirement, or criterion.
(a) WI NR 140 ES = Wisconsin Administrative Code NR 140 Enforcement Standard, October 1988.
(b) FED DWS MCL - Federal Drinking Water Standard Maximum Contaminant Level (USEPA, 1989a).
(c) FED DWS MCLG = Federal Drinking Water Standard Maximum Contaminant Level Goal (USEPA, 1989a).
(d) DWEL Drinking Water Equivalent Level (USEPA, 1989a).
(e) Proposed (other promulgated).
(f) = Secondary MCL.
* - TBC (To-Be-Considered Criteria).

- Exposure pathways, such as air, that were not dealt with quantitatively
- Generally using maximum exposure factors in the intake equation
- Using toxicity values with low confidence ratings and high uncertainty factors
- Not estimating risk or hazard quotient for the compounds with no toxicity values

Despite these uncertainties, the risk and hazard index estimates presented in Table 1 provide information sufficient to support an informed risk management decision regarding this site because the estimates are based on, wherever appropriate: the standardized assumptions, equations and values in the *HHEM*;[1] maximum exposure concentrations; and reasonable maximum exposure scenarios.

APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARS)

A summary of the chemical-specific potential ARARs and TBCs for groundwater at the Algoma Landfill site is presented in Table 2. The ARARs assessment for the Algoma Landfill followed the protocols outlined in the draft U.S. EPA guidance *CERCLA Compliance with Other Laws Manual, Part I*[4] and *Part II*.[2] Where more than one ARAR exist for a chemical, the more stringent value is reported in Table 2. If no ARAR exists, a TBC is reported. If an ARAR and a TBC exist, the ARAR is reported.

The potential ARARs for groundwater at the Algoma Landfill are, according to U.S. EPA Region V and the Wisconsin NR 140 Groundwater Standards, as follows: 1,1-dichloroethane, benzene, 1,1,1-trichloroethane, barium, iron and manganese. There are no potential ARARs or TBCs for the following: chloroethane, butylbenzyl phthalate, diethyl phthalate, potassium and sodium.

At the Algoma Landfill, the concentrations of 1,1-dichloroethane, 1,1,1-trichloroethane and barium are below the ARARs.

The ARAR for benzene (0.67 μ/L) has been proposed by the Wisconsin Department of Natural Resources (WDNR) to be revised to the MCL (5 μ/L). This change is expected to become effective in October of this year. At that time, the Algoma Landfill will be in compliance with the ARAR for benzene. However, if the ROD is signed before that time, the ARAR for the site will be frozen at 0.67 μ/L for benzene.

The ARARs for iron and manganese are public welfare related standards (NR 140.12) rather than public health related standards (NR 140.10). Iron and manganese are both essential nutrients. The iron standard is based on the aesthetic effects of taste and iron staining of fixtures and clothing. The manganese standard is based on taste and color.

CONCLUSIONS

The risk estimates for the Algoma Landfill Superfund site are below the 10^{-6} point of departure for reasonable maximum exposure and are within the range of acceptable risks (10^{-4} to 10^{-6} as defined by U.S. EPA[9] for worst case maximums. For both scenarios, the hazard indexes are below 1.0, the level of concern.[1] The site does not meet ARARs, however, for iron and manganese in the groundwater and it may exceed the ARAR for benzene. The revised state benzene standard is not an ARAR until after its effective date, which may be after the ROD is signed. The remediation plan based on ARARs for this site does not address the CERCLA mandate to protect public health and the environment and it disregards the stated purpose of the base line risk assessment which is to provide "a basis for determining whether remedial action is necessary and justification for performing remedial actions."[1] ARARs drive the cleanup even though risks from the site are low. The justification for remedial action is to meet ARARs which could have as their basis nonenforceable guidelines like SMCLs.

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Improving The Superfund Peer Review Process

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ABSTRACT

As part of the U.S. EPA efforts to implement the 90-Day Study, U.S. EPA Region II used the principles of Total Quality Management and worked closely with all U.S. EPA regional offices, 10 state Superfund programs and four U.S. EPA Superfund contractors to conduct a study of the Superfund program's peer review process nationwide. Some key recommendations for federal and state representatives and contractors which will enable them to improve the efficiency and quality of the peer review process include: early comprehensive planning; clear, documented and consistent communication; respect and understanding for different value systems and priorities; and achieving early agreement on applicable or relevant and appropriate requirements.

INTRODUCTION

In 1989, the U.S. EPA issued its report on the state of the Superfund program. The study entitled, *A Management Review of the Superfund Program* (also known as the "90-Day Study"), presented facts, observations and the best professional judgement of experts from U.S. EPA and several state Superfund programs, as well as information obtained through consultations with citizens, reporters, Congressional staff, industry and government representatives and communication professionals. The report contained a number of strategies and initiatives to improve the Superfund program, among them, the Superfund program's peer review process. As part of the U.S. EPA's efforts to implement the 90-Day Study, Region II was designated the lead for addressing how to improve the peer review process. ICF Kaiser Engineers (ICF KE) was retained by U.S. EPA Region II to study and analyze the peer review process nationwide and to develop recommendations for improving the process.

Designed to ensure QA/QC on both technical work and policy issues, the peer review process involves a series of internal (within the Superfund program) and external (i.e., other U.S. EPA divisions, the state and Trustees of the Natural Resources) reviews of work plans, investigative reports and decision documents. Ideally, it is a system of "checks and balances" to help guide U.S. EPA Remedial Project Managers' (RPM) activities and decisions. As we learned in the course of our interviews for this project, the term "peer review" has various interpretations. For this document, we use the term peer review as an all-inclusive term that applies to all phases and all groups and individuals involved in the review process for Superfund documents.

This paper describes the strong points as well as potential pitfalls of the peer review process and, more importantly, offers recommendations on how managers from federal and state environmental agencies and their consultants can improve this important area.

METHODOLOGY

Total Quality Management

In conducting this study, we utilized the principles of Total Quality Management (TQM): "a systematic approach to continuously improving the quality of services or products an organization produces." We defined the customers which include the U.S. EPA regions (primary customers) and the U.S. EPA Headquarters and the states (secondary customers). Our intent was to develop a document for the customers by soliciting customer input on program needs and project approaches. We relied on "the experts," or those who do the actual work--the RPMs, state representatives and contractors--because they are in the best position to know how the process can be improved. The tools that we used included analyzing and understanding work processes by creating flowcharts of each region's process; identifying causes of problems, or "cause and effect" using "fishbone" diagrams during interviews and brainstorming sessions; and focusing on improvement efforts by documenting success stories.

Table 1
Respondents

All Ten U.S. EPA Regions:
Region I, Boston, Massachusetts
Region II, New York, New York
Region III, Philadelphia, Pennsylvania
Region IV, Atlanta, Georgia
Region V, Chicago, Illinois
Region VI, Dallas, Texas
Region VII, Kansas City, Kansas
Region VIII, Denver, Colorado
Region IX, San Francisco, California
Region X, Seattle, Washington

Ten State Agencies:
California
Minnesota
New Hampshire
New Jersey
Oregon
Pennsylvania
South Carolina
Virginia
Washington

Four Environmental Consultants
CE Environmental/EC Jordan Company
ICF Kaiser Engineers, Inc.
Ebasco Services, Inc.
PRC Environmental Management, Inc.

Respondents and Survey Instrument

The following respondents were interviewed either in person or by telephone:

- 22 representatives from all 10 U.S. EPA regions
- 21 state environmental agency staff members from 10 states
- Four representatives from environmental consulting firms with extensive experience working with the U.S. EPA's Superfund program.

The participating entities are listed in Table 1.

Respondents were chosen based on personal knowledge of the investigators or from referrals. Given the schedule and need to collect candid, experiential information, this sampling method was considered most likely to yield high quality data. All those interviewed were in a position to know about U.S. EPA programs and policies. It is likely, however, that other viewpoints, problems and suggestions which we did not capture are available.

As a first step in this effort, U.S. EPA Region II requested information on the peer review process from designated leads within all 10 U.S. EPA regions. This information was used to develop a survey instrument with open-ended questions (Fig. 1). All responses were analyzed to uncover themes.

The U.S. EPA is looking at various Superfund processes and trying to effect improvements in Superfund efficiency. The 90-Day Study identified the Superfund peer review process as an area that needs improvement. U.S. EPA Region II has chosen to focus its attention on this area and plans to examine possible solutions to make the peer review process more efficient. This questionnaire will aid U.S. EPA Region II in learning about other regions' peer review processes and defining areas in need of improvement as suggested by the other regions.

1. What is your schedule for peer review activities from the FS stage through ROD; how does the process work; and who is involved?
2. Do you think that your region's current peer review process is adequate? Deficient? Excessive?
3. Are there places in the peer review process where you have consistently experienced delays and/or other problems? What do you attribute these delays/problems to?
4. Are there methods or procedures that you and/or your region have implemented or are planning to try to resolve these problems? What specifically has worked? What has not worked?
5. What could senior management either in your region or at headquarters do to assist you in the process?
6. Are there areas (e.g., administrative support, personnel, scheduling practices) that need improvement? What are they and how should they be improved?
7. If you could change one thing in the peer review process to make it more effective, what would it be?
8. Are there places in the peer review process where quality is lacking?
9. Does your region have a Regional Quality Assurance Officer? What QA/QC techniques does your region use? (e.g., document control)
10. Do you believe that your region's peer review process is consistent within your region? Consistent with other regions?

Figure 1
Regional Peer Review Processes for
Feasibility Studies and Records of Decision

RESULTS AND RECOMMENDATIONS

The following results and recommendations are divided into three categories: (1) general findings about the peer review process, (2) major delays and/or problems with the peer review process and (3) process-specific findings about each stage of the process. The general findings and major delays and/or problems are global in nature and pertain to all phases of the peer review process nationwide. The process-specific findings, on the other hand, pertain to particular characteristics of the peer review process from both a public and private sector perspective.

GENERAL FINDINGS

The Regional Peer Review Process Varies Significantly From Region to Region

The regional peer review process varies in both scope and focus from region to region. For example, many regions are dependent on both the management abilities and choices made by the RPM and the complexity of the site, for the design of site-specific review processes. Other regions rely on a more formal front-end peer review process that focuses on a comprehensive scientific internal scoping process of Work Assignments prior to issuance of the Work Assignments to the contractor.

Most Regions Are Streamlining Their Peer Review Process

Most regions are streamlining their process to promote efficiency and quality of review. For instance, one region is using standardized memoranda on which reviewers write their comments, while another has developed a transmittal form which accompanies review materials and identifies the areas for reviewers to focus on and time-frames for the review to be completed. Another region has developed a data base system and checklist of operating procedures to guide RPMs through the peer review process. Some regions rely on interim deliverables during the Remedial Investigation (RI) to troubleshoot problem areas early in the process.

Most Regions are Formalizing Their Peer Review Process

Many regions have restructured, or currently are restructuring, their peer review process to reflect a more formalized approach and to obtain greater internal consistency in their peer review process. One tool the regions are using to accomplish this formalization of review is a Standard Operating Procedures (SOP) document which outlines review procedures and key personnel.

RPMs Need to be Skilled Managers, Not Subject Matter Experts

Most regions said that the RPM needs to be a skilled manager, not a subject matter expert. The RPM is required to keep projects on schedule and within budget and to serve as the central contact between the internal reviewers, external reviewers, upper management and contractor. Therefore, RPMs need to have management training and experience with some environmental background and the support of an internal or external group of subject matter experts.

MAJOR DELAYS AND/OR PROBLEMS WITH PEER REVIEW PROCESS

RPM Management Experience and Training

Since the RPM is the primary decision-maker in the scoping, peer review and project specific management process, the success of the peer review process and remediation effort is very dependent on the abilities, experience and training of the individual RPM. Thus, lack of managerial ability, unfamiliarity with what is necessary to conduct an RI/FS and lack of training have been cited as leading to delays and/or problems with the peer review process.

State Review

Many regions reported that state agencies are reviewing the U.S. EPA's reports in more detail. The increased state review of Superfund documents has lengthened the time necessary to complete document reviews. This pattern can be expected to continue and become more pronounced throughout the regions as the Superfund programs within the state continue to develop.

Resource Constraints

Shortages of computers, copy machines and insufficient clerical and administrative support have been identified as a problem in several regions. Some of these problems are expected to be alleviated as additional resources resulting from the 90-Day Study become available to the regions.

Appropriate, Adequate and Timely Internal Review

Inter-divisional and inter-agency (e.g., U.S. Army Corps of Engineers)

reviews often are inconsistent. Specifically, since the peer review process is conducted with substantial discretion of the RPM, the variable level of guidance and direction for peer review given by the RPM to other non-Superfund divisions has resulted, at times, in inappropriate review by those divisions.

PROCESS SPECIFIC FINDINGS

Four key indicators have been identified as contributing components to a successful peer review process and, in turn, a successful remediation effort:

* Early comprehensive planning
* Clear, documented and consistent communication
* Respect and understanding for different agendas and priorities
* Achieving early agreement on Applicable or Relevant and Appropriate Requirements (ARARs)

Early Comprehensive Planning

One of the most important elements in ensuring timely, adequate and appropriate review of deliverables and an efficient and successful remediation effort, whether public or private sector initiated, is the early delineation of both a Project Team, to directly support the Project Manager/RPM in his/her efforts and a Review Team, to provide supplemental technical expertise and regulatory review (Table 2). It is crucial that a broad-based, multidisciplinary team be established in order to stimulate creative problem solving and to prevent narrow, provincial biases from dominating the planning process or to prevent an uninformed RPM from making decisions.

Table 2
Project/Review Team Members
Recommended members of the:

Project Team
Multi-disciplinary environmental personnel (hydrogeologist, civil/chemical engineer, risk assessment/toxicologist)
Senior management representation
Legal counsel
Public involvement specialist
Other appropriate parties within the federal or state agency

Review Team
Federal and state environmental agencies
U.S. Army Corps of Engineers
Department of the Interior
Trustees of the Natural Resources
Other Project Managers/RPMs with similar sites
Other appropriate parties within the federal or state agency
Local citizen groups (for sites with high public profile)
U.S. EPA Headquarters (for federal-lead sites)

For private-led cleanup projects, the Project Manager should request the lead government agency (i.e., U.S. EPA or the state agency) to schedule a meeting with those regulatory agencies that will be involved in the consultation and review process for the project. The entire Project Team and Review Team should participate in the meeting in order to facilitate team-building and to ensure clear, accurate communication of project goals, objectives, sampling protocols, expectations and regulatory requirements.

By designating a Project Team at the beginning of the project, the Project Manager/RPM would be creating a unified support network cognizant of every issue related to the site. The Project Team would vested interested in the site because of its "hands-on" involvement from the start of the project and would provide the Project Manager/RPM support, assistance and accountability through the life of the project.

In the case of federal- and state-led site cleanup, the Project Team would also help guide newer Project Managers during the peer review process, compensating for learning curves and inexperience. In the case of private party-initiated site cleanup the Project Team approach allows an early detection of federal and state preferences and ensures that costly delays and repetition of work plans and sampling events are avoided,

significantly reducing the cost of the site investigation.

The Review Team should be relied upon by the Project Manager/RPM to provide supplemental technical expertise and regulatory review. In addition, its involvement at the outset would give the Review Team more information on the site and the Superfund process itself, which, in turn, would enable the Review Team to give appropriate, substantive and specific comments to the Project Manager/RPM.

Clear, Documented and Consistent Communication

Contrary to popular historical practice, clear, documented and consistent communication amongst the various parties has been the single largest contributor to efficient, successful remediation efforts, whether federal, state or private parties initiate the response.

For federal- state-and private-led projects, Work Assignment (WA) and Work Plan Scoping Meetings should be held prior to retaining a consultant. The goal of the first scoping meeting, which will include the Project Manager/RPM and members of the Project Team, would be to develop a comprehensive WA and scope of work for the contractor and to discuss cost estimates and reporting procedures. The results of this scoping meeting and all subsequent meetings should be documented in a memorandum that is distributed to all attendees and placed in a centralized filing system. For subsequent meetings involving the Review Team, a request for exceptions to the meeting summary also should be included. This procedure will allow for early detection of miscommunication and will formally document legitimate differences. This technique will prevent avoidance behavior when faced with complex and controversial issues, for example Data Quality Objectives (DQOs), appropriate sampling techniques or ARARs.

Attendees at the initial Meeting should include the entire Project Team, Review Team, Project Manager/RPM and contractor. Issues and potential problem areas would be resolved during this meeting. Attendees also would discuss and verify the format, style and organization of each document clearly with the Project Manager.

Additionally, the team should consider potential remedial alternatives based on existing knowledge of the site. This point is important because the decisions made determine the type and quantity of samples taken during the RI and the level of quality assurance necessary to support the remediation objectives. The Project Manager/RPM would also provide the contractor, Project Team and Review Team with a schedule of upcoming activities and review cycles so that the contractor and reviewers could plan their schedules accordingly. In particularly large, complex and/or sensitive sites, the formal development of SOPs for coordination purposes has proven to be helpful.

Furthermore, the Project Manager/RPM in consultation with the Project and Review Teams should decide whether to direct the contractor to develop phased interim deliverable reports. This review method that has been successfully utilized, particularly in large and complex sites, to reduce costs and streamline schedules. Factors affecting whether to use phased interim deliverable reports during the RI/FS include:

* The size of the project, in terms of the duration of the RI/FS and the complexity of the site
* Public sensitivity and need to be regularly informed

Finally, the Project Manager/RPM and the Project and Review Teams should discuss and concur on the style, format and organization of all key documents thereby preventing disagreements late in the peer review process and multiple revisions.

A large component of the delay during the peer review process originates from inadequate direction to the contractor. By meeting with the contractor early and discussing components of the project with all the "key players," the Project Manager/RPM would provide the contractor with clear and accurate directions from which to develop the Work Plan and conduct the RI.

Respect and Understanding for Different Agendas and Priorities

One of the most significant miscommunications that occur during hazardous waste cleanups is the assumption that all parties have the same agenda, i.e., the successful remediation of a site. While in the broadest sense it is certainly true that all parties desire a successful

remediation effort, in today's complex and often contradictory regulatory climate, many differences, priorities and regulatory obligations may face federal agencies, private parties and even regulatory groups within one federal agency. It is naive to assume that good intentions and a broad public mandate to clean up the environment can or will mask the many contradictory priorities within and outside of government.

Successful Project Managers/RPMs are those that can integrate various agendas, priorities and administrative and regulatory obstacles into a schedule and plan for remediation. Recognizing these elements and then factoring them into the work plan and schedule early in the process, probably will be the single most effective technique in maintaining budget and schedule. Periodically, particularly at key milestones within the project, the priorities of the parties involved should be reevaluated.

While an agency such as the U.S. Army Corps of Engineers (COE) may express little interest at a project's outset, significant interest may be stimulated if the RI findings suggest an impact on wetlands. No matter how irrelevant or inappropriate other agendas may seem, the values, positions and authority of other state, federal and local agencies can either keep your project moving forward or stop it dead in its tracks.

Achieving Early Agreement on Applicable or Relevant and Appropriate Requirements

Agreement on ARARs and potential remedial alternatives is consistently a source of conflict between federal and state agencies, Trustees of the Natural Resources, environmental groups, potentially responsible parties (PRPs) and the general public. Typically, these conflicts occur at the very end of the process when the Proposed Plan is being developed and presented for comment.

To avoid the delays inherent in that conflict, ARARs and potential remedial alternatives must be discussed and agreed upon much earlier in the process. In fact, the Project Manager/RPM and Project and Review Teams should discuss ARARs as early as the Work Plan Scoping Meeting to mitigate "last-minute" conflicts or major changes, facilitate maintaining the project schedule and prevent any ARARs from being overlooked.

ARARs and potential remedial alternatives should be finalized by the Feasibility Study (FS) Scoping meeting. At this meeting, attendees would define the problem and concur on remediation goals, cleanup levels and affected media requiring cleanup. As was mentioned earlier, formal memoranda or letters of agreement for key decisions and ARARs agreed upon at these scoping meetings should be prepared and distributed to the attendees and upper management. Formalization of these decision points provides guidance to inter-divisional reviewers in delineating the parameters of their review and keeps the FS focused on project objectives.

Upper management officials, who are the key decision-makers, should be brought into the process of establishing ARARs, cleanup goals and remedial alternatives early so that they are familiar with the project goals, remedial objectives and areas of concern as voiced by the various agencies and division representatives present at the early FS meeting. By including the key decision-makers early in the project planning phase, the Project Manager/RPM will avoid time and cost delays, last minute disagreements and misunderstandings. Upper management, in addition to having a broad view of policy issues, often has significant preferences for presentation and organization. Consulting these key managers early will reduce the likelihood of substantial revisions at the last minute.

Lastly, lack of public acceptance of potential remedial alternatives can extend public comment periods and delay the peer review process. The public is not often considered a "key reviewer," though it actually is and public review and acceptance of the Proposed Plan is an important component to the successful and timely completion of a remediation effort. Early and clear communication of site issues during the process, including ARARs and potential remedial alternatives, allows the public to "own" portion of a proposed remedy and increase public acceptance. Public review can be accomplished by enlisting the aid of citizen advisory groups, conducting public or small group meetings after the completion of the RI but prior to the evaluation of alternatives in the FS and/or publicizing the availability of Technical Assistance Grants (TAG) which often are under-utilized.

Soil Cleanup Goals for Total Petroleum Hydrocarbons

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ABSTRACT

Spills of petroleum product cause contamination of soil, surface water and groundwater and can lead to human health impacts. Soil is remediated at spill sites to prevent impacts to public health. This paper presents a survey of criteria used by the southeastern states to determine soil cleanup levels for petroleum releases and the rationale for selecting these levels. Experience at a site in North Carolina is used as an example to evaluate state cleanup levels for petroleum releases.

Total petroleum hydrocarbons (TPH) is an analytical test used to determine the presence and extent of spilled petroleum products (gasoline, waste oil, etc.). Cleanup levels usually are developed for a specific compound based on human health or environmental effects. Since TPH detects a mixture of hydrocarbons, different cleanup levels have been developed using various rationales. This variability presents a problem for owners, contractors and consultants implementing cleanup at petroleum-contaminated sites. Requirements differ from state to state, in different areas of the same state or in the field based on site conditions.

Cleanup guidelines for petroleum releases were obtained from the eight states within U.S. EPA Region 4. A comparison is made of the guidelines and rationales used for setting guidelines. All states indicated soil criteria were set to prevent impacts on the groundwater, as an existing or future drinking water supply. Evaluation of data from a case study indicates that TPH is useful in evaluating the extent of a spill but does not focus cleanup on areas of greatest public health concern as indicated by BTEX. A case study shows that the area indicated for remediation based on a state criterion of 10 ppm for BTEX (South Carolina and Tennessee) is less than half of the area indicated by a cleanup level of 100 ppm TPH (Alabama, Georgia and Tennessee) and about one fifth the area indicated by a cleanup level of 10 ppm TPH (North Carolina). Cleanup criteria are inconsistent between states, which can result in substantial differences in the extent and cost of remediation.

INTRODUCTION

Public health and environmental impacts from releases of petroleum products represent a significant problem. In the states within U.S. EPA Region 4, investigated in this report, as well as in many other states, petroleum releases have been shown to be the cause of the largest number of site investigations. Contamination by petroleum products is of concern due to potential health and environmental effects from some constituents which adsorb to soil or migrate into air or groundwater. This paper reviews established cleanup levels used to remediate organic compounds in contaminated soils. While criteria for metals are available, this paper only evaluates criteria for organic compounds.

There are no federal standards for soil cleanup. Individual states have promulgated their own standards or guidance levels to determine whether remediation of soils is necessary. Various factors go into the selection of cleanup levels. These include the composition of different petroleum products, geological and hydrogeological characteristics of the site and land and water uses in the area. TPH analysis has been used to determine if soil cleanup is necessary. This analysis does not specifically identify concentrations of contaminants that pose a health risk.

IDENTIFICATION AND CHARACTERIZATION OF CONSTITUENTS IN PETROLEUM PRODUCTS

Petroleum products include a wide range of fuels and oils such as crude oil; natural and liquified gases; gasolines; middle distillates such as kerosene, jet fuel, diesel fuel and heating oils; lubricating oils; and residual oils. This paper considers those in liquid form at standard temperature and pressure. The chemical composition of different fuels and oils varies and in most cases is not completely defined; the composition varies depending on the type of crude oil and fractionation process used to produce the product. Constituents include paraffinic, naphthenic, aromatic and sulfur-containing hydrocarbons; some nitrogen and oxygen-containing compounds; and a variety of metals.[1] From 100 to 150 compounds have been identified in gasoline, although more are known to be present.[2]

The most toxic components of petroleum products have been described by some as the aromatics, including benzene, toluene, ethylbenzene and xylene (BTEX), with toxicity decreasing from olefinics to naphthanes and paraffins.[1] Benzene in gasoline and carcinogenic polycyclic aromatic hydrocarbons (caPAHs) in certain heavy residual oils have also been identified as the components of greatest concern due to their carcinogenicity.[3] CaPAHs include benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene and indenopyrene.

Given the range of chemicals that make up petroleum products, the behavior of oils and fuels in the environment is not fully understood. Components that are soluble in water and have low adsorption coefficients, such as aromatics (BTEX), have the greatest potential to migrate into the groundwater. Compounds with higher molecular weight (carcinogenic PAHs) are less water soluble, have higher adsorption coefficients and, as a result, tend to remain adsorbed to the soil for longer periods of time. Lower molecular weight compounds such as BTEX also have higher vapor pressures, indicating a tendency to volatilize into the air, resulting in surface contamination, or into soil pores.[3] Modeling by Fleischer et al.,[4] provides information on the environmental partitioning of thirteen petroleum constituents. Table 1 presents the partitioning of the thirteen constituents and Table 2 presents the migration pathways of the different compounds.

STATE CRITERIA

Soil cleanup criteria for Alabama, Florida, Georgia, Kentucky,

Table 1
Relative Environmental Partitioning of Petroleum Constituents

Petroleum Compound	Adsorption onto Soil Particles (%)	Volatilization (%)	Soluble Portion in Groundwater and Soil Moisture (%)
Benzene	3	62	35
Ethylbenzene	21	59	20
(n)Heptane	0.1	99.8	0.1
(n)Hexane	0.1	99.8	0.1
(n)Pentane	0.1	99.8	0.1
Benzo(a)anthracene	100	0	0
Benzo(a)Pyrene	100	0	0
Napthalene	61	8	31
Phenanthrene	68	2	10
1-Pentene	0.1	99.8	0.1
Phenol	9	0.01	91
Toluene	3	77	20
(o)Xylene	15	54	31

Source: Fleischer et al., 1986[4]

Table 2
Categories of Migration Pathways

Adsorb to Soil Particles	Volatize in Air	Solubilize in Groundwater	Multiple Pathways
Benzo(a)Pyrene	(n)Hexane	Phenol	Benzene
Phenanthrene	(n)Heptane		Ethylbenzene
Benzo(a)anthracene	(n)Pentane		Napthalene
	1-Pentene		Toluene
			(o)Xylene

Source: Fleischer et al., 1986[4]

Mississippi, North Carolina, South Carolina and Tennessee (U.S. EPA Region 4) are summarized in Table 3. All of the states set soil criteria based on the prevention of groundwater contamination. In addition, certain states have also set criteria to protect surface waters and prevent exposures to contaminated surface soils. In most cases, states will consider variances or modifications of criteria based on land use, site-specific geologic and hydrogeologic conditions and results of a risk assessment. Soil criteria are available for:

* Total petroleum hydrocarbons - 7 states
* Benzene, toluene, xylene (BTX) or BTX and ethylbenzene (BTEX) 5 states
* Halogenated hydrocarbons - 1 state
* Polycyclic aromatic hydrocarbons (PAHs) 1 state
* Volatile organic compounds (VOCs) 1 state

Three states provide different soil criteria depending on the type of fuel contamination. State criteria are discussed in greater detail below.

Alabama

In Alabama, TPH cleanup levels are only used for underground storage tank (UST) sites.[5] The soil cleanup concentration is 100 ppm TPH, provided that the soil is at least 5 feet above groundwater. At non-UST sites, cleanup is determined on a case-by-case basis. Factors evaluated are background concentrations; surrounding site conditions such as land use and well supplies; and applicable or relevant and appropriate requirements. The state's goal is to develop a reasonable program using site circumstances and potential risk.[5]

Florida

Laboratory methods of determining contamination, as opposed to field screening techniques, were rejected by the state of Florida due to the turnaround time, cost and a lack of numerical standards, as is explained in the state's guidelines document.[6] Measurement of total hydrocarbons was selected over measurement of individual compounds because toxicological data are limited and additional health effects may be identified. A flame ionization detector (FID) was chosen for measurement because it is sensitive to hydrocarbons of interest. U.S. EPA data from gasoline spill sites were used to establish that a FID reading of 500 ppm was roughly equal to a total hydrocarbons concentration of 10 to

20 ppm in soil. This concentration has been shown by U.S. EPA and the state of California to not result in adverse groundwater effects.[6] The FID measurement is made in the headspace of a jar sample. State regulations are supplemented by more stringent criteria in different counties of Florida due to local aquifer protection plans. Cleanup levels as low as 10 ppm on the FID are required in some areas.

Georgia

The main factor in selecting soil-cleanup levels for Georgia is distance from well supplies.[7] If a public supply well is within three miles or a private supply well is within a half-mile, then the cleanup level is 100 ppm TPH or 20 ppm BTEX. Groundwater contamination is assessed only where soil remediation is required. When sites are not within the distances to well supplies given above, soil cleanup is required when TPH concentrations are above 500 ppm or BTEX concentrations are above 100 ppm. In these cases, monitoring of the groundwater is required.

Kentucky

Recent state regulations include a provision to propose soil cleanup levels based on the results of site-specific risk assessments; however, since the regulations are new, no risk-based cleanup levels have been submitted to date.[8] Historically, the state has required cleanup to background levels, generally meaning to nondetectable levels. The constituents to be monitored depend on the spill material: BTEX is required at gasoline spill sites; PAHs at diesel fuel and motor fuel sites; and TPH at waste oil sites.[9] State guidelines require sampling of soil, groundwater, surface water and sediment potentially affected by contaminant migration from the site.[9]

Mississippi

A soil criterion of 100 ppm TPH is used at virtually every UST diesel fuel site. For gasoline spills and leaks, there are no criteria for TPH; instead the criterion of 100 ppm BTEX in soil is used. Land use is considered and could result in higher cleanup levels. For example, at an automotive garage or a wood preservative plant, the criterion used could be higher, given sufficient technical basis.[10] Documents are not

Table 3
State Criteria

STATE	SOIL CLEANUP LEVELS	COMMENTS
Alabama	• 100 ppm TPH in soil if more than 5 ft above groundwater	Set to protect groundwater Variances from criteria based on risk assessments
Florida	• 500 ppm on FID • 10 to 500 on FID if groundwater affected	Set to protect groundwater Dependent on location in the state, aquifer conditions and future use of the site
Georgia	• 100 ppm TPH or 20 ppm BTEX within 1/2 mile of private well or 3 mi of public well • 500 ppm TPH or 100 ppm BTEX for other cases	Set to protect groundwater Dependent on proximity to well supplies
Kentucky	• Background levels or detection limits • Analysis for gasoline BTEX • Analysis for diesel/motor fuel PAH • Analysis for waste oil TPH	Set to protect groundwater and surface water Recent changes in the state regulations include a provision for a risk assessment
Mississippi	• Diesel fuel. 100 ppm TPH in soil • Gasoline 100 ppm BTEX	Set to protect groundwater. Value could increase on site-by-site basis, based on land use
North Carolina	• TPH - 10 ppm • Halogenated hydrocarbons - Det limit	Set to protect groundwater and prevent surface soil exposure Could increase based on site sensitivity evaluation • potential for direct exposure • proximity to water table • contaminant class • soil characteristics
South Carolina	• Gasoline and light products 10 ppm BTEX • Heating oil and heavy products 100 ppm TPH	Set to protect groundwater Variances based on site-specific conditions and a risk assessment
Tennessee	• Drinking water area BTEX 10 - 100 ppm TPH 100 500 ppm • Non-drinking water area BTEX 50 - 500 ppm TPH 250-1000 ppm	Set to protect groundwater Level based on soil permeability Variances based on land use, depth to bedrock, aquifer characteristics, chemical constituents, and toxicity

available to explain the technical basis for the criteria; however, ground-water cleanup goals are associated with soil cleanup goals, indicating that the soil criteria are based on preventing migration into groundwater.

North Carolina

State guidelines state "...soil remediation shall be conducted in order to eliminate potential threats to human health and/or welfare resulting from exposure to contaminated materials and prevent further environmental degradation resulting from leaching of contaminants into the groundwater."[11] Action levels are provided for TPH (10 ppm) and halogenated hydrocarbons (detection limit). The guidelines indicate that while screening methods for VOCs, including ion detectors, are useful in the field, they cannot replace recommended laboratory analytical methods for final cleanup. A site-sensitivity evaluation (SSE) allows for higher action levels where contaminated soils are five or more feet above the seasonal high-water table or bedrock and where direct contact with the soil does not occur.[11] The SSE is based on soil pH, grain size, contaminant class, distance from seasonal high water table and bedrock, presence of a confining layer, time since the release occurred, presence of sedimentary structures and textures and presence of artificial conduits within the zone of contamination. Criteria based on site-specific conditions or a risk assessment would also be considered.[12]

South Carolina

Cleanup levels for soil in South Carolina are guidelines, not legal regulations. Criteria were developed from those used by other states in the southeast.[13] Different analyses and concentrations are used for light and heavy petroleum products. The guideline for gasoline and similar substances is 10 ppm BTEX. For heating oil and heavy substances, the guideline is 100 ppm TPH. Other factors, such as groundwater use in the area, depth to the water table and soil conditions, are assessed to determine the necessary site cleanup.

Tennessee

State criteria are dependent on whether the site is located in a drinking water or nondrinking water area and the permeability of soil in the vicinity of the site. The state provides two technical documents outlining the determination for drinking water area and soil permeability classifications. The following criteria are available.

Criteria can be modified based on other site-specific variables, however no site-specific variances have been submitted to date.

DISCUSSION

Soil criteria for TPH are available for seven of the eight states investigated and range from detection limits to 500 ppm. Protection of groundwater for use as a drinking water supply is the basis for the criteria; however, a calculation of TPH levels in soils from safe groundwater levels is not available from the states. Instead, reference to criteria used in other states within and outside of Region 4 and an interest in being as protective or more protective is made.

Guidance provided by the state of California has been cited in conversations with personnel from agencies within the states investigated. The California guidelines are based on preventing migration of BTEX into groundwater. A model is used to predict the potential for leaching of BTEX and the percentage of BTEX in gasoline and diesel fuel is used to estimate a TPH level that prevents BTEX impacts on groundwater. Other investigators have evaluated whether a commonly used TPH criterion is likely to result in groundwater concentrations of BTEX below federal drinking water standards.[3] These investigation showed, through modeling, that soils with TPH levels of 100 ppm can result in benzene concentrations above groundwater standards for some petroleum releases, specifically petroleum naphtha, gasoline and waste oils.

Compound-specific analytical testing is required by four of the states. Criteria for BTEX and PAHs have been provided, with the goal of focusing cleanup efforts on chemicals that affect human health. In some cases, such as in the state of Kentucky, a requirement to analyze for specific compounds is dictated by the type of petroleum product released into the environment, with the intent to focus the cleanup on the toxic

components felt to be the most prevalent in the petroleum product.

The state of Tennessee provides a range of cleanup levels depending on the soil permeability at the site being investigated. North Carolina goes a step further by providing a range of cleanup levels dependent upon a variety of site conditions such as soil pH, grain size, contaminant class and other conditions described above.

CASE STUDY

In August and September 1989, an investigation was conducted at a fire fighting training area within an air force base in North Carolina. The primary petroleum product used at the site was jet fuel, a middle distillate similar to kerosene with some components of light distillates like gasoline. Thirteen borings and five monitoring wells were completed. A total of 57 soil samples from the borings and monitoring wells and a groundwater sample from each of the wells were analyzed. Several seeps were observed issuing from the hillside below the site; three samples of the seeps and their associated sediment were collected. All samples were analyzed, using the U.S. EPA methods for total petroleum hydrocarbons, volatiles and semivolatiles. The data were used to write a preliminary report on site contamination.

Geologic and hydrogeologic conditions at the site are fairly simple. There is a surficial sandy aquifer 20 to 30 feet thick comprised of 90% fine to medium sand and 10% silt and clay. Underlying this is a relatively impermeable unit at least 40 feet thick comprised of 55% clay, 31% silt and 14% fine sand. The groundwater table ranges from 2 to 5 feet below ground. Flow direction is downhill in the direction of the topography. Slug tests in two wells indicate the velocity of flow is approximately 0.06 feet per day in the upper sandy aquifer.

Analysis of soil and sediment samples indicated that concentrations of TPH were present at numerous locations. Of the 60 samples of soil and sediment analyzed, 10 had TPH levels below the detection limit (4 ppm), 8 had TPH between the detection limit and 10 ppm, 15 had TPH concentrations between 10 and 100 ppm, 8 had concentrations between 100 and 999 ppm and 19 had concentrations of 1,000 ppm or higher. The highest concentration measured was 44,000 ppm.

In spite of such widespread TPH concentrations, almost no benzene was detected in the soil. Of the 60 soil samples analyzed, only 6 had a benzene concentration greater than 1 ppm and only two had a concentration greater than 5 ppm. These samples contained 6.4 ppm and 9.9 ppm benzene and occurred near the highest TPH concentrations. A review of total BTEX data indicates that 8 soil samples had a concentration greater than 10 ppm and 2 of these were greater than 100 ppm.

The high TPH concentrations did not reflect high caPAH concentrations in the soil. CaPAHs were detected in only one sample at low concentrations of 1.8 ppm for chrysene, 1.6 ppm for benzo(a)anthracene, 1.2 ppm for both benzo(b)fluoranthene and benzo(a)pyrene and less than 1 ppm for benzo(k)-fluoranthene and indenopyrene. The sample containing caPAHs was in a different location from those containing benzene.

Prior to drilling borings and monitoring wells, a soil-gas survey was conducted to determine the area of contamination. An area of approximately 55,000 ft^2 contained OVA readings greater than 500 ppm. This area is similar in size and location to the one containing BTEX readings greater than 10 ppm (Table 4). Although an OVA is nonspecific in measuring organic vapors, it was sensitive to the BTEX compounds in soil.

To illustrate how the criteria from states within Region 4 would affect

Table 4
Approximate Cleanup Areas in the Case Study

Criteria	Area (ft^2)
BTEX over 100 ppm	16,000
BTEX over 10 ppm	55,000
VOC over 500 ppm*	55,000
TPH over 100 ppm	140,000
TPH over 10 ppm	265,000

* Total volatile organic compounds as measured with an OVA.

the level of cleanup at this site. Table 4 presents criteria for BTEX, TPH and total volatile organic compounds (VOCs), as measured on an OVA and the corresponding areas of remediation. The areas indicated for cleanup based on BTEX concentrations greater than 10 ppm and OVA readings greater than 500 ppm are similar. The TPH cleanup levels of 100 ppm and 10 ppm would result in a cleanup of an area 2.5 and 5 times larger than the area required using a BTEX cleanup level of 10 ppm.

Data from the site have shown:

* Soil at petroleum-spill sites can have high TPH levels and little or no benzene present. This contain may be due in part to partitioning of the benzene so that almost all is either volatilized into air or leached into groundwater.
* High TPH levels do not indicate high caPAH levels in soil at this site where the release is mainly jet fuel.   The OVA data greater than 500 ppm correlated well with data on BTEX concentrations greater than 10 ppm. This supports work presented by Florida and its use of this field-screening method. This method provides no specific information on BTEXs and would not be suitable where a mixture of petroleum spills and solvents has occurred.
* The extent of site remediation required varies greatly depending on which state's criterion is used. Soil remediation of 140,000 ft² area would be necessary at the case study site based on state criteria of 100 ppm for TPH. Less than half that area would be remediated using a cleanup criteria of 10 ppm BTEX and about one tenth the area using 100 ppm BTEX.

CONCLUSIONS

States within U.S. EPA Region 4 have established different soil cleanup levels, using various rationales, for petroleum release sites. Soil cleanup criteria generally are based on laboratory analysis of TPH or FID measurements of VOCs. A few states provide chemical-specific criteria for BTEX and PAHs. Additional criteria are based on the type of petroleum product released, groundwater use and soil permeability. TPH criteria have been estimated based on the percentage of and the leaching potential of BTEX in petroleum products and precedence set by other states.

Cleanup criteria are inconsistent between states which can result in substantial differences in the extent and cost of remediation. Data from a site in North Carolina indicate that a soil cleanup criterion of 10 ppm for BTEX will limit the cleanup to less than one half the area required if a TPH criterion of 100 ppm were used and approximately one fifth the area required if the TPH criteria of 10 ppm were used.

If soil cleanup levels are to be based on health concerns, then analysis of toxic components of petroleum products and cleanup criteria for the

same components are needed. At sites with gasoline and light and middle distillate products, samples should be analyzed for BTEX. Evaluation of caPAH was found not to be useful at a site contaminated with jet fuel. Others have indicated that sites with oils and heavier products samples should be analyzed for caPAHs. Given the number of petroleum release sites investigated and the variety of site conditions and petroleum products encountered, a range of criteria for different chemicals in different solutions should be established.

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Hanford Site Past Practice Investigation Strategy

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ABSTRACT

The Department of Energy's Hanford Site contains over 1000 CERCLA and RCRA past practice mixed waste sites which must be cleaned up under the Hanford Federal Facilities Agreement and Consent Order. These sites have been grouped into 78 source and groundwater operable units and many of the units also contain RCRA TSD units which must be closed or permitted to operate under Washington State's Dangerous Waste Regulations. Each operable unit must undergo either a RI/FS under CERCLA or a RCRA Facility Investigation/Corrective Measures Study (RFI/CMS) under the RCRA Corrective Action Program.

The complexity of working with mixed wastes, the need to conduct numerous RI/FSs simultaneously and the focus on obtaining large quantities of data to provide a high degree of certainty for decision-making, has caused the schedules to become very long (ranging from 3.5 to nearly 7 yr) and the costs to grow well beyond initial expectations. Further, because the initial efforts have shown that excessive time is required to gather data, the parties to the Agreement have become concerned that actual cleanup could not begin in an appropriate and timely manner. In response to these problems, a new strategy is being developed to integrate CERCLA and RCRA requirements into a singular process for Hanford, to provide for expedited response actions and to provide a streamlined study process which maximizes use of existing data for decision-making and at the same time manages uncertainty effectively.

INTRODUCTION

In May 1989, the U.S. EPA, the Washington Department of Ecology (WDE) and the U.S. Department of Energy (DOE) entered into an Interagency Agreement to provide a legal and procedural framework for cleanup and regulatory compliance at numerous hazardous waste sites at the DOE Hanford Facility located in southeastern Washington State. This Interagency Agreement, called the Hanford Federal Facility Agreement and Consent Order (Agreement), divided the Hanford Facility into four aggregate areas (the 100, 200, 300 and 1100 Areas), each of which has been included on the U.S. EPA's NPL.

Under the Agreement, the more than 1000 inactive waste disposal and unplanned release sites have been grouped into 78 past practice operable units (74 source operable units and four groundwater operable units which underlie the source units). The contamination, a result of past disposal practices and other releases, is in the form of solely hazardous waste, radioactive mixed waste and other hazardous substances defined by CERCLA.

Also covered by the Agreement are 55 RCRA TSD groups which will be closed or permitted to operate under the state's RCRA authority. Some of these RCRA TSD groups are physically located within the past practice operable units. Past practice operable units which contain a RCRA TSD unit as the primary contributor to the contamination have been designated as RCRA Past Practice subject to cleanup under the RCRA Corrective Action authority. Conversely, those operable units which involve primarily CERCLA releases are designated as CERCLA Past Practice subject to cleanup under CERCLA authority.

The Agreement requires that Hanford cleanup programs integrate the requirements of CERCLA, the federal RCRA/HWSA and the dangerous waste program enforced by the state. The Agreement includes all CERCLA removal and remedial actions and RCRA/HSWA corrective measures and requires integration of RCRA interim status compliance, RCRA permitting and RCRA closure activities which apply to the TSD units.

While the U.S. EPA maintains authority for CERCLA, WDE has received authorization from the U.S. EPA to implement the state's dangerous waste program in lieu of the federal RCRA program. In addition, the state has received authorization to implement the U.S. EPA's radioactive mixed waste program. The state does not yet have HSWA authority, and that authority remains under the U.S. EPA. The U.S. EPA is the lead regulatory agency for CERCLA Past Practice operable unit cleanup and WDE is the lead agency for RCRA Past Practice cleanup.

As a result of the complex regulatory involvement coupled with the sheer size of the cleanup program, a major challenge of the Agreement is to coordinate, in a cost-effective and timely manner, the different requirements of CERCLA, RCRA corrective action and RCRA TSD activities, in many cases at the same physical location.

The Agreement requires that comprehensive work plans for conducting either RI/FS or RFI/CMS be submitted for each of the 78 operable units according to a predescribed priority defined in the Agreement and that each operable unit be treated as a separate entity for the purposes of conducting the RI/FS. The Agreement requires that 20 RI/FS or RFI/CMS work plans be submitted to the regulatory agencies by April 1992 and that six per calendar year be submitted thereafter until all operable units are covered. RCRA Part B permit applications and/or closure plans must be submitted for all 55 RCRA TSD units by May 1996. Specific milestones are defined in the Agreement for the near-term work plans and RCRA permit/closure plans. A major milestone is included in the Agreement for completion of all RI/FS (RFI/CMS) by 2018.

Experience to Date

The experience gained to date on developing the work plans and permit applications has shown a need for refining the strategy of RCRA/CERCLA integration beyond that specified in the Agreement to provide for greater uniformity in the applicability of requirements

to the Hanford Facility. Because of the complexity of working with mixed wastes, because the need to conduct numerous large RI/FSs simultaneously strains available resources, and because the Agreement requires data collection which provides a high degree of certainty for decision-making, the schedules for the initial few RI/FSs have become very long, ranging from 3.5 to nearly 7 yr. For the same reasons, the costs of the RI/FS programs have shown growth well beyond initial expectations. Further, because the initial work plans have not provided for any cleanup actions to commence until after the ROD following the RI/FS, DOE and the regulatory agencies have become concerned that too much time and resources would be spent before evidence of actual cleanup could be demonstrated.

The lessons learned from development of the first few work plans have also shown that there is a need to more closely integrate source and groundwater operable units such that the information gained from each of the investigations is in sync and available for input into the source and groundwater risk assessments to be conducted in parallel. Also, since a groundwater operable unit covers an area which encompasses several source operable units, many of which are scheduled for investigation much later in the program, there is a need for early identification of the specific sites within each operable unit which are significant contributors to groundwater contamination. The three parties to the Agreement acknowledge that these significant contributor sites, even though not scheduled to be addressed for a long time, should be brought forward into the overall investigation and risk assessment for the aggregate area.

All parties to the Agreement have now recognized that past practice investigations must be managed and implemented under one characterization and remediation strategy regardless of the regulatory agency lead and the applicable regulations (CERCLA or RCRA Corrective Action). A need also has been identified to better coordinate and integrate past practice investigations and schedules with RCRA permitting and/or closure activities.

Finally, the long schedules and resultant high costs associated with traditional past practice investigations have given the parties a new perspective on the need to streamline the RI/FS and RFI/CMS processes.

Armed with the knowledge gained by past experience, the parties to the Agreement have set out in a cooperative effort to formulate a new strategy for addressing Hanford's cleanup problems which would streamline the programs for greater schedule and cost-effectiveness while minimizing lengthy investigations and paper studies.

STRATEGY

The acceptability and use of existing environmental data is a pivotal element to making the RI/FS process work more efficiently. There is a huge body of existing environmental information at Hanford dating back to the beginnings of the facility in the early 1940s. While much of the data were not collected under the rigorous procedures in use today, there exists a wealth of information. Although the data utility could be limited if viewed only for the utility and validity of individual data points, taken as a whole, the data are good for showing trends, for use in planning and possibly for making action decisions. Making maximum use of existing data and providing for uncertainties in the decision-making process would reduce the number of new samples required, which would in turn allow expediting treatability and feasibility studies as well as cleanup actions. Accepting that a level of uncertainty will ultimately exist in the data and data analyses for each decision is imperative if the process is to be streamlined.

Remedial investigations tend to be conducted for long periods of time because data uncertainty makes the highly subjective decision of when to stop sampling very difficult and hard to defend.

Methodical approaches for addressing the issues of data acceptability and uncertainty will draw from two existing concepts: the U.S. EPA's Management Systems Review[1] (MSR) and the Observational Approach.[2] The MSR concept proposes to limit field sampling episodes by defining objectives and acceptable uncertainty through structured planning and quantification. The Observational Approach proposes to address uncertainty of data and data analyses in the decision-making process by first defining the expected (probable) conditions and reasonable deviations to those conditions. The decision can then be

proposed with contingencies defined to address the probable deviations. The uncertainties remain, but the uncertainties are now quantified and contingencies are in place such that timely action can proceed without first having to conduct lengthy investigations and studies.

Three basic tenets of the observational approach are:

- Characterization should be undertaken for a specific purpose, such as the selection of a remediation technology, not just to study contamination or site characteristics
- More data do not necessarily lead to less uncertainty
- Convergence on a response action as early as possible is the goal.

Acceptance of uncertainty, within reasonable constraints, and reasonable contingency planning are synergistic in this approach.

The U.S. EPA Management System Review identifies a process to expedite the feasibility and treatability study processes. Feasibility studies are proposed to be initiated in the scoping stage, where possible, and are limited to as few realistic technologies as possible. In this way, evaluation of remedial alternatives becomes a process of starting with what is likely to work (based on existing information) and making adjustments later if significantly different contaminants or conditions are found. This approach has considerable advantage over the traditional methods of identifying and screening large arrays of alternatives and justifying why the unselected alternatives are unlikely to work. Early consideration of probable remedial technologies and alternatives thus allows focused data collection to obtain only the data needed to evaluate and implement the most probable remedial alternatives, thus limiting multiple field sampling episodes.

The MSR also proposes to conduct treatability studies during the early stages of the RI. Since treatability testing is costly and time consuming, a limited number of promising technologies, identified in the early feasibility studies, would be tested.

Another major aspect of the Hanford strategy is the initial evaluation of existing data on an aggregate area basis. These aggregate areas would provide the basis for detailed assessment of all operable units contained within the aggregate area prior to the development of RI/FS or RFI/CMS work plans. The aggregate area would be delineated to encompass the geography necessary to define and understand the local hydrologic regime, the distribution and migration of contaminants emanating from the target source terms, the interaction of those source terms and the area necessary to provide defensibility for both conceptual and numerical models. Existing data would be gathered and interpreted for the entire aggregate area. These data include all that are normally presented in RI/FS reports. The quality of existing data would be assessed and any need for verification would be identified. Conceptual models would be developed. Data needs would be assessed for: full development of the conceptual model; input to numerical models that assess performance and risk; and completion of site characterization, treatability studies, etc. Process information for the facilities would be gathered and assessed so that contamination potential is factored into site characterization.

Having defined the key concepts to be followed, the strategy now ties the concepts together into a methodical approach to decision-making. Paths are defined for conducting the decision process to tailor studies to site-specific conditions, situations and regulatory requirements. The objective here is to find the shortest path to a decision on a permanent solution to the problem and the shortest path to interim remedial actions or removal actions which start solving the problem as quickly as possible. Each path in the decision process constantly searches for the minimal amount of validated data adequate to justify the decision and provide confidence that the proposed solution will solve the problem. Uncertainty is recognized, but a process is in place to manage that uncertainty by providing contingency solutions.

The approach thus developed, which is referred to as the Hanford Past Practice Strategy, is embodied in the decision flow chart given in Figure 1. The decision chart encompasses an aggregate area as the basic unit for study and application of the principal concepts of the strategy. Each of the major elements and decision blocks of the chart is described below:

The Aggregate Area Management Study

In the first element of the strategy, an Aggregate Area Management Study (AAMS) is performed for a given aggregate area. The AAMS is similar in nature to a scoping study as defined in 40 CFR 300.430(b) and proposed 40 CFR 264.511. Both of these regulations are designed to characterize the release of hazardous substances at sites considerably less complex than Hanford. The intent of the AAMS is to:

- Assemble, validate and evaluate existing data
- Identify the need for interim response actions
- Identify likely contaminants, response scenarios and likely remedial technologies, i.e., perform a limited feasibility study
- Focus and minimize new work
- Identify data gaps and uncertainties
- Provide for the opportunity to perform limited new site characterization work if critical data gaps exist and/or uncertainty needs to be reduced. This procedue is similar in concept to Preliminary Assessment/Site Investigation (PA/SI) studies or the RCRA Facility Assessment (RFA) process
- Build defensible conceptual models for further site characterization and for the development of performance assessment models and proposed remedial actions

A key element to the AAMS process is conduct of a limited FS. Existing site and contaminant knowledge would be used to identify and screen likely remedial alternatives as early as possible. Early identification of remedial alternatives and technologies allows for focused data collection during early preliminary studies or during the early RI phase.

The AAMS culminates with the AAMS Report. This document, similar to RI/FS or RFI/CMS reports, contains the knowledge gained from the AAMS. The intent of the report is to present to the regulators and to the public data and analyses so that specific additional studies and analyses can be agreed upon.

If an AAMS Report is prepared, it would be fully integrated with subsequent operable unit work plans which would be focused on confirmatory or verification studies. The AAMSR would address the entire aggregate area, whereas the RI/FS (RFI/CMS) work plan would only address those sites or operable units for which additional work is necessary.

Expedited Response Actions

Concurrent with the AAMS, and throughout the duration of the AAMS, the question of whether an expedited response action is justified would be addressed. The assessment of this question would be iterative and continuous as new data are collected and analyzed. Expedited response actions (ERA) are one of several methods the U.S. EPA is looking at to improve the efficiency and effectiveness of Superfund response actions.[3] Revisions of the NCP redefine the response categories of removal actions and remedial actions so that removals now include all activities formerly considered immediate removals, planned removals and Initial Remedial Measures (IRMs). The purpose of the ERA is to accomplish rapid cleanups by streamlining the RI/FS process for operable units or sites where the most effective mitigation method is readily evident.

If there is justification for an ERA, then it must be decided whether immediate action is justified because of an imminent and substantial endangerment situation or whether an expedited response action is necessary but not time-critical.

The data would be assessed and judgement would be applied to evaluate the potential threat to human health (public and Hanford workers) and the environment. Consideration would be given to the immediacy and the magnitude of the threat, the nature of available actions and the implications of delaying the action until after the ROD is issued. In addition, the value gained from implementing the action would be evaluated in light of impacts to the overall Hanford cleanup effort.

If an imminent and substantial endangerment situation is found to exist and the decision is made to perform a removal action, the action would not preclude continuation of the AAMS. The AAMS would proceed in tandem with the abatement process. To respond rapidly,

activities would be carried out in parallel. These activities would include collection of data relating to selection and design of the preferred remedial alternative. Performance standards would be set by the regulators within their regulatory authority.

An assessment would be made of the removal action performance when it is possible to do so. If performance is judged adequate to justify terminating the remedial investigation process, a limited feasibility report and a risk assessment adequate to support the no-further-action decision would be prepared to support the record of decision. The decision to terminate the RI process would be made by the lead regulatory agency in consultation with the other regulatory agency.

A removal action which does not involve an imminent and substantial endangerment situation could cover a wide range of actions. Such action might involve relatively simple actions such as removal of surface contamination or buried drums. Other cases might involve relatively complex and more significant actions such as pump-and-treat groundwater cleanup efforts for source containment or mass reduction, in situ stabilization of waste sources, or managing groundwater injection and withdrawal to stabilize contaminant plumes. Such actions might also be designed to assist in gathering data useful in later feasibility or treatability studies if and when further action becomes necessary. Analogous to the previous discussion concerning imminent and substantial endangerment abatement decisions, these non-time-critical removal actions would not necessarily stop the ongoing investigation process. The investigation would continue in parallel to the removal action.

RI/FS

Once the AAMS Report is issued, a decision would be made whether to proceed with a full RI/FS or whether one or more elements could be bypassed depending upon the state of knowledge at that point. If sufficient validated data exist from the AAMS to complete a more formal FS without conducting a full RI, then the path diverts to completing the FS and writing the FS report. If necessary, additional focused field work could be done to obtain only those validated data necessary to support and complete the FS.

The fundamental principle involved here is that it is not necessary to fully characterize a site before cleanup decisions can be made. The NCP and proposed RCRA Subpart S regulations do not actually require completion of the RI/FS or RFI/CMS before taking corrective actions, i.e., these are only means to an end. The requirement is only that sufficient information be known from which a defensible decision (the ROD) can be made. This requirement means that the process can be streamlined with a certain degree of risk taking shared by all parties involved.

If the AAMS shows that substantial additional validated data are necessary before the FS could be completed, then the path reverts to a more typical RI/FS or RFI/CMS process requiring a complete work plan. The objectives of the work plan would be to describe the field and interpretive techniques needed to fill gaps in the available data, provide verification of data quality (existing and new) and, if necessary, refine the conceptual model identified in the scoping studies. Information gained through removal actions, remedial actions and expedited feasibility and treatability studies also would be factored into the work plan.

Groundwater investigations would be performed under a groundwater (or aggregate area) operable unit work plan. A parallel effort covering vadose zone investigations would be included in the priority (most significant contributor) source operable unit work plan. The groundwater/aggregate area work plan would provide for a screening investigation of potentially significant source term areas outside the priority source operable unit. This approach would be taken when there is a high probability that such source terms are contributing or may significantly contribute to near-term groundwater contamination. Reprioritization of operable unit rankings might result from this process. In such a situation, it would be appropriate to consider performing a definitive and exhaustive RI/FS on the first operable unit of each type. Subsequent investigations would use the findings of the definitive RI/FS to refine data needs for investigations of similar operable units.

These subsequent operable unit studies would be used to verify

findings and assumptions of the primary RI/FS or RFI/CMS investigations as they apply to similar operable units, in addition to providing site-specific information necessary to support a ROD or permit modification. Documentation in work plans, investigation reports, RODs and associated review requirements would thus be reduced. Additionally, reviews of work plans and reports would be performed in parallel by DOE and the regulatory agencies. This process could significantly reduce the time required to produce these documents, thus accelerating the decision-making process.

The U.S. EPA has recognized efficiencies in expediting treatability studies when obvious technologies can be selected early in the process.[1] Once the need for treatability testing is identified in the AAMS, collection of samples needed for bench-scale treatability tests can be scheduled to occur early in the RI. Results could be available for use during detailed evaluation of remedial alternatives and would indicate whether a technology would or would not meet ARARs and other risk-based criteria. If not, there would be less time lost in the evaluation of other alternatives.

CONCLUSION

The Hanford cleanup is a highly complex and massive effort involving compliance with a great number of laws, regulations and procedures whose application and integration are virtually unprecedented on this scale. Cleanup will be long and costly. Existing regulatory frameworks for conducting studies and for making decisions must be reshaped to allow for more efficient use of existing data, for more timely cleanup actions and for better management of uncertainty.

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Waste Reduction Technical Assistance Programs: Supporting Business & Industry in Ensuring A Sustainable Future

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INTRODUCTION

Waste minimization, waste reduction, source reduction and pollution prevention are terms with one underlying philosophy: it makes far more sense not to produce waste than to develop costly schemes to control it. This concept is receiving a tremendous amount of attention these days. William Reilly has stated that pollution prevention is one of the U.S. Environmental Protection Agency's top priorities, several corporate pollution prevention programs are being highly publicized, including 3M's Pollution Pays program, and several states are considering legislation to enforce waste reduction by industry. It appears that pollution prevention will be the environmental issue of the 1990s.

Indeed, pollution prevention is an environmentally sound strategy for companies to control their waste production. But pollution prevention is not just an environmental issue; pollution prevention is an economic issue. Pollution prevention is the premier waste management strategy because, unlike pollution control which costs money, pollution prevention saves money. Reduction in the production of wastes reduces treatment, transportation and disposal fees, energy and fuel costs, water and raw materials expenses, long-term liability and insurance, and the administrative costs of record-keeping and reporting requirements. The "waste" in waste minimization is not just waste material, but wasted resources and money. It is rather self-evident that producing less waste reduces all the costs associated with wastes. However, less evident is the fact that the analysis of industrial processes involved in identifying pollution prevention opportunities almost always results in a higher quality product, greater process efficiency and less process downtime. These process advantages all favorably affect the bottom line of a business.

Why then have not all businesses implemented pollution prevention programs? A common response by industry is that pollution prevention is a highly technical issue requiring research to identify new and innovative methods to institute pollution prevention techniques. Pollution prevention thus is viewed as requiring major process changes and the installation of capital-intensive equipment. Yet experience has shown that some of the greatest gains in pollution prevention are made with little or no capital expense, and data indicate that waste generation across all industries can be reduced by 50% with existing technology.

What has become apparent is that the greatest barrier to pollution prevention is old attitudes. For many years, we have thought of waste management as an unfortunate cost of doing business. We grudgingly hired engineers to handle waste control problems and invested a great percentage of our revenues into environmental compliance. As the regulations grew in number and complexity, we increased our environmental staff and budget. We are finding, however, that this is not a road which leads to a sustainable future. Industry cannot afford the costs and liabilities associated with coping with unabated pollu-

tion. The old attitudes must be replaced by the new attitude that waste reduction is a sound investment both ecologically and economically.

Where then does this scenario lead us? Very few companies can implement a pollution prevention program without assistance. The initial need is for technical assistance programs to supply the support system needed to reshape the long-held end-of-pipe perspective of today's businesses. Education, information and tools will enable the industrial community to effectively reduce their wastes. Technical assistance programs cannot provide all the answers. Pollution prevention methods are highly case-specific, and there is no single technology applicable in all situations even within a specific industrial process. Therefore, taking advantage of the enormous opportunities for pollution prevention requires that the desire to reduce waste be part of the everyday consciousness of all employees. What technical assistance programs can, and should, provide are the tools and the methodology for implementing pollution prevention techniques.

In response to the urgent need for nonregulatory technical assistance in waste minimization and pollution prevention, the not-for-profit Center for Hazardous Materials Research (CHMR) at the University of Pittsburgh operates a comprehensive, state-wide technical assistance program in Pennsylvania. Although there is room for all sectors of society to become involved in pollution prevention, there is a particularly great need for nonregulatory technical assistance programs to provide pollution prevention assistance. The fear of federal regulation authorities that permeates most of the business and industrial community continues to frustrate the best intentions of many pollution prevention programs in regulatory agencies.

CHMR was established in 1985 to provide users of hazardous materials and generators of hazardous waste with cost-effective, practical information on waste management and waste reduction. Since then, the program has expanded to include cross-media pollution prevention. Pennsylvania has a particular obligation to provide solutions to some of the pressing hazardous waste problems. Pennsylvania currently is ranked fourth in the nation in the production of hazardous waste and second in the number of Superfund sites. As an agricultural state, Pennsylvania is a major user of pesticides and fertilizers, and 60% of the population depends on groundwater for drinking water.

Funded by $35,000 in seed money from the University of Pittsburgh, CHMR set out to solve these problems in partnership with industry and government. CHMR now has a staff more than 50 drawn from industrial, regulatory and academic communities. In 1986, CHMR was awarded a $259,000 grant by the U.S. EPA to create and implement the state-wide Technical Assistance Program. This program, currently funded in part by a grant from the Pennsylvania Department of Environmental Resources, continues to focus on waste minimization as the primary method of pollution abatement.

The experience of CHMR's Technical Assistance Program has demonstrated that technical assistance services are needed to respond to businesses whether they are completely unaware of pollution prevention or have already instituted a successful program. Pollution prevention assistance can be divided into three phases: motivate, educate and support.

First, businesses that are unfamiliar with pollution prevention most often request a definition of the concept and its application. This definition of what the words mean is essential as a first step, as is preaching the pollution prevention ethic. If you do not succeed in motivating a company to pursue pollution prevention opportunities, a successful program, even if instituted by coercion or enforcement, is unlikely to be successful. It cannot be overstated that committed management and employees are essential to any pollution prevention program. Inspiring businesses, government officials or employees to embrace pollution prevention is a key challenge involving the human component of the pollution prevention picture.

Second, once inspired to pursue pollution prevention, businesses need to be educated in the tools and resources with which to proceed. It is not enough to haphazardly apply pollution prevention techniques. An understanding of the thought processes involved in pollution prevention is essential.

Third, once businesses proceed with instituting a pollution prevention program in their facility, ongoing technical support is necessary. Inevitably, questions will arise as to the availability of particular chemical substitutes or alternative technologies. CHMR's Technical Assistance Program has informational services, training and engineering services that provide a complete support system including motivation and education for pollution prevention.

MOTIVATE

To inform the business and industrial community of both the existence of CHMR's technical assistance program and to motivate companies to investigate the benefits of pollution prevention, CHMR has established a network of organizations assisting in an outreach effort including trade associations, manufacturing associations, chambers of commerce, small business development centers, industrial resource centers, Pennsylvania Department of Environmental Resources and U.S. EPA Region III.

Trade associations have proven to be a major vehicle for reaching the business community. Press releases describing the Technical Assistance Program and announcing new services are sent periodically to associations which, in turn, publicize the program in their organization's publications.

CHMR also publishes articles on pollution prevention in journals, association publications, bulletins, magazines and newsletters. CHMR's speakers' bureau provides experts on pollution prevention to speak at conferences and meetings. In these ways, CHMR reaches out to the business community to promote the value of pollution prevention.

CHMR's quarterly newsletter, *The Minimizer*, currently is mailed to more than 2,000 business people, researchers, legislators, regulatory officials and other states' waste minimization personnel. This four-page publication includes articles written primarily by CHMR staff on waste minimization techniques, recycling, new CHMR services and publications, and other environmental and health and safety issues.

The goal of these services is to inspire businesses to pursue the benefits of pollution prevention.

EDUCATE

Businesses often become convinced of the benefits of pollution prevention, but do not know where to begin. To meet this need, CHMR has established a pollution prevention clearinghouse containing fact sheets, articles, government publications, reports and manuals. The clearinghouse includes CHMR's publications such as industry-specific pollution prevention packets and fact sheets and CHMR's 300-page *Hazardous Waste Minimization Manual for Small Quantity Generators* which received the U.S. EPA Region III's Environmental Education Achievement Award. This easy-to-read manual covers topics such as: how to conduct a pollution prevention audit, financing a pollution prevention program and sources for waste reduction and recycling equipment.

CHMR's pollution prevention seminars and workshops have been attended by more than 400 regulatory personnel, industry representatives and members of the academic community. The first state-wide conference in Pennsylvania addressing waste minimization issues, held by CHMR in the fall of 1987, attracted representatives of government, business, academia and public interest groups. The second conference is being planned for the spring of 1991.

For more complete training, CHMR has developed a 16-hour pollution prevention workshop designed to improve participants awareness and ability to incorporate pollution prevention concepts in their day-to-day job functions. Workshops have been customized for the U.S. EPA regulatory personnel, industry representatives and students. Participants receive a mix of classroom instruction and interactive group exercises with an emphasis on learning the thought processes required to identify pollution prevention opportunities and on recognizing the role of human attitudes in implementing pollution prevention in the workplace. Through workshop activities, participants gain the tools and resources necessary to perform a pollution prevention assessment and institute a pollution prevention program in their own facility.

SUPPORT

Once a business has embraced the pollution prevention perspective, an avenue for ongoing support is essential. The lifeline of the Technical Assistance Program is a confidential, toll-free telephone number (1-800-334-CHMR) which receives more than 150 calls per month. Callers receive answers to their questions on pollution prevention issues as well as regulatory and other environmental and health and safety topics. The Center's telephone is staffed by CHMR technical staff who can either provide the technical assistance immediately or, in the case of more complicated questions, research the particular problem and provide the necessary information within an average of 2 hours.

The telephone center uses a computerized data base system for the logging and tracking of calls. This data base allows the staff to search previous calls for information obtained which may be applicable to other calls. The database includes information about the caller's business such as address, number of employees, business type (SIC code) and inquiry topic. As CHMR develops new services or obtains more updated information, specific mailing lists are developed to target mailings to callers who are in need of the particular service or information.

By providing CHMR with a direct communications link with the business community, the telephone center enables CHMR to design programs in response to the needs that are identified through the calls. Each month internal reports are produced which summarize the types of callers and their concerns or questions. This information is then used to target additional support programs to meet the needs identified by the callers.

The toll-free number is particularly useful to individuals who have specific questions that develop concerning the institution of a pollution prevention program or specific techniques. This type of ongoing support is essential. If a question or problem is too complex to answer by telephone, CHMR provides on-site pollution prevention consultations and assessments. CHMR pollution prevention specialists review facilities' waste streams and processes, identify pollution prevention options and advise facilities how to begin or continue a pollution prevention program. Assistance may include training for employees or the development of guidance manuals. In some instances, research into available alternative technologies for a particular process may be conducted.

To address the need for financial support in demonstrating and instituting pollution prevention technologies, CHMR is managing the U.S. EPA's Office of Small and Disadvantaged Business Utilization's "Pollution Prevention By and For Small Business" grant program. Under this program, approximately $800,000 in grants will be made available to small businesses over a 2-year period.

CONCLUSION

The key challenge for business and industry today is ensuring a sustainable future. Economic development and environmental protection

cannot remain mutually exclusive. To support the business and industrial communities in this effort, technical assistance programs must supply the necessary services for motivating, educating and supporting these communities in their pollution prevention efforts. The opportunities for pollution prevention are great, and it will be through the cooperation of business, government and academia that full advantage of these opportunities can be taken. The present and future role of technical assistance programs is pivotal in this venture. With the support systems in place, all sectors of the business community can discover and implement this lucrative alternative to waste control.

Regulating Hazardous Waste on Indian Lands

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ABSTRACT

Enforcing RCRA Subtitle C regulations on Indian lands is a challenge for both the U.S. EPA and for Indian tribes. The task is to define Indian land, determine regulatory authority and identify hazardous waste on Indian lands. These issues have not been properly addressed by either the Indian tribes or by the regulatory community. As a result, hazardous waste has gone largely unregulated on Indian lands.

To correct these problems, U.S. EPA Region 5 initiated a study of Indian lands. The key goals of Region 5's study are to identify hazardous waste on Indian lands and to educate the tribal governments about RCRA. Information request letters will be sent to the tribal environmental contacts, to the Indian Health Service and to the Bureau of Indian Affairs.

INTRODUCTION

Enforcing RCRA Subtitle C regulations on Indian lands is a challenge for both the U.S. EPA and for Indian tribes. Tribal governments are considered to be sovereign entities, subject to federal jurisdiction. U.S. EPA holds a federal trust responsibility to protect human health and the environment on Indian lands. The challenge is to define Indian land, determine regulatory authority, identify hazardous wastes on Indian lands and promote technology transfer to the Indian tribes.

The term "Indian land" refers to all land within the exterior boundaries of an Indian reservation. Within each Indian reservation, however, there are several types of land ownership, including ownership by non-Indians. This variety of ownership complicates the problem of defining regulatory authority. In addition, most information about hazardous waste operations is tracked by the Hazardous Waste Data Management System (HWDMS). Partly because of errors in HWDMS, there is very little information available on the types of hazardous waste operations on Indian lands. The lack of technology transfer to Indian tribes is a problem because even if RCRA clearly delegated authority to tribal governments, the tribes would need to meet training and health and safety criteria in order to become authorized to regulate RCRA on the reservations. Currently, it would be nearly impossible for most tribes to meet such criteria.

Because of the complexity of these issues, hazardous waste on Indian lands has been addressed at only a few sites, typically after problems have been identified.

To meet the challenges described above, U.S. EPA Region 5 initiated a study of Indian lands. The key goals of Region 5's study are to identify hazardous waste on Indian lands and to educate the tribal governments about RCRA. Information request letters will be sent to the tribal environmental contacts, to the Indian Health Service and to the Bureau of Indian Affairs.

What Is Indian Land?

The problem in defining Indian land is that both Indians and non-Indians can own land on the same reservation. The Indian reservations that were created by Congress during the mid-1800s have undergone significant changes in the intervening years. Non-Indian ownership of land within reservation boundaries is a result of the General Allotment Act of 1887 (also known as the Dawes Act). The Dawes Act divided up land within reservation boundaries and allotted ownership of land to individual tribal members. The concept of property ownership was completely foreign to the Indians, and the concept of property tax was even more so. Many individual Indians subsequently sold their lands to non-Indians or lost their lands because of failure to pay their property taxes. Although allotment ceased by the 1930s, the legacy of policy legacy can be seen today in the checkerboard pattern of Indian and non-Indian ownership that characterizes most reservations.[1]

This complexity of property ownership on Indian lands adds to the problem of determining regulatory authority on Indian lands.

Who Holds Regulatory Authority On Indian Lands?

Although Indian reservations and tribal governments are considered to be sovereign entities, the question of who actually holds environmental regulatory authority on Indian lands is a very complicated issue. Until recently, there has been no clearly defined authority set forth in the environmental regulations. For example, although Section 1004(13) of RCRA includes Indian tribes within the definition of "municipality" and Section 3006 gives state hazardous waste management programs authority over municipalities, Section 3006 does not grant states authority over Indian lands.[2] The Indian Self-Determination and Education Act of 1975 clearly illustrates the intent of Congress to delegate Indian regulatory programs away from the federal government and to the tribal governments as much as possible. The contradictory language between these and other regulations creates the perception of a regulatory "gap" on Indian lands. Despite this perceived gap, the U.S. EPA still holds a federal trust responsibility to regulate hazardous waste on Indian lands. The U.S. EPA's federal trust responsibility extends over more than 83,807 square miles of Indian land and more than 100 federally-recognized tribal governments throughout the United States.

The U.S. EPA has taken the lead among federal agencies in developing policy to interpret regulations such as the Indian Self-Determination and Education Act of 1975 and the President's Federal Indian Policy (January 24, 1983). On November 8, 1984, the U.S. EPA established an Indian lands policy pursuant to the President's Indian policy. The U.S. EPA's Indian policy is based on a nine-point approach that stresses that the Agency will work directly with the tribes on a government-to-government basis, and that the Agency recognizes tribal governments

as "the primary parties for setting standards, making environmental policy decisions and managing programs for reservations, consistent with agency standards and regulations." The overall goal of the U.S. EPA's 1984 Indian land policy fits within the overall Agency goal to protect human health and the environmental quality for all people and all geographic areas in the nation.[4]

In addition to the U.S. EPA's Indian policy, several legal decisions have served to reinforce federal and tribal government authority as opposed to state jurisdiction over Indian lands. For example, in the case of the *State of Washington vs. U.S. EPA*, the Ninth Circuit Court of Appeals affirmed that the U.S. EPA, not the state, is responsible for "ensuring that federal standards are met on the reservations."[3]

Although the U.S. EPA arguably holds both the responsibility and the authority to regulate hazardous waste on Indian lands, very little work has been done on Indian lands to date. Environmental problems can be found in all media on Indian lands. On most Indian reservations, the only types of solid waste disposal are open dumping and burning of garbage, and many reservations are not able to restrict access to the dumps. The potential magnitude of this problem is just beginning to be realized by the regulatory community. There is growing concern that the magnitude of the unregulated waste may be larger than previously anticipated.

In order to address these waste problems, the U.S. EPA and the tribal governments must be able to located and identify hazardous wastes on Indian lands.

Identifying Hazardous Waste on Indian Lands

Identifying hazardous wastes on Indian lands is difficult because the Hazardous Waste Data Management System (HWDMS) data base system, which often is used to track hazardous waste generators, transporters and disposal facilities, has proven to be inadequate for tracking facilities on Indian lands. This is often because either the original Notification of Hazardous Waste form or the Part A Application form was filled out incorrectly. These two forms are the source of much of the HWDS data, and therefore the source of most errors in the data base.

A common HWDMS error that interferes with tracking waste on Indian lands is in the area of property ownership. Both the Notification and Part A application forms include codes that specify the type of ownership - whether a facility is privately owned Indian land (PI), federally owned Indian land (FI) or (M) municipal property. On the Notification form, the "M" code is used to indicate municipally-owned land. However, on the Part A Application form the code "M" is used to indicate that a facility is operated on "public, other than federal or state" land. Therefore, the M code is often incorrectly substituted for the PI or FI codes for facilities or operations located on Indian lands.

This error and other errors commonly found in the HWDMS data base make tracking hazardous waste operations on Indian lands difficult. Most RCRA implementation has been conducted through the states' programs, and since states do not have regulatory jurisdiction on Indian lands, there are very little data available to indicate what types of hazardous waste operations and facilities may exist on Indian lands.

Technology Transfer

Even if RCRA clearly delegated authority to tribal governments, the tribes still would need to meet training and health and safety training criteria in order to enforce RCRA on the reservations. Most tribes currently do not meet the equivalence and capability requirements as stated in RCRA (CITE REG), owing to a lack of resources and the absence of a program of technology transfer from the U.S. EPA to the tribes. To correct this shortfall, technical assistance must be made available to the tribes so that they can exercise their sovereign right to self-regulation. The same resources that have been made available to the states during their regulatory development should now be made available to the tribes.

REGION 5's APPROACH

PRC Environmental Management, Inc. (PRC) was asked by the U.S. EPA Region 5 RCRA Enforcement Branch (REB) to identify opera-

tions located on Indian lands that are subject to RCRA Subtitle C. These operations might then be the subjects of compliance evaluation inspections (CEI).

To identify RCRA Subtitle C operations, the U.S. EPA sorted the HWDMS data base by the ownership codes. Of the 32 Indian reservations in Region 5, seven facilities or operations were found to show either PI, FI or M codes.

PRC contacted each of the identified facilities or operations and determined that of the seven facilities or operations, only two were actually located on Indian lands and subject to RCRA Subtitle C. For five out of the seven facilities or operations, the Notification forms had been completed incorrectly. Table 1 below summarizes the data collected by PRC and the U.S. EPA. The table shows the names of the facilities or operations as they appear in the HWDMS data base. In some cases the names appeared as specific facilities, and in some cases the Notification appeared to be for the entire reservation.

Table 1
Summary of Indian Land Facility Status

Facility Name	State	U.S. EPA Notification Form Code	Located on Indian Lands?
Bookcrafters, Inc.	MI	PI	No
Champion International	MN	M	Yes (Leech Lake IR)
Fort Howard Paper Company	WI	M	Partially (Oneida IR)
Hagglunds Dennison Corp.	OH	PI	No
Koch Fuels	MN	PI	No
Lac Du Flambeau	WI	FI	Yes (Lac Du Flambeau IR)
Red Lake PHS Hospital	MN	FI	Yes (Red Lake IR)

Note:
PI = Privately Owned, Indian Land
FI = Federally Owned, Indian Land

In July 1989, PRC performed CEI inspections at the Lac du Flambeau Indian Reservation in Wisconsin and at the Red Lake Indian Reservation Public Health Service (PHS) Hospital in Minnesota. These inspections identified two small quantity generators that were previously unknown to the EPA. Both of these facilities are located on the Lac du Flambeau reservation. No additional RCRA facilities were identified on the Red Lake Indian Reservation. Both of the reservations inspected had completed their Notification of Hazardous Forms incorrectly.

The project approach was revised after the screening and inspection activities described above. The revised approach involves direct contact with reservations and coordination with various Indian related agencies, such as the Bureau of Indian Affairs and the Indian Health Service. The reservations and concerned agencies will be sent a questionnaire which will request information and assistance in identifying hazardous waste generators on Indian lands. This information request is consistent with Section 3007 of RCRA, which authorizes the U.S. EPA to collect information for enforcement purposes, and it also qualifies as a government-to-government request under the U.S. EPA's 1984 Indian policy.

The approach of coordinating among various agencies and involving the tribal governments directly is a more efficient approach than trying to access information about hazardous waste operations through HWDMS. This approach will also facilitate technology transfer to the reservations.

CONCLUSION

The issues raised in this paper have implications that reach beyond the scope of regulating RCRA Subtitle C on Indian lands. These questions must be addressed in enforcing any environmental statute on Indian lands.

The U.S. EPA Region 5 REB has initiated a study to collect data on the types of operations located on Indian lands and subject to RCRA Subtitle C. As part of this study, an information request letter will be sent to all tribal environmental contacts. This letter will be written both to request information and to provide information and should serve to educate the Indian tribes about RCRA and waste problems in general.

The study conducted by Region 5, and other programs being im-

plemented by Regional Indian Work Groups in other Regions, will help to close the "regulatory gap" on Indian lands. By identifying hazardous waste generators on Indian lands, and promoting technology transfer, the U.S. EPA to can better meet its objectives of working on a "government-to-government basis" with tribal governments, while protecting human health and the environment on Indian lands.

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DISCLAIMER

The contents and conclusions of this paper are those of the author and do not necessarily reflect those of the U.S. EPA.

Active Site Discovery Using a Geographic Information System

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ABSTRACT

Concerns about the potential universe of CERCLA sites has led the U.S. Environmental Protection Agency to take a more active role in determining those sites currently not included in the U.S. EPA site inventory. As a result, Ecology and Environment, Inc. (E & E) was tasked to develop an active site discovery mechanism in the State of Oregon.

The discovery mechanism developed by E & E consisted of: utilizing several discovery methods to obtain a complete inventory of active or abandoned potential Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites; screening and locating the new sites; and focusing on vulnerable areas as defined by the revised Hazard Ranking System (rHRS) model. To accomplish the latter, a Geographic Information System (GIS) was used to store, manage, manipulate and display the gathered data necessary to model rHRS factors. Preliminary Assessments (PAs) were performed on a representative fraction of the discovered sites in an attempt to evaluate the correlation between the GIS model vulnerability values and the rHRS model scores.

INTRODUCTION

The U.S. EPA is in the process of evaluating different mechanisms for discovering potential Superfund sites. Ecology & Environment (E & E) was tasked by the U.S. EPA to develop an active site discovery mechanism to be applied in the State of Oregon. The main objective of the Region 10 Pilot Site Discovery Project was to identify potential CERCLA sites in areas considered vulnerable based on rHRS model factors (proposed Rule 53 FR 51962).

Current methods of site discovery used by the U.S. EPA typically consist of identifying potential Superfund sites through a combination of citizen's complaints, referrals from other government branches and agencies and identification through the Preliminary Assessment/ Site Inspection (PA/SI) work (Table 1). These site discovery methods are considered passive since they do not require regions or states to use a systematic approach in identifying potential hazardous waste sites. This system of site discovery has worked reasonably well to date, given the U.S. EPA's current inventory of potential hazardous waste sites. However, passive methods are dependent on random site discovery and on individuals to channel the information to the appropriate agency. Active site discovery requires the dedication of resources to find previously undiscovered hazardous waste sites (Table 1). Previous active discovery efforts have been limited to specific geographic areas (i.e., cities, counties and sole-source aquifers) and/or specific contaminant/facility types (i.e.,

known area-wide problems related to wood preserving, coal gasification, coal fields, and solvent and TCE contamination).[2][4][7]

Table 1
Passive versus Active Discovery Methods

Passive Site Discovery Mechanisms	Active Site Discovery Mechanisms
Citizen Complaint	Remote Sensing
Referrals by Other Agencies	Aerial Photograph Interpretation
PA/SI Byproduct	Selected Geographic Area
Responsible Party Report	Historical Searches
Property Transfer Regulations	Selected Pollutant Searches
Solicitation of Information (Random)	Solicitation of Information (Specific)
Response to Emergency Situation	Selected Industry Study
Survey Review	File Review
	Documentation Search

The active discovery mechanism developed targets a variety of industries as potential CERCLA sites. This mechanism utilized several discovery methods to obtain a complete inventory of active or abandoned potential CERCLA sites, screened and located the new sites, and delineated vulnerable areas using a Geographic Information System (GIS).

SITE DISCOVERY CONCEPT

A GIS was used to store, manage, manipulate and display data necessary to model and map the air, surface water and groundwater pathway factors of the rHRS model. Areas mapped using GIS were ranked in an attempt to correspond with rHRS model values so that areas delineated as highly vulnerable correspond to areas most likely to receive significant weighting under the rHRS model if contamination is present at a site located in these areas.

Site discovery methods consisted of using a general documentation search for all active facilities in Oregon by specified Standard Industrial Code (SIC) and an abandoned site search in areas considered highly vulnerable. The SICs selected for general documentation search represent those facilities commonly found on the NPL and the CERCLA Information System (CERCLIS), and typically generate hazardous wastes. Sites discovered using the various methods were screened in a series of steps to generate a final list or universe of potential CERCLA sites.

This paper provides a summary of the site discovery mechanism completed for the Willamette Basin, Oregon. The Willamette Basin was selected as the first basin in Oregon to implement this concept

since it contains approximately 70% of the discovered sites on the final list and 80% of Oregon's population.

IMPLEMENTATION OF SITE DISCOVERY CONCEPT

GIS Model Development

A GIS can be defined as an organized collection of computer hardware, software, geographic data and personnel designed to efficiently capture, store, update, manipulate, analyze and display all forms of geographically referenced information.[6] ARC/INFO GIS software was used to develop the GIS vulnerability model. In ARC/INFO software, a digital version of a single map sheet layer is the basic unit of storage and is termed a "coverage." A coverage contains both the locational data and thematic attributes for map features in a given area.[6] In this paper, a "coverage" and a "map" are interchangeable terms.

Data used in the GIS vulnerability model were acquired from several sources, such as: the U. S. Geological Survey (USGS); the United States Census Bureau; Oregon Fish and Wildlife; and the U.S. EPA. The rHRS model uses site-specific and waste-specific information; therefore, it was necessary to simplify the model in order to integrate rHRS factors into the GIS vulnerability model.

The rHRS model groundwater, surface water and air migration pathways were evaluated for nonsite-specific factors. The pathway factors were grouped into two primary categories: contaminant migration factors and target factors. For a given migration pathway, a GIS pathway module was developed to account for contaminant factors. Target factors were then integrated into the GIS pathway modules. Each migration pathway was developed independently resulting in a pathway vulnerability coverage. For each pathway map (i.e., groundwater, surface water and air) the pathway vulnerability values were standardized to a 0 to 100 point scale. These three pathways were then overlayed to produce an overall vulnerability coverage. Five ranking categories were chosen for each vulnerability coverage. Table 2 summarizes these ranking categories.

Table 2
Ranking Categories of GIS Vulnerability Coverages

Category	Percent Distribution of Pathway Vulnerability Values
Low Vulnerability	Lower 10
Moderately Low Vulnerability	Lower 20
Moderate Vulnerability	Middle 40
Moderately High Vulnerability	Upper 20
High Vulnerability	Upper 10

Groundwater Pathway Module

Two options exist for evaluating the groundwater contaminant migration factors. The first is to use the rHRS environmental factors (i.e., net precipitation, depth to aquifer, hydraulic conductivity and sorptive capacity), weight them according to the rHRS model and combine the weighted factors. The second option is to use the parameters in the DRASTIC model to map groundwater contaminant migration factors. The DRASTIC parameters (i.e., depth to aquifer, net recharge, aquifer media, topography, impact of vadose zone and hydraulic conductivity) reasonably correlate with the rHRS factors (Table 3). DRASTIC was selected because of wide use of the model by USGS, the U.S. EPA and other government agencies.

DRASTIC parameters were weighted and combined to create a contaminant migration coverage. Table 4 summarizes groundwater pathway factors and weights. Since the data were not available, two DRASTIC factors (depth to aquifer and topography) were not used.

The groundwater pathway target factor was accounted for by using a coverage of population served by municipal wells. The well locations were "buffered" to a 1-mile radius by changing a point representation to an area representation of a circle with a 1-mile

radius. A 1-mile radius buffer was chosen by examining the rHRS distance weights. The groundwater drinking population necessary to maximize the rHRS groundwater target score is 32,000 at a 1/2-mile distance; 62,000 at a 1-mile distance; and 115,000 at a 2-mile distance. It was determined that the 1-mile radius was the best compromise distance for rHRS dilution weights.

Table 3
rHRS Model and Drastic Model Weight Comparison

rHRS Parameter Weights (%)*	DRASTIC Parameter Weights (%)*	
Depth to Aquifer (35%)	Depth to Aquifer (22%)	
Hydraulic Conductivity (35%)	Aquifer Media (13%) Vadose Zone (22%) Hydraulic Conductivity (13%)	(48%)
Net Precipitation (20%)	Net Recharge (16%) Topography (4%)	(20%)
Sorptive Capacity (10%)	Soil Media (9%)	

* Numbers in parenthesis represent the percentage of the total maximum value possible for the rHRS and DRASTIC models.

Table 4
Groundwater Vulnerability Pathway Factors

Contaminant Migration Factors/DRASTIC (PGV)	Weights
Soil Media (SM)	2
Aquifer Media (AM)	3
Net Recharge (NR)	4
Vadose Zone Media (VZM)	5
Hydraulic Conductivity (HC)	3
Topography	
Depth to Aquifer	-
Groundwater Pathway Vulnerability	
Groundwater Population Factor (PF)	2
Contaminant Migration Factor/DRASTIC (PGV)	5

- Not used.

This groundwater-use population coverage was then overlaid with the contaminant migration coverage (DRASTIC) to create a groundwater pathway vulnerability coverage (Maps 1 and 2). Figure 1 illustrates the development of the groundwater pathway vulnerability module.

Surface Water Pathway Module

To incorporate the surface water pathway contaminant migration factors, a model was developed that takes into account rHRS factors for which data were available. This model incorporated soil texture, 2-year 24-hour rainfall and land-use type. These factors were overlaid and weighted according to rHRS factor weights to develop a surface water contaminant migration coverage. In order to define run-off limits, it was necessary to incorporate an areal hydrographic boundary. This hydrographic boundary, a sub-sub-basin coverage, represents drainage areas on a 1:24,000 scale.

The contaminant migration coverage was overlaid with the hydrographic boundary coverage, and an area weighted average score of the contaminant migration factor was developed for each sub-sub-basin.

The rHRS target factors used in developing the surface water pathway vulnerability module consisted of surface water use population, fish production and sensitive environments. Each target factor was overlaid with the hydrographic boundary coverage. The value of each target factor was summed per sub-sub-basin.

The target coverages were then combined with the contaminant migration coverage to produce a surface water pathway vulnerability coverage (Map 3). Figure 2 illustrates the development on the surface water vulnerability module.

INPUT DATA LAYER

RANGE	RATING
Thin or Absent	10
Gravel	10
Sand	9
Peat	8
Shrinking and/or Aggregated Clay	7
Sandy Loam	6
Loam	5
Silty Loam	4
Clay Loam	3
Muck	2
Nonshrinking and Nonaggregated Clay	1

SOIL MEDIA (SM)

RANGE	RATING
Massive Shale	1 - 3
Metamorphic / Igneous	2 - 5
Weathered Metamorphic Igneous	3 - 5
Glacial Till	4 - 6
Bedded Sandstone, Limestone and Shale Sequence	5 - 9
Massive Sandstone	4 - 9
Massive Limestone	4 - 9
Sand and Gravel	4 - 9
Basalt	2 - 10
Karst Limestone	9 - 10

AQUIFER MEDIA (AM)

(GPD / FT²)

RANGE	RATING
1 - 100	1
100 - 300	2
300 - 700	4
700 - 1000	6
1000 - 2000	8
2000+	10

HYDRAULIC CONDUCTIVITY (HC)

RANGE	RATING
Confining Layer	1
Silt / Clay	2 - 6
Shale	2 - 5
Limestone	2 - 7
Sandstone	4 - 8
Bedded Limestone, Sandstone, Shale	4 - 8
Sand and Gravel with significant Silt and Clay	4 - 8
Metamorphic / Igneous	2 - 8
Sand and Gravel	6 - 9
Basalt	2 - 10
Karst Limestone	8 - 10

VADOSE ZONE MEDIA (VZM)

(INCHES)

RANGE	RATING
0 - 2	1
2 - 4	3
4 - 7	6
7 - 10	8
10+	9

NET RECHARGE (NR)

OVERLAYED COVERAGES

Calculated a potential for groundwater contamination factor (PGW) as follows

$$PGW = SM(2) + AM(3) + HC(3) + VZM(5) + NR(4)$$

Standardized factor (PGW) to a 0 - 100 scale

Keyed a population factor (PF) per HRS II factor breaks

> 62,000	100
46,801 - 62,000	80
31,001 - 46,800	60
15,001 - 31,000	40
≤ 15,000	20

GROUNDWATER USAGE POPULATION

Buffered point data to a 1 mile radius

OVERLAYED COVERAGES

Calculates the groundwater route vulnerability factor ( ) as follows:

$$GWV = PGW(5) + PF(2)$$

Standardized the groundwater vulnerability route factor (GWV) to a 0 - 100 scale

Figure 1
Schematic of Module Development, Groundwater Route

LEGEND

- LOW VULNERABILITY
- MODERATELY LOW VULNERABILITY
- MODERATE VULNERABILITY
- MODERATELY HIGH VULNERABILITY
- HIGH VULNERABILITY

Scale 1 : 1000000

Miles

Map 1
Drastic Model Results
Willamette Basin

LEGEND

- LOW VULNERABILITY
- MODERATELY LOW VULNERABILITY
- MODERATE VULNERABILITY
- MODERATELY HIGH VULNERABILITY
- HIGH VULNERABILITY

Scale 1 : 1000000

Miles

Map 2
Groundwater Route Vulnerability
Willamette Basin

LEGEND

- LOW VULNERABILITY
- MODERATELY LOW VULNERABILITY
- MODERATE VULNERABILITY
- MODERATELY HIGH VULNERABILITY
- HIGH VULNERABILITY

Scale 1:1000000

Miles

Map 3
Surface Water Route Vulnerability
Willamette Basin

LEGEND

- LOW VULNERABILITY
- MODERATELY LOW VULNERABILITY
- MODERATE VULNERABILITY
- MODERATELY HIGH VULNERABILITY
- HIGH VULNERABILITY

Scale 1:1000000

Miles

Map 4
Air Route Vulnerability
Willamette Basin

INPUT DATA LAYER

SOIL MEDIA (SM)

RANGE	RATING
Thin or absent, sand, gravel	3
Sandy loam, loam, aggregated clay	5
Silty loam, clay loam	7
Silty clay, clay	9

LANDUSE (LD)

RANGE	RATING
Urban	9
Cultivated	7
Open grains, pasture, range	5
Woods, forest	3

2-YEAR / 24-HOUR RAINFALL (RF)

INCHES	
RANGE	RATING
> 3.0	10
> 2.5 - 3.0	8
> 2.0 - 2.5	6
> 1.5 - 2.0	4
1.0 - 1.5	2
< 1.0	1

OVERLAYED COVERAGES

Calculate a potential for surface water runoff factor (PSW) as follows

PSW = SM(3) + LD(4) + RF(5)

Overlayed and calculated a PSW factor per sub-sub-basin as follows

$$PSW_{ssb} = \sum^{n} \frac{PSW \ (area)}{sub\text{-}sub\text{-}basin \ area}$$

n = number of areas within a sub-sub-basin

Standardized PSW (sub-sub-basin) to a 0 - 100 scale

HYDROGRAPHIC BOUNDARY (HB)

SURFACE WATER USAGE POPULATION (SWP)

Overlayed coverages calculated total SWP per sub-sub-basin

Rated SWP factor per HRS II breaks

Population	SWP Factor
> 60,000	100
45,001 - 60,000	80
30,001 - 45,000	60
15,001 - 30,000	40
< 15,001	20

SENSITIVE ENVIRONMENTS (SE)

Keyed HRS II sensitive environment values

Overlayed coverages calculated total SE per sub-sub-basin

Standardized values to a 0 - 100 scale

OVERLAYED COVERAGES

Calculated a surface water route vulnerability factor (SWV) sub-sub-basin as follows

SWV_ssb = PSW_ssb (3) + F_ssb (2) + SWP_ssb (2) + SE_ssb (1)

SWV standardized to a 0 - 100 scale

FISHERIES (F)

Overlayed coverages calculated total fisheries per sub-sub-basin

Rated F factor per HRS II breaks

lbs. of fish	F factor
> 1,000,000	100
100,001 - 1,000,000	80
50,001 - 100,000	60
1,001 - 50,000	40
< 1,001	20

Figure 2
Schematic of Module Development,
Surface Water Route

Air Pathway Module

The air pathway contaminant migration factor used in the rHRS model is the Thornwaite Precipitation-Effectiveness Index (P-E Index).[3] The P-E Index is a surrogate measure of the relative moisture content of surface material. The P-E Index is constant throughout all of the Willamette Basin; therefore, it was not necessary to develop this data layer at this time.

The target factors incorporated into the GIS air pathway vulnerability model are population density and sensitive environments. The population density coverage was developed using Geographic Exposure Model (GEMS) data. The GEMS data base has a population per municipality variable. These point data were processed into area data with a population density attribute by creating polygons around each point and dividing the population variable by each polygon area. A more complete U.S. Census data layer will be used when made available.

As demonstrated in Figure 3, the sensitive environments coverage was then overlaid with the population density coverage to produce an air pathway vulnerability coverage (Map 4).

The groundwater, surface water and air pathway vulnerability coverages were overlaid and all module vulnerability factors were added to create the overall vulnerability coverage (Map 5). Figure 4 illustrates the development of the overall vulnerability coverage.

Universe Development

Categories of facility types that were targeted for site discovery were identified by the U.S. EPA based on past definitions, regulatory authority, site activity, waste type and NPL and CERCLIS characterization of sites. The hazard potential associated with these facility categories can be evaluated based on a typical site in each category. The hazard potential rank (i.e., low, medium or high hazard) is determined by evaluating four major factors:
• Documented evidence of hazards/risks associated with inclusion or absence of sites in the category on the NPL, the number and type of documented damage cases caused by releases at sites in the category, and previous conclusions by the U.S. EPA or other government agencies regarding hazard or risk
• Characteristics of the generated waste, such as waste quantity, concentration, and toxicity

• Typical containment and management practices associated with sites in the category
• Potential for exposure, given a release

The following is a list of facility categories considered to be high and/or medium hazard potential.

Categories With High/Medium Hazard Potential
1. Closed Municipal Solid Waste Landfills (High Hazard)
2. Hazardous Waste Generators (Medium Hazard)
   • Large quantity generators such as:
     - Fabricated metal facilities
     - Metal manufacturing facilities
     - Chemicals and allied products
       Electrical equipment
     - All other manufacturing
3. Subtitle D Industrial Process Waste Facilities (Medium Hazard)
   • Manage waste on-site such as:
       Pulp and paper
     - Inorganic and organic chemicals
       Transportation equipment
     - Rubber and miscellaneous products
     - Leather products
       Plastics and resins manufacturing
     - Fertilizer and agricultural chemicals
       Petroleum refining
4. Other Site Categories (Medium Hazard)
   • Nonfuel mining and processing
   • Class IV and Class V
     (industrial/commercial/utility) disposal wells
   • Open/illegal dumps
   • Coal gasification plants
   • Wood-preserving facilities
   • Tanneries
   • Pesticide formulators
   • Electroplating facilities
   • Aerial pesticide applicators
   • Drycleaners
   • Metal/transformer salvage yards

Figure 3
Schematic of Module Development
Air Route Vulnerability Module
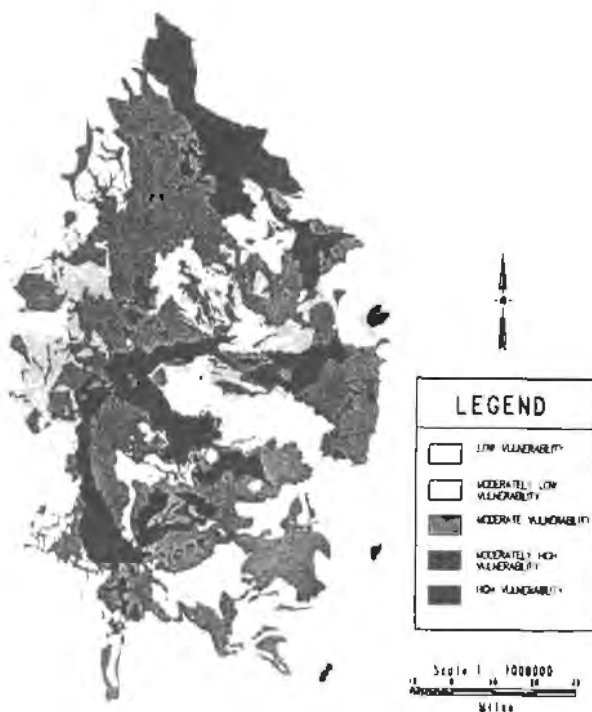
Map 5
Overall Vulnerability
Willamette Basin
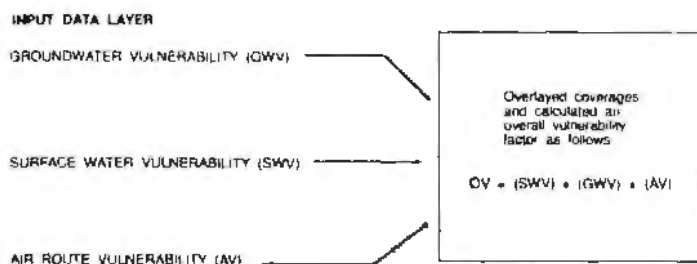
Figure 4
Schematic of Module Development
Overall Vulnerability Module

These types of facilities were targeted for the site discovery process. Not all individual sites in the categories listed above are sufficiently hazardous to warrant priority U.S. EPA concern under Superfund. In fact, there probably are few if any site categories in which all individual sites will require U.S. EPA attention, and some categories may have very few sites that warrant concern. The two main methods used in the discovery process were documentation search and geographic survey.

A documentation search consists of researching available data sources to obtain information regarding the existence of potential hazardous waste sites. The sources of data used include: U.S. EPA regional files, state files, commercial data bases and trade group publications. Abandoned sites can be identified by using County Business Patterns (U.S. Bureau of Census) and Directory of Chemical Producers (SRI) data bases to establish business patterns from 1961 to the present. State files were reviewed to locate closed municipal landfills. The facility information contained in the different data bases was cross-checked to eliminate facility duplication.

A geographic survey consists of canvassing specific areas in an effort to locate potential hazardous waste sites. The abandoned site search for closed landfills was limited to highly vulnerable areas as defined by the GIS vulnerability model. Geographic surveys were used to confirm potential waste sites identified through the documentation search and to identify other potential sites in the area.

Site discovery by documentation search uses five different data sources to obtain a thorough listing (i.e., universe) of active facilities and closed municipal landfills. These sources include: the American Business List (ABL), the Oregon Department of Environmental Quality site inventory (ODEQ list), the U.S. EPA Facility Index Numbering Data System (FINDS) and Title III data bases and the ODEQ Solid Waste branch files.

The ABL data base is a yellow page listing of active manufacturers by SIC code. The types of facilities acquired from the ABL correspond to the categories discussed earlier. The ODEQ list consists of active and abandoned facilities currently on the ODEQ site inventory. The FINDS data base includes all active and abandoned sites currently on the U.S. EPA's site inventory. Title III data contain a list of facilities with emissions of chemicals reported under Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986. Files from the Solid Waste branch of the ODEQ were reviewed to obtain a list of closed municipal landfills located in/near highly vulnerable areas as defined by the GIS vulnerability model.

The five data sources of potential CERCLA sites were processed to produce the final Universe of "discovered" sites. The first stage of the site discovery screening process was to compare each data source with an inventory of current CERCLA sites to eliminate those facilities already on CERCLIS. Following the purge of CERCLA facilities from each data source, the data bases were compared with each other to eliminate duplication. By eliminating U.S. EPA FINDS, ODEQ and Title III duplicate sites from the ABL data base, the ABL list represents potential CERCLA sites that are currently in neither the state nor the U.S. EPA site inventories. The U.S. EPA FINDS data base was processed by selecting RCRA generators not on CERCLIS and selecting those U.S. EPA sites not under RCRA or CERCLA (Other U.S. EPA).

The second phase of the screening process is to eliminate those facilities that do not fit the medium and high hazard categories discussed earlier from the ODEQ list, the U.S. EPA FINDS (i.e., RCRA generators and Other U.S. EPA sites) and the Title III list. The remaining ABL, ODEQ list, U.S. EPA FINDS, Title III and closed landfill sites comprise the universe of "discovered" sites. The final screening is designed to prioritize "discovered" sites. Sites in cities that are located in highly vulnerable areas are prioritized for confirmation and review.

Approximately 6,000 potential sites were discovered in Oregon using the screening process discussed above. The U.S. EPA emphasizes that the vast majority of sites may not contain hazardous waste or be of concern to the U.S. EPA. Seventy percent (4,198) of the discovered sites were located in the Willamette Basin. A summary of the number of sites contributed by each data source for the Willamette Basin is as follows:

- ABL = 3,072 sites (73.2 %)
- RCRA = 637 sites (15.2 %)
- Other U.S. EPA = 316 sites (7.5 %)
- ODEQ List = 98 sites (2.3 %)
- Closed Landfills = 48 sites (1.1 %)
- Title III = 27 sites (0.6 %)

In a study that summarizes discovered sites by industrial category (SIC code) and vulnerability rankings (as defined by the GIS model), the majority of the sites (97%) are located in the moderate to high vulnerability rankings. This could be a result of the fact that the moderately low and low vulnerability areas represent rural or low population centers. Fabricated metals and industrial machinery manufacturers comprise 38% of the sites. It was also noted that the

federal data sources have incomplete SIC designations for approximately 57% of the sites. To account for the lack of SIC codes in federal data sources, all facilities without SIC codes were included in the "discovered" universe.

PAs were performed on 79 of the 4,198 potential sites in an attempt to evaluate the legitimacy of the universe of "discovered" sites. A second objective of the PAs was to provide a field check for the GIS vulnerability model. Three criteria were used in selecting PA candidates from the 4,198 potential sites. The first criterion was to select PAs from each of the vulnerability rankings (high, moderately high, moderate, moderately low and low) in an attempt to test the GIS vulnerability model. The next criterion in the PA selection was to choose facilities from each of the data sources (ABL, ODEQ List, RCRA, Title III, Other U.S. EPA and closed landfills). Finally, PAs were selected to represent a cross section of industry type by SIC code.

A summary was compiled of 57 PA sites. Of the remaining 22 sites, drive-by surveys were performed on 19; the other three sites could not be located. It was determined that of the 57 sites evaluated, 27 sites generating hazardous waste were recommended as no further action (NFRAP), 19 facilities did not generate hazardous waste and were recommended as NFRAP and 11 sites were recommended as requiring a PA evaluation.

Table 5 summarizes the industrial code (SIC) and vulnerability ranking of the 11 facilities recommended for PA evaluation. Factors that determined which sites warranted a PA evaluation include: waste quantity, disposal practices, waste type, years of operation, spill history, visual appearance and past agency involvement.

Table 5
Summary of Preliminary Assessment Facilities

Industry Type	Data Source	Vulnerability Class
Pesticide Appl.	RCRA (1 site)	Moderately High
Chemical Products	RCRA (1 site)	High
	ODEQ (2 sites)	High
	Title III (1 site)	High
Lumber and Wood	ABL (2 sites)	High
Electronic Products	RCRA (1 site)	Moderate
Primary Metals	RCRA (1 site)	High
Drycleaners	ABL (1 site)	High
	ABL (1 site)	Moderate

CONCLUSIONS

Of the 79 potential PA candidates, PAs were performed on 11 sites. This indicates a success rate of 14% for the initial PA screening effort in the Willamette Basin. Based on this success rate and the current Level of Effort (LOE) expended to date, the cost of implementing this active site discovery mechanism in the Willamette Basin is approximately 7 LOE hours per discovered site. Nine of the 11 PA evaluations were recommended for Screening Site Inspections (SSIs).

The SSI results will be used to further evaluate the correlation between the GIS vulnerability model and the rHRS model.

PAs were performed on sites from four of the five data sources (ABL, RCRA, ODEQ List and Title III). This indicates that the data sources used to generate the universe of "discovered" sites appear to contain potential CERCLA sites. PA sites that scored the highest (i.e., rHRS potential scores of 31.80 and 30.07) are located in highly vulnerable areas. However, a site scored in the moderate vulnerability class exceeded some site scores in the moderately high and high vulnerability categories. Additional tests on the GIS vulnerability model are necessary to correlate vulnerability rankings with rHRS scores.

Since environmental and target type data are already in the GIS system, this allows for a reduction of resource requirements to calculate rHRS scores and perform PAs. Based on the 11 PAs performed in this study, a 40% reduction of LOE hours was achieved by using rHRS data in the GIS system, as opposed to collecting rHRS data in the field.

These GIS environmental and target data layers can be used for other agency applications, such as risk assessments, environmental impact statements and specific environmental studies (pesticide groundwater vulnerability study). The developed GIS data layers also are accessible to the State of Oregon for use in prioritizing state resources.

The results of the Willamette Basin project will be incorporated as this active discovery mechanism is applied to the remaining basins in Oregon. This discovery mechanism also can be applied, partially or as a whole, to other areas or states.

ACKNOWLEDGEMENTS

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Highway Right-Of-Way Considerations
Near Superfund Sites in Delaware

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ABSTRACT

State transportation departments are responsible for state ownership of roadway right-of-way and for acquiring new right-of-way and related properties. Some state-owned highway right-of-way properties lie adjacent to uncontrolled hazardous substance release sites. Due to potentially high implementation costs (from construction scheduling, operations impacts and future liability associated with acquiring portions of an uncontrolled hazardous substance release site or encountering contaminants on existing right-of-way), the Delaware Department of Transportation (DOT) has instituted a program to evaluate environmental constraints before purchase decisions are made. Where possible, phased environmental investigations are performed on properties considered for acquisition. The ultimate objectives are: (1) to provide right-of-way negotiators with cleanup cost estimates for consideration in the purchase agreements and (2) to evaluate design and construction constraints should the property be purchased. Most of the properties investigated to date have been underground storage tank (UST) sites, although a number of industrial and commercial facilities have been evaluated. This paper examines case studies of Delaware DOT highway projects planned near three Superfund sites: Sealand Limited, Tybouts Corner Landfill (NPL No. 2) and Dover Air Force Base. Substantial technical and legal effort are is associated with addressing right-of-way issues near each of the three sites. Due to the complexity of the issues and considerable time required for resolution, early attention to Superfund impacts by environmental professionals is recommended.

IMPACTS TO STATE RIGHT-OF-WAY

State-owned roads and highways exist adjacent to, or near, many uncontrolled hazardous substance release sites. Most commercial and industrial facilities require road access or frontage to conduct business. The nature of vehicular transportation attracts some environmentally sensitive businesses, i.e. to road frontage gasoline stations. In planning, acquiring, constructing and maintaining roadway right-of-way, increasing attention is being given to resolving matters related to impacts from environmental regulations and releases of hazardous substances on State-owned rights-of-way. State transportation departments (the planners and custodians of state-owned rights-of-way) must confront the issues of environmental compliance and responsible management of affected road projects and properties.

The right-of-way development process is important when evaluating environmental impacts and actions. Figure 1 illustrates a five-stage development process of a roadway from its conceptualization to completion.[1] Note that eventual property management (Stage 5) is only one stage of concern. The first four stages—location planning, design, acquisition and construction—are associated with development of a new or expanded roadway. These four stages may be significantly affected

by environmental considerations. Generally, the earlier that potential environmental problems are recognized and evaluated, the less disruptive they are to later stages. For instance, discovering an environmental problem during the construction stage may not only delay the construction and require special operations, but the road design (Stage 2) might require modification and the value/liability of the subject state-owned property (Stage 3) may change at the taxpayers' expense. Furthermore, if the environmental condition is known earlier, a more feasible and potentially more cost-effective roadway alternative may be selected (Stage 1). Unforeseen environmental problems can cause substantial time and cost impacts to the roadway project.

Often with existing road upgrades, it is not feasible to avoid a problem site because of the high cost of developing a totally new road corridor. Recently in Delaware, upgrade projects have constituted the majority of new road projects and have been the most affected by hazardous substance environmental problems. For these projects, environmental issues are assessed with regard to liability of ownership and design and construction impacts.

Property owners could be liable for necessary environmental compliance (e.g., site cleanup), handling and disposing of special or hazardous wastes generated by site development (e.g., being named as a responsible party due to the link with state-generated waste, third party law suits by construction workers exposed to waste) and additional administrative costs (e.g., negotiation or litigation). Historically, efforts have been made to quantify environmental compliance cost and to avoid, rather than estimate, potential liabilities associated with waste issues and additional administrative costs.

Environmental impacts to road design and construction have motivated Delaware DOT to establish a hazardous substance evaluation program. The presence of contaminated soil or groundwater on a right-of-way construction site can significantly disrupt planned operations and cause delays and contractor claims.

ENVIRONMENTAL EVALUATION PROCESS

Delaware DOT has instituted a multiphased right-of-way evaluation process that is similar to the environmental evaluation process for real estate property transfers. A number of other states, including California and New Jersey, have similar programs.[2]

Delaware DOT is in the midst of a Relief Route Project, a new 46-mile, north-south limited access highway. Due to the size and complexity of the project scope, Delaware DOT retained Century Engineering, Inc. International (CEII), a civil engineering consultant, to manage the design and construction.[3] CEII subcontracted with EA Engineering, Science and Technology, Inc. to perform environmental services for the Relief Route Project. CEII and Delaware DOT representatives screened the proposed road alignment for suspect sites based on current site usage

and Delaware DOT records.

Other state road projects are managed internally by the Location Studies group of Delaware DOT. Traditionally, this group has administered the environmental impact aspects of road preconstruction activities (e.g., wetlands and noise). In 1988, their responsibilities were expanded to include administering hazardous substance evaluations. Between 1987 and 1988, the Delaware DOT retained EA to provide technical assistance for selected projects. After fulfilling several small contracts dealing only with individual sites during 1987, EA was contracted in 1988 by Delaware DOT under a task-order basis to provide investigative and remedial design/implementation environmental services. Currently, environmental specialists in the Location Studies group screen various road project right-of-way acquisition plans and proposed subsurface construction. Properties designated as environmentally suspect are assigned to EA for phased investigation. For major new corridor projects requiring an Environmental Impact Statement (EIS), the Location Studies group now requires more consideration of hazardous substances release sites by the EIS consultant.

The multiphased approach is designed to identify and evaluate potential areas of contamination on the suspect properties.[3] A three-phased approach is used:

- Phase I—Preliminary assessment
- Phase II—Site characterization, remediation assessment
- Phase III—Remedial design and implementation

Figure 2 illustrates a sequential flow of environmental activities.
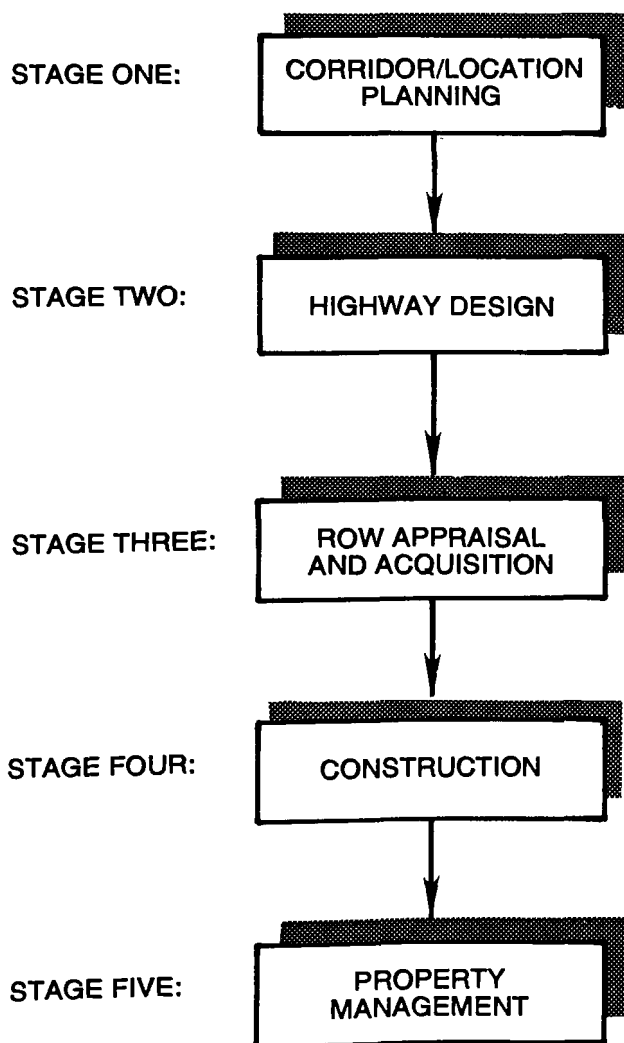
Figure 1
Right-of-Way Development Process

STAGE ONE: CORRIDOR/LOCATION PLANNING

STAGE TWO: HIGHWAY DESIGN

STAGE THREE: ROW APPRAISAL AND ACQUISITION

STAGE FOUR: CONSTRUCTION

STAGE FIVE: PROPERTY MANAGEMENT

The purpose of Phase I is to establish whether or not an environmental problem exists on the subject property. Often the right-of-way to be acquired is a "strip-take," that is, a strip of property adjacent to the existing road. Investigation may be limited to that strip. Records, site inspections and interviews, limited sampling and metallic tank location surveys are used in Phase I investigations. Because many of the sites (e.g., gas stations) are associated with volatile organic compound usage or storage, soil vapor surveys are a valuable investigative technique. Often during Phase I, several shallow soil samples are obtained by hand-augering in proposed trench lines. In some cases, existing information is sufficient to omit some or all of the Phase I components and proceed directly to Phase II or III.

Phase II investigations are implemented if contamination is identified or suspected and further characterization is necessary. Detailed investigations, such as hydrogeologic assessments, may be performed. Once the site is adequately characterized to evaluate hazards and/or remediation needs, a cleanup cost estimate is generated to assist Delaware DOT property acquisition personnel. The cost estimate is used to help appraise the value of the property if Delaware DOT purchases it unremediated. In some cases, the responsible party has initiated cleanup and site closure. In other cases, the estimated cleanup costs are used to establish escrow funds deducted from the purchase price, pending future cleanup.

Phase III, remedial design and implementation, can be implemented if Delaware DOT accepts responsibility for the identified environmental problem. Delaware DOT has pulled a number of USTs at various sites, some with associated soil excavation and above-ground remediation. Delaware DOT has not initiated any multimedia site cleanups, such as pumping or venting, although such projects are possible in the future.

Delaware DOT (through EA) has performed Phase I investigations at 50 properties, Phase II investigations at 17 properties and tank pull oversight with some soil remediation at 10 sites. The majority of properties investigated are UST-related; however, several road project locations are affected by Superfund sites. Presently, environmental issues are being evaluated for road projects adjacent to three NPL sites. Due to the technical and administrative complexity associated with environmental issues of Superfund sites, these cases are good illustrations of how such sites can affect the road right-of-way development process.

CASE 1—SEALAND LIMITED

The Sealand Limited site located in New Castle County, Delaware, was recently added to the NPL. Prior to 1983, the Sealand facility recycled waste oils, coal tar, inks and other waste organics. The property was owned by Conrail and leased to Sealand. Operations closed in 1983 when a U.S. EPA Emergency Removal Action was initiated. Past analysis of site groundwater and soil have indicated the presence of trace metals, VOCs and base neutral organic compounds (notably polycyclic aromatic hydrocarbons—PAHs). The property is narrow, approximately 100 ft wide and 1,000 ft long. An RI/FS is being conducted now with numerous off-property sampling locations. Delaware DOT is planning a road upgrade near Sealand. The route is heavily used by commercial and commuter traffic. Figure 3 depicts three road upgrade alternatives, Alternates 2, 3 and 4 (Alternate 1 is not discussed here). All three alternatives have hazardous substance concerns, as well as other substantial considerations (e.g., wetlands, property cost). The favored Alternate, No. 4, skirts the north end of the Sealand property on a new alignment. An effort was made by Delaware DOT planners to avoid potential property acquisition of the Superfund site itself, due to legal ramifications, delays and association with an NPL-listed site. However, subsurface contaminants may be migrating toward the Alternate 4 right-of-way. Alternate 3 is an upgrade of the existing road, but requires acquisition of property strips along the Sealand site and other environmentally suspect sites. Alternate 2, the southern-most route, bisects an operating grainery.

Investigations on each alternative have discovered subsurface contamination. Aside from the legal aspect of acquiring a section of a Superfund site, Delaware DOT is concerned about purchasing neighboring properties with contamination sources and ultimately being drawn into the Superfund process due to mingling contaminants. Although in some

cases the contamination has been small and probably of low risk to human health or the environment, the proximity to the Sealand site exacerbates future liability concerns.

A significant quantity of oil-stained soil was discovered on Alternate 4, possibly related to former asphalt batching operations. The discovered compounds of concern are the same as those on Sealand—PAHs and total petroleum hydrocarbons. The oily soil lies near a stream headwater and wetland, so road construction through the area would require careful design and construction to minimize surface water impacts.

Alternate 3 requires strip-takes of the Sealand property, a former gas station and an operating grainery. Soil and groundwater samples at the former gas station showed aromatic petroleum hydrocarbons (benzene, toluene and xylenes) in the former tank field area. The former tank field may be upgradient of the Sealand site. Past sampling at Sealand

has shown benzene and toluene in soil. Soil vapor and shallow groundwater samples at the grainery indicate the presence of 1,1,1-trichloroethane. From the limited sampling to date, the compound appears to be ubiquitously distributed across the site. Solvents may have been used in the past as carrier agents for grainery pesticides. This environmental condition also affects Alternate 2.

Environmental evaluations of the right-of-way development process began more than 1.5 years ago (during Stage 1) for this project; the final alternative still has not been selected, partially due to the complexity of the above environmental issues.

CASE 2—TYBOUTS CORNER LANDFILL

Tybouts Corner Landfill is located in New Castle County, Delaware and was originally No. 2 on the NPL. The 50-acre site originally was a sand and gravel pit and subsequently was used as a landfill for

1. Site characterization may include hydrogeologic assessment, waste distribution assessment, and ecological assessment.

2. Hazard assessment is a qualitative mini-risk assessment.

3. Remedial assessment is a quantitative mini-feasibility study.
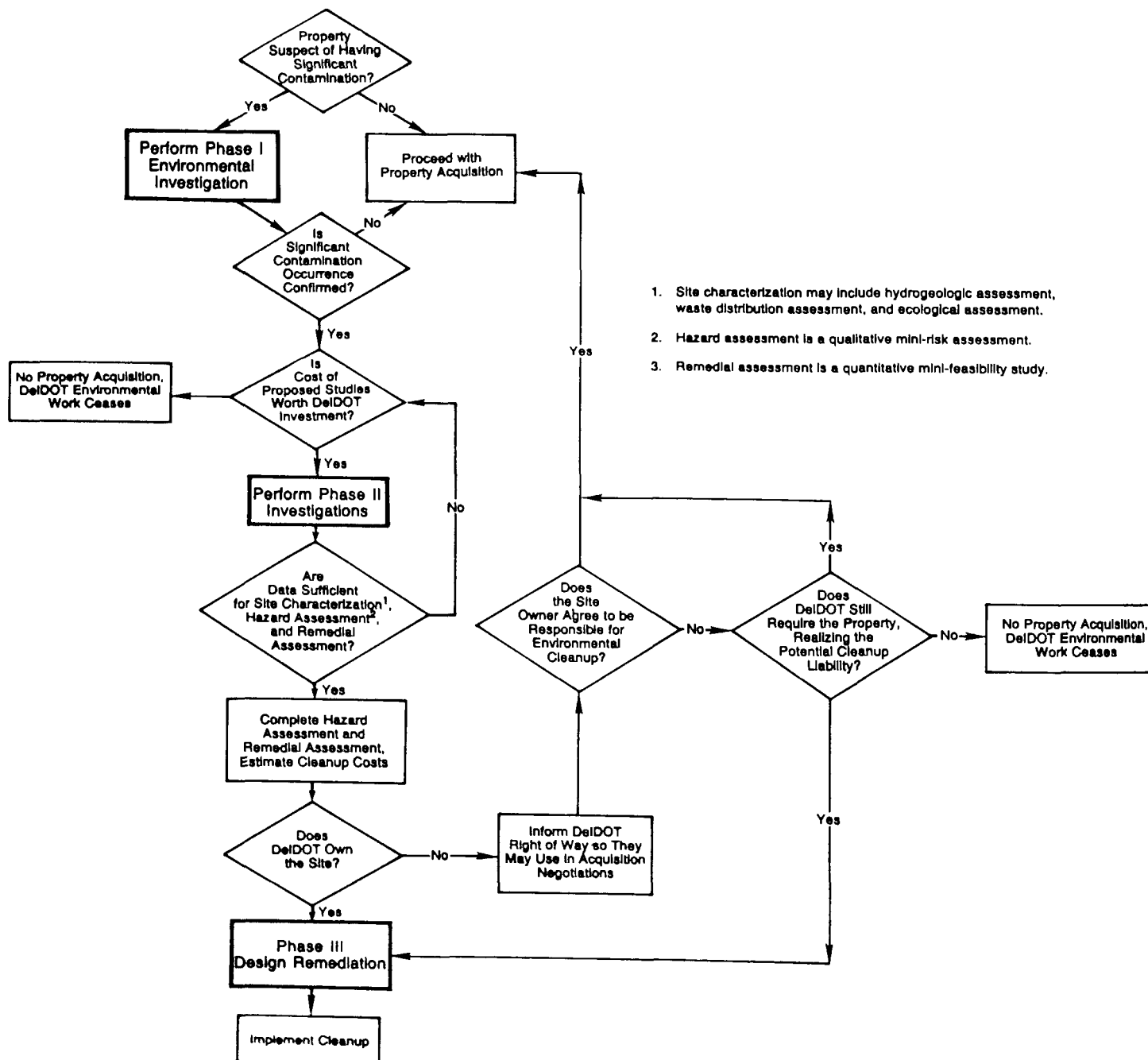
Figure 2
Environmental Activities Flow Chart

Figure 3
Road Alternatives Near Sealand Limited

penetrated, so stringent borehole sealing and decontamination procedures were required. Because drilling was performed in the existing highway right-of-way (shoulders and median), special attention was given to maintaining traffic. After several iterations of a work plan, geotechnical borings were completed in Spring 1990, almost two years after they were originally planned.

Subsurface samples were obtained during drilling to evaluate other design and construction operation considerations. Concerns include foundation design, road and bridge drainage design, waste generation and disposal, health and safety for construction operations and construction materials compatibility. These issues are being evaluated now. Because driven piles were an original foundation design alternative, consideration will be given to methods that may minimize cross-contamination of subsurface units if retarding units must be penetrated. Many of the issues still require discussion with regulators and PRPs. For instance, it is still uncertain as to which party should be responsible for wastes generated (e.g., soil and groundwater from excavations). Also, construction health and safety measures will be established by assessment of the chemical data, but it has not been determined if road construction should fall within the Tybouts Corner Landfill approved Safety and Health Plan.

CASE 3—DOVER AIR FORCE BASE

Dover Air Force Base (DAFB) is a large military cargo handling facility. The base recently was included on the NPL: it has numerous uncontrolled hazardous substance problems, including jet fuel and motor fuel spills and leakage of dissolved organic compounds from surface impoundments. RT. 113, part of the Relief Route Project, borders the base. To expand the existing roadway into a limited access highway, numerous property acquisitions are necessary near the base. A commercial strip exists on the southwest side of the road, across the operational part of DAFB and several subsurface contaminant sources have been or will be acquired as part of the Relief Route (Fig. 4). Namely, parts or all of two former gas stations and one active gas station, several
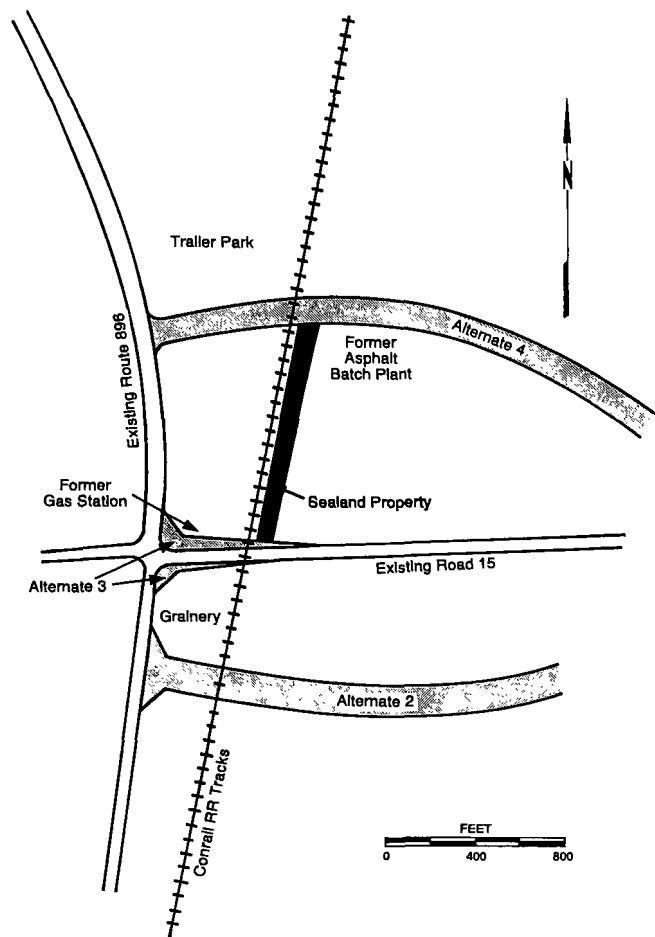
municipal and industrial waste in the 1960s and 1970s. A number of refineries are nearby and solvent and hydrocarbon wastes were documented to be disposed at the site. The RI/FS was completed in 1985 and the ROD was signed in 1986. The PRPs are now in the design phase of remediation. The cleanup will ultimately incorporate capping, excavation and pump-and-treat technologies.

Route 13, a major north-south highway, lies immediately east and downgradient of the landfill. Expansion for the limited access Relief Route will require acquisition of only the property to the east of the existing right-of-way. No Tybouts Corner Landfill property will be acquired. The problems associated with road development thus far have centered on design considerations and impact on future road construction. The road work also may affect the off-site remediation and monitoring, such as compliance well placement. The project has required substantial coordination effort between Delaware DOT and its consultants, The Delaware Department of Natural Resources and Environmental Control (DNREC), U.S. EPA Region 3 and the PRPs and their consultants.

Problems began in the summer of 1988, when a geotechnical drilling crew encountered suspicious odors while drilling in the road median downgradient of the site. The drillers were pulled off the site and EA and CEII performed an environmental evaluation using existing information. It was discovered that an existing right-of-way area near a bridge over a creek probably was underlain by aqueous leachate plumes from the landfill. Also, underlying aquifers had varying degrees of hydraulic confinement and contamination from the landfill. These conditions present several potential problems for road design and construction.

First, the geotechnical borings, which were necessary for new bridge design, had to be completed with regard for environmental considerations. Several retarding units separating subsurface hydraulic units were
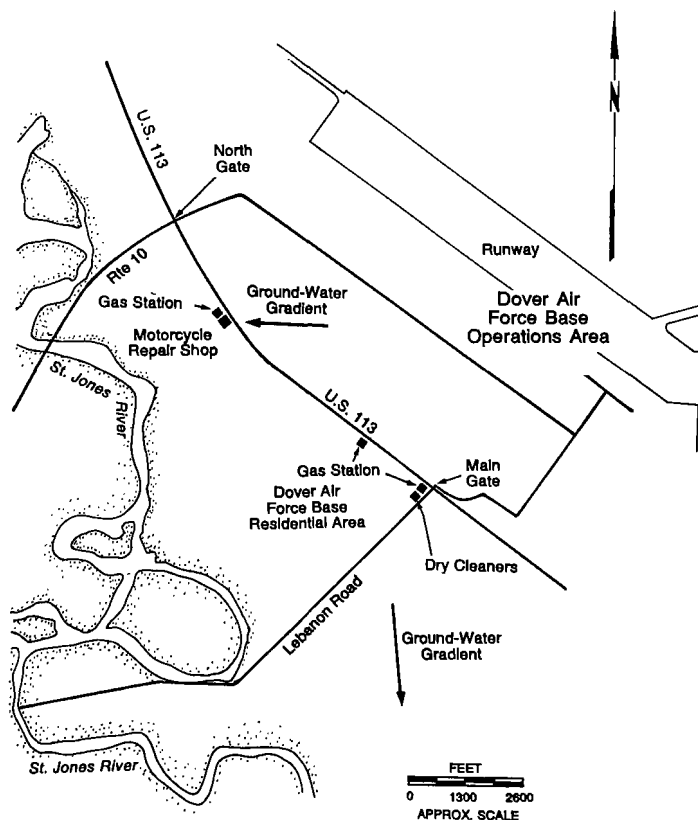
Figure 4
Properties Considered for Acquisition Near Dover Air Force Base

former drycleaners and a large motorcycle repair and salvage business are included in the project.

The three gas stations are documented to have had leaking USTs. Two sites are being remedied by the PRPs, while one is being handled by Delaware DOT under an escrow arrangement. All gas station environmental activities fall under Delaware DNREC UST Management Group primacy. Subsurface chlorinated solvent contamination existing on a former drycleaner site and motorcycle facility fall under Delaware DNREC CERCLA Management Group primacy. The U.S. Air Force is presently completing RI/FS activities at DAFB under state and U.S. EPA scrutiny.

A central issue in developing the subject properties is the potential mingling of aqueous plumes from the right-of-way sites with DAFB plumes and the possibility of having to jointly allocate plume responsibility. Near the highway, the shallow groundwater gradient is from the DAFB operations area toward the subject properties. DAFB sources with similar contaminants have been documented to be migrating toward one gas station and the motorcycle business. Preliminary results of investigations near the drycleaners have found contaminated shallow groundwater upgradient of the known source sites. A substantial amount of site characterization work is being performed just to obtain a baseline of contamination location and the costs of investigation and probable remediation are greater than the value of the assets of some of the responsible properties. Delaware DOT is now weighing how best to appraise and acquire the properties. A large uncertainty exists as to what corrective action objectives and criteria will be set for DAFB and how they may affect cleanup requirements from other downgradient sources. The value of properties and future liabilities can differ substantially different from those perceived now if stringent corrective action is required. Where possible, Delaware DOT is altering plans to avoid acquisition of potential source areas.

LESSONS LEARNED

Subsurface contamination originating on the right-of-way of highways and migrating from off-site sources can pose a problem. Dealing with uncontrolled hazardous substance impacts to the right-of-way development process takes more time and effort than that to which highway planners are accustomed. Confronting the environmental issues as early as possible during the staged right-of-way development process will minimize disruptions to plans, designs and construction operations. Environmental expertise is essential to understanding the complex technical and regulatory environmental issues as they apply to the highway process, as well as prudently managing the public's property and interests.

Road development near Superfund sites has been especially sensitive due to the complexity of regulatory and multiple-party interaction and uncertainties in how the Superfund process may affect right-of-way projects. Furthermore, the thoroughness and QA/QC requirements of field and laboratory activities necessary for work associated with Superfund sites often exceeds that for other programs, such as state UST investigations. Therefore, an extra effort must be made to communicate environmental plans to the appropriate regulators and interested parties and to coordinate a mutually agreeable action.

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Conducting Remedial Investigations/Feasibility Studies at CERCLA Municipal Landfill Sites

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ABSTRACT

Approximately 20% of the sites on the National Priorities List (NPL) are municipal landfills which typically share similar physical and chemical characteristics. Because of this similarity, the Superfund Program anticipates that their remediation will involve similar waste management approaches.[1]

As stated in the National Contingency Plan, the U.S. EPA expects that containment technologies will generally be appropriate for waste that poses a relatively low long-term threat or where treatment is impracticable [NCP Sec. 300.430(a)(iii)(A)]. Therefore, containment has been identified as the most practicable alternative because of the volume and heterogeneity of waste within CERCLA municipal landfills, which often makes treatment impracticable. In addition, the U.S. EPA expects treatment to be considered for identifiable areas of highly toxic or mobile material that constitute the principal threat(s) posed by the site [NCP Sec. 300.430(A)(iii)(C)]. Treatment of hot spots within a landfill should therefore be considered and evaluated. The similarity in landfill characteristics and the NCP expectations make it possible to streamline remedial investigations and feasibility studies for municipal landfills with respect to site characterization, risk assessment and the development of remedial action alternatives.

INTRODUCTION

A broad framework for the Remedial Investigation/Feasibility Study (RI/FS) and selection of remedy process has been created through the National Contingency Plan and the *EPA RI/FS Guidance*.[2] With this framework now in place, the U.S. EPA's Office of Emergency and Remedial Response's efforts are being focused on stream,lining the RI/FS and selection of remedy process for specific classes of sites with similar characteristics.

One such class of sites is municipal landfills which compose approximately 20% of the sites on the Superfund Program's National Priorities List (NPL). Municipal landfill sites currently on the NPL typically contain some combination of municipal and hazardous waste and range in size from 1 to 640 acres. Nonhazardous waste disposed in municipal landfills is a heterogeneous mixture of materials primarily composed of household refuse such as yard and food wastes, and commercial waste such as paper, plastic, glass and metals. There are four ways in which hazardous wastes may have been disposed in municipal landfills. First, landfills that operated before the implementation of RCRA in 1980 typically accepted and codisposed of both liquid and solid hazardous waste; second, small quantity generators contribute varying quantities of hazardous wastes to municipal landfills; third, some household wastes such as batteries and paints are hazardous; and fourth, biodegradation of wastes within the landfill can create new compounds that are hazardous.

Potential threats to human health and the environment resulting from municipal landfills may include:

- Leachate generation and groundwater contamination
- Soil contamination
- Landfill contents
- Landfill gas
- Contamination of surface waters, sediments, and adjacent wetlands

A conceptual model of the potential pathways of exposure that may exist at municipal landfill sites is presented in Figure 1.

Because these sites share similar characteristics, they lend themselves to remediation by similar technologies. The National Contingency Plan (NCP) contains the expectation that containment technologies generally will be appropriate remedies for wastes that pose a relatively low long-term threat or where treatment is impracticable. Therefore, because of the volume and heterogeneity of waste within CERCLA municipal landfills, treatment often will be impractical. The NCP also contains an expectation that treatment should be considered for identifiable areas of highly toxic and/or mobile material (hot spots) that pose principal threats. Therefore, treatment of hot spots within a landfill will be considered and evaluated.

With these expectations in mind, a study of municipal landfills was conducted with the intent of developing methodologies and tools to assist in streamlining the RI/FS and selection of remedy process. Streamlining may be viewed as a mechanism to enhance the efficiency and effectiveness of decision-making at these sites. The goals of this study to meet this objective include: (1) developing tools to assist in scoping the RI/FS for municipal landfill sites, (2) defining strategies for characterizing municipal landfill sites that are on the NPL and (3) identifying practicable remedial action alternatives for addressing these types of sites.

STREAMLINING SCOPING

The primary purpose of scoping an RI/FS is to divide the broad project goals into manageable tasks that can be performed within a reasonable period of time. The broad project goals of any Superfund site RI/FS are to provide the information necessary to characterize the site, define site dynamics and develop a remedial program to mitigate current and potential threats to human health and the environment. Scoping of municipal landfill sites can be streamlined by focusing the RI/FS tasks on just the data required to evaluate alternatives that are most practicable for municipal landfill sites. Scoping of municipal landfill site RI/FS tasks can be streamlined by:

- Developing preliminary remedial objectives and alternatives based on the NCP expectations and focusing on alternatives successfully implemented at other sites
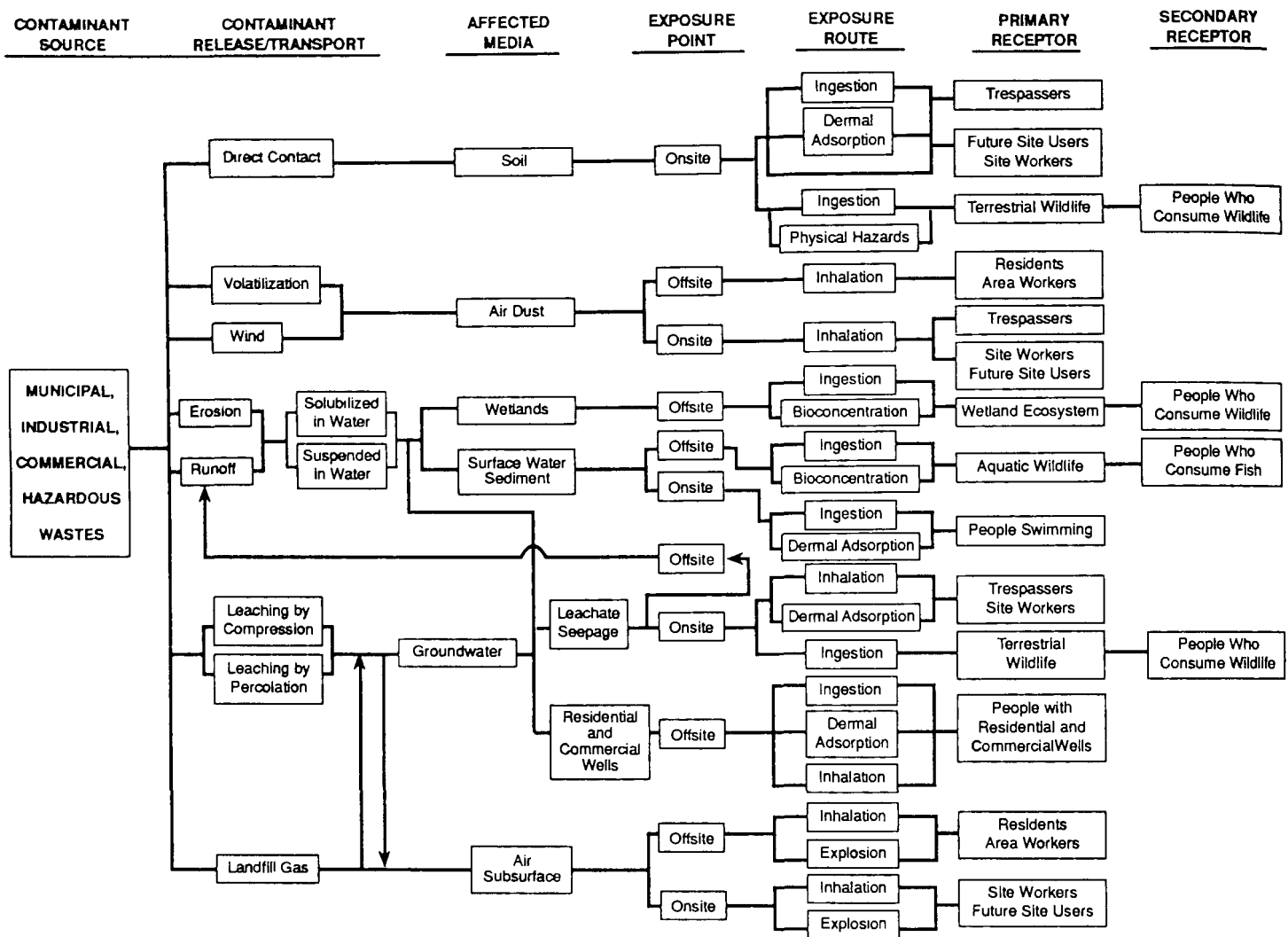
Figure 1
Potential Exposure Pathways for Municipal Landfills

- Using a generic conceptual site model developed for municipal landfill sites (based on their similarities) and modifying it as necessary to reflect site conditions
- Conducting limited field investigations to assist in targeting future fieldwork (Table 1)
- Identifying clear, concise RI objectives in the form of field tasks to ensure sufficient data are collected to adequately characterize the site, perform the necessary risk assessments(s) and evaluate the practicable remedial action alternatives
- Identifying data quality objectives (DQOs) that result in a well-defined sampling and analysis plan, ensure quality of the data collected and integrate the information required in the RI/FS process
- Limiting the scope of the baseline risk assessment as discussed below

Streamlining the Baseline Risk Assessment

The purpose of the baseline risk assessment is to determine whether a site poses risks to human health and the environment that are significant enough to warrant remedial action. Because options for remedial action at municipal landfill sites are limited, it may be possible to streamline or limit the scope of the baseline risk assessment by:

- Using the conceptual site model and RI-generated data to perform a qualitative risk assessment that identifies contaminants of concern in the affected media, contaminant concentrations and their hazardous properties that may pose a risk through the various routes of exposure.
- Identifying pathways that are an obvious threat to human health or the environment by comparing RI-derived contaminant concentra-

tion levels to standards that are potential chemical-specific applicable or relevant and appropriate requirements (ARARs) for the action. These ARARs may include:

— Non-zero maximum contaminant limit goals (MCLGs) and MCLs for ground water and leachate
— State air quality standards for landfill gas

- When potential ARARs do not exist for a specific contaminant, risk-based chemical concentrations should be used.
- Where established standards for one or more contaminants in a given medium are clearly exceeded, the basis for taking remedial action is clearly warranted (i.e., quantitative assessments that consider all chemicals, their potential additive effects or additivity of multiple exposure pathways are not necessary to initiate remedial action).
- In cases where standards are not clearly exceeded, a more thorough risk assessment will be necessary before initiating remedial action.[3,4]

This streamlined approach may facilitate early action on the most obvious landfill problems (groundwater and leachate, landfill gas and the landfill contents) while analysis continues on other problems such as affected wetlands and stream sediments. However, the effect of early action on obvious problems should be factored into any ongoing risk assessment. For example, if leachate seepage that had been contaminating surface water and wetlands is stopped as a result of an early action, then the risk assessment developed subsequently for the stream sediments and wetlands should assume no further loading. Any early actions also need to be designed for flexibility so that they will

Activity	Objectives	Action
Hydrogeologic Investigation	Evaluate usefulness of existing monitoring well network	Conduct a well survey for all wells (residential, commercial, industrial). Determine local uses of groundwater and accessibility of existing wells. Obtain permission for use. Determine, by sounding to the bottom of the well if existing wells are obstructed.
	Review preliminary locations for new monitoring wells	Perform fracture-trace analysis in areas with fractured bedrock (can be done through EPIC study).
	Determine location of residential wells and their construction	Perform well survey for all residential wells adjacent to, and downgradient from, the landfill. Obtain well logs from federal, state, local utilities, or municipal agencies.
	Determine direction of groundwater flow and estimate gradients	Record water level measurements from existing wells.
	Determine rate of groundwater flow in strata and bedrock fractures	Perform hydraulic conductivity tests on existing wells.
	Confirm previous sampling results for both existing monitoring and residential wells and collect additional data as necessary. Identify areas of groundwater contamination and types of contaminants.	Collect and analyze samples from monitoring and residential wells. Record quality parameters for the samples analyzed. Compare new results with values from previous studies.
	Determine if residential wells adjacent to, and downgradient from, the landfill are contaminated	Collect and analyze tap water samples before any filtration unit and conduct preliminary risk assessment.
General Investigation	Identify previous site owner/operators and delineate site boundaries. Estimate uncertainties in boundaries	Conduct property survey or perform a title or identify property ownership from tax records, or plat maps.
	Locate existing monitoring wells	Perform location and elevation survey of existing monitoring wells.
	Evaluate site drainage patterns	Perform a topographic and hydrologic survey.
	Evaluate site-cover conditions and surface water drainage	Perform visual surface inspection with topographic maps. Conduct surface emissions survey.
	Evaluate gas migration, potential, if applicable	Measure explosive gas levels in nearby residences, or onsite buildings, if present. Also measure in water meter boxes and utility corridors, if landfill gas poses a threat.
	Locate sampling locations	Survey a grid for the site and cross-reference to sample locations.
	Determine landfill subsidence, if survey is otherwise required	Measure elevations along crown of fill or install benchmarks in areas of potential subsidence (requires repeat visits by surveyor).
Geotechnical Investigation	Describe geologic features, classify soil	Conduct visual observation of mechanical erosion, slope instability, differential settlement,, and ponding caused by subsidences and cracking.

be consistent with subsequent actions. For example, it may be necessary to adjust a groundwater pump-and-treat early action designed to attain MCLs to achieve even lower levels, determined to be necessary under a subsequent risk assessment, in the interest of protecting environmental receptors in the wetlands into which the groundwater discharges.

Ultimately, it will be necessary to demonstrate that the final remedy,

once implemented, will in fact address all pathways and contaminants of concern, not just those that triggered the remedial action. The approach outlined above facilitates rapid implementation of protective remedial measures for the major problems at a municipal landfill site.

STREAMLINING SITE CHARACTERIZATION

Site characterization for municipal landfills can be expedited by focusing field activities on the information needed to sufficiently assess risks posed by the site and to evaluate practical remedial actions. Media-specific recommendations to help streamline site characterization of media that are unique to landfills are discussed below.

Leachate/Groundwater Contamination

Characterization of a site's geology and hydrogeology will affect decisions on capping options as well as on extraction and treatment systems for leachate and groundwater. Data gathered during the hydrogeologic investigation are similar to those gathered during investigations at other types of NPL sites. Groundwater contamination at municipal landfill sites may, however, vary in composition from that at other types of sites in that municipal site groundwater often contains high levels of organic matter and metals.[5,6]

Leachate generation is of special concern when characterizing municipal landfill sites. The main factors contributing to leachate quantity are precipitation and recharge from groundwater and surface water. Leachate is characteristically high in organic matter as measured by chemical oxygen demand (COD) or biochemical oxygen demand (BOD). Information to be gathered during characterization of leachate may be limited to:

* Surface water drainage patterns
* Climatological characteristics (for example, precipitation and evapotranspiration)
* Leachate characteristics [for example, TCL organics, TAL metals, BOD, COD, pH, total dissolved solids (TDS), total suspended solids (TSS) and oil and grease]
* Identification of Class I and II aquifers and their associated water levels, flowrates and chemistry

In many landfills, leachate is perched within the landfill contents, above the water table. Placing a limited number of leachate wells in the landfill is an efficient means of gathering information regarding the depth, thickness and types of the waste; the moisture content and degree of decomposition of the waste; leachate head levels and the composition of the landfill leachate; and the elevation of the underlying natural soil layer. Additionally, leachate wells provide good locations for landfill gas sampling. It should be noted that, without the proper precautions, placing wells into the landfill contents may create health and safety risks. Also, installation of wells through the landfill base may create conduits through which leachate can migrate to lower geologic strata, and the installation of wells into landfill contents may make it difficult to ensure the reliability of the sampling locations.

Landfill Contents

Characterization of a landfill's contents generally is not necessary because containment, which often is the most practical technology, does not require such information. Certain data, however, are necessary to evaluate capping alternatives. The needed data include:

* Contour maps
* Fill thickness, lateral extent and age
* Estimate of landfill settlement rate
* Estimate of rate of landfill gas production and landfill gas composition
* Soil characteristics, including permeability, grain size, Atterberg limits and erosion rates
* Climatic conditions, including frost depth, and the appropriate storm event to assess the potential for significant erosion
* Geologic and hydrogeologic characteristics, particularly the permeability of the layer underlying the landfill; depth to groundwater; thickness of waste below the water table; and groundwater flow through the waste, if the waste is partially below the water table
* Physical characteristics of any existing cap, including thickness, area,

slope stability, evidence of freeze/thaw protection and soil characteristics
- An evaluation of the ability of an existing cap to reduce surface gas emissions and odors, prevent oxygen intrusion into the refuse, prevent surface water infiltration, provide erosion control and improve site aesthetics
- Potential future uses of the site

Hot Spots

Hot spots may lend themselves to more extensive remedial alternatives such as thermal treatment or stabilization.[7] In order to consider treatment of hot spots, a waste type or mixture of wastes must be in discrete, accessible locations of a landfill and must be highly toxic and/or highly mobile and present a principal threat to human health or the environment. A hot spot should be large enough that its remediation would significantly reduce the risk posed by the overall site, but small enough that it is reasonable to consider removal or treatment. A landfill containing a low to moderate volume of waste (for example, 100,000 cubic yards or less), and where treatment of the entire landfill contents might be practical, may be treated as a hot spot.

To determine if treatment is practicable, hot spots should be characterized if documentation and/or physical evidence exist to indicate the presence and approximate location of the hot spots. Hot spots may be delineated using geophysical techniques or soil gas surveys and typically are confirmed by excavating test pits or drilling soil borings. When characterizing hot spots, soil samples should be collected to determine waste characteristics, including target analytes list metals, target compound list organics, RCRA waste characteristics, total BTU content and weight of the material. Treatability or pilot testing may be required to evaluate treatment alternatives.

Landfill Gas

Several gases typically are generated by decomposition of organic materials in a landfill. The composition, quantity and generation rates of the gases depend on such factors as refuse quantity and composition, placement characteristics, landfill depth, refuse moisture content and amount of oxygen present. The principal gases generated in municipal landfills are carbon dioxide, methane, nitrogen, trace thiols and, occasionally, hydrogen sulfide. Volatile organic compounds may be present in landfill gases, particularly at co-disposal facilities. Data generated during the site characterization of landfill gas should include:

- Contour drawings and rate of settlement
- Geologic and hydrogeologic characteristics, including permeability, moisture content, geologic strata, pH, depth to bedrock and depth to groundwater
- Presence of off-site subsurface migration
- Surface emissions
- Ambient air monitoring
- Landfill gas characteristics, including composition, moisture content, quantity, temperature and methane content

STREAMLINING THE DEVELOPMENT OF ALTERNATIVES

Figure 2 identifies remedial technologies and process options that frequently have been implemented for achieving remedial action objectives at CERCLA municipal landfill sites. The following points should be considered in order to streamline the development of remedial action alternatives for landfill contents, hot spots, landfill gas, contaminated groundwater and leachate:

- The most practicable remedial alternative for landfills is containment (capping). The type of cap would likely be either a native soil cover, single barrier cap, or double barrier cap. The appropriate type of cap to be considered will be based on remedial objectives for the site. For example, a soil cover may be sufficient if the primary objective is to prevent direct contact and minimize erosion. A single or double barrier cap may be necessary where infiltration is a significant concern. Figure 3 is a simplified decision-tree for selecting the appropriate type of cap.
- Treatment of soils and wastes may be practicable for hot spots. Consolidation of hot spot materials under a landfill cap is a poten-

tial alternative in cases when treatment is not practicable or necessary.
- Extraction and treatment of contaminated groundwater and leachate may be required to control off-site migration of wastes. Additionally, extraction and treatment of leachate from landfill contents may be required. Collection and treatment may be necessary indefinitely because of continued contaminant loadings from the landfill.
- Constructing an active landfill gas collection and treatment system should be considered when: (1) existing or planned homes or buildings may be adversely affected through either explosion or inhalation hazards, (2) final use of the site includes allowing public access or (3) the landfill produces excessive odors. Most landfills will require at least a passive gas collection system (venting) to prevent buildup of pressure below the cap and to prevent damage to the vegetative cover.
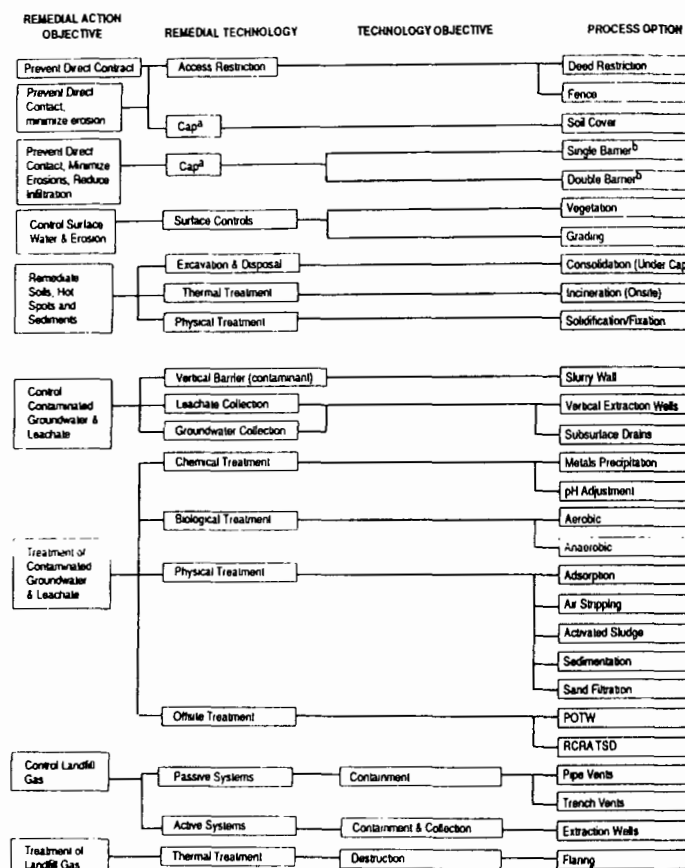
Figure 2
Technologies Frequently Implemented for Remedial Action at CERCLA Municipal Landfill Sites

CONCLUSIONS

Evaluation and selection of appropriate remedial action alternatives for CERCLA municipal landfill sites are functions of a number of factors including:

- Sources and pathways of potential risks to human health and the environment.
- Potential ARARs for the site.[8,9] Significant ARARs might include RCRA closure requirements (Subtitle D requirements will be applicable unless Subtitle C is determined to be applicable or relevant and appropriate)[8] and federal or state requirements pertaining to landfill gas emissions.
- Waste characteristics.
- Site characteristics (including surrounding area).
- Regional surface water (including wetlands) and groundwater characteristics and potential uses.

LANDFILL CHARACTERISTICS	REMEDIAL OBJECTIVES	COVER TYPE

Minimal Hazardous Substances in Landfill and Minimal Contamination of Groundwater

Significant Percentage of Hazardous Substances in Fill Are Below the Water Table, And Lowering the Water Table Is not Practicable

Leaching of Hazardous Substances to Groundwater Is Expected to Contribute to Unacceptable Human Health or Environmental Risks, and Reliability of Single Barrier Is Considered Adequate c

Significant Contaminant Mass in Fill, and Risks of Hazardous Substances Leaching to Groundwater Are Great

High Degree of Reliability Needed in Method of Minimizing Leaching of Hazardous Substances to Groundwater

Prevent Direct Contact; Minimize Erosion a → Native Soil Cover

Prevent Direct Contact; Minimize Erosion; Minimize Infiltration → Single Barrier Cap b

Prevent Direct Contact; Minimize Erosion; Prevent Infiltration → Double Barrier Cap

a Primary objective is to prevent direct contact, although the soil cover can be designed to reduce infiltration.

b Single barrier caps may include additional layers that provide protection to that barrier.

c Examples include situations where infiltration is not the primary concern and may include sites containing a small volume of contaminant mass, regions with low annual precipitation, or sites where groundwater is not being used as a source of drinking water.

Figure 3
Landfill Cover Selection Guide

Because these factors are similar for many CERCLA municipal landfill sites, it is possible to focus the RI/FS and selection of remedy process. In general, the remedial actions implemented at most municipal landfill sites include: (1) containment of landfill contents (i.e., landfill cap) (2) remediation of hot spot areas, (3) control and treatment of contaminated groundwater and leachate and (4) control and treatment of landfill gas. Other areas which commonly require remediation include surface waters, sediments and adjacent wetlands.

NOTICE

The policies and procedures set out in this paper are intended solely for the guidance of response personnel. They are not intended, nor can they be relied upon, to create any rights, substantive or procedural, enforceable by any party in litigation with the United States. The U.S. EPA officials may decide to follow this guidance, or to act at variance with these policies and procedures based on an analysis of specific site circumstances, and to change them at any time without public notice.

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Improving the Remedy Selection Process:
An Explicit and Interactive Process

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ABSTRACT

This paper summarizes the results of a year-long project to study the process of selecting remedies at Superfund hazardous waste sites. One key to getting a larger number of sites cleaned up is making the remedy selection process work as effectively and rationally as possible. The choice of a remedy determines the total cost of cleanup and the level of protection it will afford. The current process has been widely criticized as inconsistent.

The Clean Sites project identified that a key problem with the current process of selecting remedies is that it works backwards—the U.S. EPA explores in depth all the alternative cleanup methods it plans to consider before it determines the level of protection necessary for the site. Part of the problem is that program goals and requirements of site cleanup are poorly defined.

In its report, Clean Sites recommends that the U.S. EPA move to a process that explicit defines cleanup requirements and requires cleanup objectives be developed for each site before alternatives are developed. Clean Sites also recommends that the U.S. EPA adopt a more interactive approach to decision-making that elicits and responds to citizens' and states' comments as part of setting site cleanup objectives and before selecting a preferred alternative.

INTRODUCTION

Following the October 1986 reauthorization of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), members of the Superfund community criticized many of the remedies being selected by the U.S. Environmental Protection Agency (U.S. EPA) for Superfund sites. The U.S. Office of Technology Assessment (OTA) and a number of other government, industry and environmental organizations released reports charging that the U.S. EPA was not complying with the specific provisions for remedy selection developed as part of the Superfund Amendments and Reauthorization Act of 1986 (SARA).

In light of these criticisms, Clean Sites developed a project to bring together representatives from all areas of the broad Superfund community to discuss their concerns regarding Superfund remedy selection and to identify improvements to the current process. The project was initiated in the summer of 1989 under grants from the U.S. EPA and the Andrew W. Mellon Foundation, with additional support from private contributions. Nearly 100 individuals participated in a series of meetings and workshops in 1989 and 1990 to generate ideas for improving remedy selection in Superfund. The input of the many individuals who participated in this project was invaluable to the development of our recommendations. However, the recommendations presented in this report are those of Clean Sites.

As expected, the project revealed a great deal of continuing disagree-ment among the many participants in the Superfund program regarding the key requirements and goals of remedy selection—and of the Superfund program itself. Fortunately, there is also a great deal of common ground from which to build an effective remedy selection process.

THE CHALLENGE OF REMEDY SELECTION

For any remedy selection process to be effective, it must direct decision-makers to answer two fundamental questions at each Superfund site:

- What level of cleanup is required to achieve overall protection of human health and the environment?
- How will this level of cleanup be achieved?

The answers to these questions are not straightforward. The factors that are taken into consideration vary among sites and include risks to public health and the environment, statutory preferences, available technology, cost, liability and political sensitivities. Very often these issues create conflicting considerations for site cleanup.

At every site there are a number of interested parties with a stake in the decision. At most sites, these parties include the U.S. EPA, state environmental agencies, local citizen groups and potentially responsible parties (PRPs). Additional stakeholders may include other federal and state agencies, local governments, and national environmental groups. Naturally, each group approaches site cleanup from a different perspective. These different perspectives often result in differing opinions as to the cleanup requirements of the site.

In addition to the challenge of balancing the many issues and the range of interests involved in remedy selection, the U.S. EPA faces several fundamental challenges as a result of its decision to implement the Superfund program in a decentralized fashion. Paramount among these challenges is the tension between the desire for program consistency and the need for site-by-site flexibility. The challenge confronting the U.S. EPA as it attempts to implement a successful remedy selection process is to balance all of the site-specific and program-wide considerations of Superfund to protect human health and the environment, meet statutory directives and respond to stakeholder concerns — without creating a bureaucratic quagmire.

The U.S. EPA's current approach to remedy selection is presented in the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The U.S. EPA remedy selection process centers on the application of nine evaluation criteria representing the statutory requirements for Superfund cleanups and other considerations identified by the U.S. EPA for remedy selection. The overall process was developed to provide a great deal of flexibility to the site decision-maker.

MAJOR ISSUES

The results of Clean Site's project indicate that a number of specific

impediments exist to the implementation of effective and consistent remedy selection. The most significant issues and the resulting problems created in remedy selection are summarized below.

Issue 1

There is no program definition and little consensus among stakeholders as to "overall protection of human health and the environment." Overall protection is the primary objective of Superfund, yet there is no overall program definition or comprehensive site-specific process to establish this level of protection. In fact, the current remedy selection process does not require determination of site-specific cleanup levels to achieve protection of human health and the environment until after a remedial alternative has been selected.

The use of applicable or relevant and appropriate requirements (ARARs) in conjunction with site-specific risk assessment to establish cleanup levels has not been sufficiently developed or consistently applied at Superfund sites. The use of ARARs is confusing and time-consuming because most of these standards were developed to address different types of environmental problems. More specific guidance is needed before site-specific risk assessment can be used with any consistency to establish cleanup levels.

The results that remedy selection decision-making often works backwards—potential remedies are developed and evaluated before the level of cleanup necessary to achieve protection of human health and the environment is established. The lack of explicit standards or an explicit process to determine "how clean is clean" at specific sites results in insufficient attention to this issue. As a result, decision-makers are often inexplicit and local citizens and other interested parties are not informed as to the level of cleanup that is required to protect human health and the environment.

Issue 2

The nine criteria approach does not provide for the explicit evaluation of the statutory requirements for Superfund remedies. In particular, insufficient definitions exist for "permanence," "treatment," "long- term effectiveness" and "cost-effectiveness." The current process makes little distinction between long-term effectiveness and permanence and defines both concepts on a continuum. No specific process exists to guide the decision-maker in making the determination of cost-effectiveness. The use of treatment has been much debated and often has focused on the use of treatment for its own sake. The result of the above-cited problem is that the application of the statutory requirements is inconsistent and ambiguous. Inexplicit definitions have generated semantic arguments that obfuscate program objectives. Focus is often diverted from the actual results that the overall site cleanup will achieve. The outcome is a lack of consistency in the application of "permanence," "treatment," "long-term effectiveness" and "cost-effectiveness." In particular, the preference for permanence is often ignored.

Issue 3

The use of "modifying criteria" to formally address state and community concerns focuses much of the site communication at the end of the process in the record of decision (ROD). Currently, the U.S. EPA does not communicate the majority of important information regarding remedy selection until a remedy is proposed. Communities are not involved in the setting of objectives or goals for the site. The result of the foregoing is that communities generally believe they have no opportunity for meaningful input into decision-making. Because of the focus of communication in the ROD, important site information and decision-making rationale is not communicated in a clear and timely fashion. The use of the "modifying criteria" has created unnecessary friction between the U.S. EPA and states and communities by creating the impression that the only chance for input occurs after the U.S. EPA has proposed a remedy. As a result, communities often are reluctant to accept any remedy that may be proposed.

RECOMMENDATIONS FOR IMPROVING REMEDY SELECTION

Clean Sites believes that a long-term view of the hazardous waste cleanup problem should be adopted. Initiatives taken today may not assist the cleanup of those sites currently on the National Priorities List, but there are thousands of sites to be cleaned up and the more effort put toward the problem now, the faster the cleanups will be in the future, not just for Superfund but for all waste site cleanups. In response to the issues identified as a result of the project activities, Clean Sites believes that for remedy selection to be effective, the U.S. EPA approach to decision-making must do the following:

- Require the explicit determination and communication of site risks and objectives for cleanup as early in the process as feasible
- Clearly define the statutory requirements of Superfund and identify how they are to be achieved
- Enforce a consistent process which recognizes the need to incorporate site-specific considerations
- Provide for interactive communication throughout the process to generate input from all stakeholders, particularly the community

To address each of these desired characteristics, Clean Sites has developed the following recommendations:

1. U.S. EPA should establish an explicit process to focus on the identification of the level of cleanup necessary to achieve site-specific protection of human health and the environment. Such a process is presented in the following section. The purpose of an explicit process is to clearly identify the goals of the program and explain for each site how those goals have been achieved or why they cannot be achieved.

2. U.S. EPA should improve the usefulness of ARARs by more clearly identifying which standards apply to Superfund sites. A clearly applicable subset of available environmental standards will be much more useful than the current approach by allowing for quicker and more consistent application. Also important, this will allow for the comprehensive identification of specific site conditions for which no usable standards exist.

3. U.S. EPA should set a long-term goal, and focus the necessary resources, to develop standards to fill the gaps in currently available ARARs wherever possible. A practical set of nationally-developed standards applicable to the cleanup of even some categories of hazardous waste sites would greatly improve the cleanup process by reducing the time and conflict of selecting cleanup levels.

Clean Sites recognizes the time and effort that creating such standards would entail, but believes the size of the cleanup program and the long-term nature of the problem warrant a significant investment in investigating its feasibility. At least, the U.S. EPA should attempt to develop concentration levels for that subset of chemicals that are most commonly encountered. Setting the development of standards as a national long-term goal with the appropriate resource commitment will help to stimulate the development of the fundamental scientific base that ultimately can contribute to the quantification of risks to human health and the environment. During the life of Superfund, which may well exceed the professional careers of many current decision-makers, this effort would improve the certainty with which site cleanups are performed.

These standards would need to operate within a total framework that allows for different levels of site use and recognizes the highly variable conditions at hazardous waste sites. Part of developing standards should be to focus more strongly on the cleanup levels that are being selected at specific sites. When conditions are encountered at a site for which no standards are available, decisions made at that site should guide future decisions at similar sites. It is time to incorporate much better use of past experience into Superfund decision-making. The use of each site decision as a potential precedent for future decisions will result in a greater focus on the cleanup levels being selected and speed up future decision-making.

4. The U.S. EPA should develop a specific and detailed approach to using risk assessment procedures to establish site cleanup levels. Clean Sites recognizes that there are many conditions for which national standards are not feasible. Site-specific risk assessment will continue to be one of the primary tools for setting cleanup levels. The U.S. EPA should develop specific procedures and specific exposure scenarios that

provide the flexibility to select different future land uses.

5. The U.S. EPA should give greater weight to the so-called "point of departure" in the residual risk range. To increase the consistency of using risk assessment and to increase the explicitness of remedy selection, more stringent rules should be developed for deviating from the excess upperbound lifetime cancer risk of one-in-one-million (10^{-6})—the U.S. EPA's "point of departure." The current risk range of one-in-ten-thousand (10^{-4}) to 10^{-6} provides a very large variance in cleanup levels. By calling the entire range fully protective, the U.S. EPA has created a source of contention. Many PRPs logically take the position that if 10^{-4} is "fully protective," then they should not be required to achieve a higher level of protection. The NCP identifies 10^{-6} as a "starting point," which suggests that its attainment will be an exception. Clean Sites believes the point of departure should be viewed more seriously. Deviations should be permitted based upon site conditions, but the reasons for these deviations should be clearly explained and objectives for the site (including the future land use) should be revised as necessary.

6. The U.S. EPA should clearly define permanence as a goal of Superfund cleanups. Permanence will not be achieved at every site, but the statutory requirement to achieve permanence "to the maximum extent practicable" suggests that the feasibility of achieving a permanent solution should be specifically evaluated at each site. Permanence for Superfund should present a stringent but attainable goal. The dictionary definition of "permanent" is "intended to last indefinitely without change." Clean Sites believes this concept should be transferred to the evaluation of permanence with regard to Superfund sites. The application of permanence Clean Sites proposes is as follows:

> "Permanent solutions return the site to a usable condition by irreversibly eliminating the threat of any future release that would increase the risk to human health or the environment above cleanup levels identified for the site. Permanent solutions must conform with the statutory preference that waste not be disposed off-site without treatment."

This definition does not allow containment remedies to be considered permanent, but does allow remedies that achieve less than pristine levels of cleanup to be considered permanent when justified by site conditions.

7. Because permanence will not be achieved in many cases, long-term effectiveness should be the primary criterion in the evaluation of remedial alternatives. Long-term effectiveness is the ability of a remedy to maintain the desired level of protection over time. This, in effect, represents the "next best thing" to a permanent solution if a permanent solution is not practicable. In order to fully evaluate the long-term effectiveness of each alternative, the expected useful life of each alternative should be calculated (in years).

8. Treatment should not be used as a stand-alone criterion, but rather evaluated as a means to achieve permanence or long-term effectiveness. It is not the use of treatment, but the result of using treatment, that is important. Treatment options should be developed to clearly demonstrate the increased protection and long-term effectiveness they provide relative to containment remedies.

9. The consideration of cost should be more clearly evaluated against the overall result of site cleanup. Consideration of costs should be the last step in remedy selection. A cost-benefit approach for Superfund should compare costs against the primary benefit of long-term effectiveness. This approach would provide a relative measure of the long-term value of each alternative from which to make a decision.

10. The U.S. EPA should establish an interactive remedy selection process to incorporate the views of both the community and the state throughout remedy selection. The only way for these viewpoints to be fully considered is to involve the community and state in decision-making activities by regularly discussing issues and options regarding site cleanup. Round table discussions among all parties should be used to promote a greater understanding of site conditions and a mutual understanding of the concerns of each of the parties.

11. The U.S. EPA should disclose all site information as soon as it is available. The community needs detailed information early in the cleanup process. In order for an interactive process to work, all stakeholders must be well informed about site problems and activities.

12. U.S. EPA should develop a headquarters task force to assist in remedy selection. In a delegated program seeking consistency, some central source of guidance and assistance needs to be created to ensure quality and consistency in remedy selection. This group would not second-guess decisions, but would provide a clearinghouse for information and assistance and monitor the consistency of decision-making among U.S. EPA regions.

AN EXPLICIT PROCESS FOR REMEDY SELECTION

Remedy selection is influenced by all site characterization activities. Community relations, the remedial investigation (RI), the feasibility study (FS), and the ROD are all interrelated and should be considered components of a single remedy selection process. However, the current timing of these activities does not promote a logical decision-making process or provide discrete points for communication and interaction. The remedy selection process should promote an understanding of how all these activities are linked and focus decision-makers on the relevance of these activities to the overall determination of the appropriate response action.

To help achieve this goal, Clean Sites recommends that the decision-making process used by the U.S. EPA for remedy selection be reoriented to focus on the major issues that must be resolved at every site. These are:

* What are the risks to human health and the environment that require remediation?
* What is the level of cleanup necessary to achieve protection of human health and the environment in response to these risks?
* What alternatives are available to achieve the identified level of cleanup?
* Which alternative best fits the site conditions?

Clean Sites recommends that the U.S. EPA adopt a four-step process directed at explicitly answering these questions. Such a process would not require changing the content of the RI or the FS, but would simply reorient key decision-making points. The application and importance of each of the nine criteria would be strengthened through their explicit consideration at appropriate points throughout the process. The process Clean Sites recommends is presented below.

Step 1: Clearly Define the Problem

The site characteristics and risks identified in the RI and the base line risk assessment need to be clearly and consistently communicated because they play a key role in remedy selection. Site risks will guide the development of site cleanup objectives by focusing the decision on what specific problems of the site require remediation. A clear description of site risks also provides the community with a basis of understanding for subsequent site decisions. Early communication of these risks to the community should provide the U.S. EPA a vehicle to gain an understanding of the fears and concerns of the community.

Step 2: Establish Site Cleanup Objectives

The most critical point of remedy selection is establishing site-specific cleanup objectives. These objectives are: (1) the level of cleanup necessary to protect human health and the environment and (2) the expected use of the site. Clean Sites recommends that the U.S. EPA's "threshold criteria" (overall protection of human health and the environment and compliance with ARARs) be specifically identified and evaluated through explicit objective-setting.

Cleanup objectives should be detailed and explicit enough to guide the development of alternatives and to provide outside parties an understanding of what is to be achieved at the site. Developing cleanup objectives is an iterative process. Initial objectives should be realistic and sensible in light of the site conditions and, therefore, achievable. However, there will always be instances when initial objectives are determined not to be feasible from a technical or cost standpoint once alternatives are developed. In these cases, the objectives should be revised

and new objectives developed in light of the new information.

The revision of objectives should be as explicit an activity as the original development of objectives. It should also be recognized that there are cases when a higher level of cleanup is achievable at a small incremental cost, and this also must be considered as the process progresses. It is important that final cleanup objectives be developed before a remedy is selected.

Step 3: Develop Remedial Alternatives

Comprehensive cleanup alternatives should not be developed until after the objectives are established so that all alternatives, at a minimum, meet the site objectives. (This does not mean that all of the activities of the FS must wait until after the RI, as there are many data gathering and preliminary design steps that can proceed prior to the development of objectives.) Also at this point in the process, explicit consideration of permanence, treatment and long-term effectiveness is required so that these criteria can be fully considered in the evaluation of alternatives. At least one permanent remedy should be developed.

Step 4: Evaluate Alternatives and Select a Remedy

Alternatives should be evaluated considering cost, permanence, long-term effectiveness and the concerns of the community and state. To frame the problem, Clean Sites recommends a cost-benefit approach which compares the cost of alternatives to their overall long-term effectiveness. Permanent solutions represent the highest level of long-term effectiveness.

Since all of the alternatives under consideration must achieve site objectives, the task of selecting an alternative will be to select the alternative that achieves the greatest long-term value (protection over the longest number of years for the lowest cost). In some cases, one alternative will stand out. In other cases, several alternatives may provide similar long-term value. In such cases, community and state preferences would then be used to choose among the remaining alternatives.

CONCLUSION

The remedy selection process presented by Clean Sites forces the explicit communication of important site decision-making information early in the process. It is directed at eliciting and incorporating the views of all stakeholders. As such, much of the site controversy will occur earlier in the process than currently. Clean Sites believes this will force the U.S. EPA and the stakeholders to focus more deliberately on the difficult issues that must be resolved and be more explicit about the decisions that are reached. While this may slow the process somewhat in the beginning, it will ultimately lead to better decision-making, more community trust and more effective implementation of remedial actions.

Title III Of SARA: The Facts You Need To Know

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INTRODUCTION

Any business that handles or uses chemicals is potentially regulated by Title III of SARA, the Emergency Planning and Community Right-to-Know Act (EPCRA). This paper is designed to help facility owner/operators comply successfully with all of EPCRA's requirements and avoid enforcement actions.

The discussion will concentrate on each reporting requirement with significant detail. For the emergency planning requirements under Section 302 of EPCRA, the paper focuses on the responsibilities given to facilities and also to local emergency planners.

The EPCRA, Section 304 emergency release reporting requirements encompass both the extremely hazardous substances and the CERCLA hazardous substances subject to the CERCLA Section 103(a) provisions. The paper discusses the differences between the two reporting requirements and how to correctly report releases. Under Sections 311 and 312 of EPCRA, any facility that is subject to the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard (HCS) is subject to the inventory reporting requirements of EPCRA.

The EPCRA, Section 313 toxic chemical release reporting is probably the most well-known and most complex of the EPCRA requirements. The discussion will explain how to make an accurate threshold determination and how to properly complete U.S. EPA Form R. Under Section 322, of EPCRA there are provisions to claim and substantiate as trade secret a particular chemical identity an owner or operator wants withheld from the public or competitors. Lastly, there is a brief section on how the information collected is made available to the public under EPCRA.

SECTION 302: EMERGENCY PLANNING

According to SARA Title III, the Local Emergency Planning Committee (LEPC) is primarily responsible for developing and maintaining an emergency plan for its district. The State Emergency Response Commission (SERC) is responsible for coordinating the district plans together into a comprehensive statewide emergency plan. Section 302 of EPCRA was developed because no matter how broad-based the membership of the LEPC and SERC, it would be very difficult for them to identify every potential chemical hazard in their community. EPCRA, Section 302 provides a mechanism for identifying facilities that the planners should take into account in their planning efforts.

Who Is Subject

Since emergency planning is important to entire communities, the EPCRA, Section 302 requirements apply to all sectors of the community, from private residences to large businesses. There are very few facilities not included in the scope of Section 302 of EPCRA.

Exemptions

Ships and federal facilities are the only types of facilities not subject to Section 302 or any other section of EPCRA. Federal facilities are not included in the scope of EPCRA due to the following regulatory language: a "facility" for SARA Title III purposes must be "owned or operated by the same person" (40 CFR 355.20). The definition of "person" at 40 CFR 355.20, however, does not include the federal government. This unintentional exclusion applies only to federal facilities operated by Federal employees. This exclusion does not include government owned-contractor operated facilities (GOCOs) even though these GOCOs may be operating on Federal property.

Similarly, there is only one category of substances excluded from Section 302 and the other sections of EPCRA, except Section 304 emergency release notification. The substances in this category are those in transit. These substances in transit were given a statutory exemption by Congress. Section 327 of EPCRA reads: "Except as provided in Section 304, this title does not apply to the transportation, including the storage incident to such transportation, of any substance or chemical subject to the requirements of this title, including the transportation and distribution of natural gas." Therefore, if a substance is under active shipping papers, whether it is actively in transit, in storage during transit or in a distribution pipeline, it is considered to be in transit and not included in the scope of EPCRA (except for Section 304). However, once the substance is delivered and the shipping papers are signed, that substance is no longer exempt under the above provision. The substance must then be included in any applicable threshold determinations. Similarly, once a substance in a pipeline reachs an end-of-the line holding tank and is no longer in the pipeline, it is no longer part of the transportation exemption and must be included in any applicable threshold determinations.

De Minimis

In order to make threshold determinations for mixtures and solutions easier to calculate, the U.S. EPA set a minimum concentration level below which a person can disregard the EHS. This level is called the de minimis. The de minimis for Section 302 of EPCRA is 1%. Any amount in a concentration greater than 1% must be factored into a threshold determination. Any amount less than or equal to 1% can be excluded from the threshold determination (40 CFR 355.30(e)(1)).

Facilities (excluding ships or vessels and Federal facilities) are subject to the emergency planning provisions of Section 302 of EPCRA if they are a facility at which there is present an EHS equal to or exceeding its Threshold Planning Quantity (TPQ) or if they are a facility that has been designated by the SERC under the authority of SARA Section 302(b)(2) to become subject to the requirements of emergency

planning. The following discussion will focus on the substances covered and the thresholds for reporting.

The Extremely Hazardous Substances (EHS) List

The EHS list was originally developed by the U.S. EPA under the voluntary Chemical Emergency Preparedness Program (CEPP) as the acutely toxic chemicals list. The purposes of the EHS list were, and still are, to identify substances which, if released, could cause serious, irreversible health effects and to provide emergency planners with a starting point for their efforts. In order to identify these substances, the U.S. EPA developed criteria that would be used to identify short- and long-term health effects resulting from short, term exposure. These criteria were then applied to the Registry of Toxic Effects of Chemicals Substances (RTECS) data base. Any substance that met one or more of the criteria was then included on the EHS list.

Threshold Planning Quantity (TPQ)

In order to further assist emergency planners, the U.S. EPA developed a Threshold Planning Quantity (TPQ) for each EHS. This TPQ does not represent a cutoff above or below which a substance is or is not a danger. Rather, the TPQ was developed as a preliminary cutoff that local emergency planners could use to further prioritize facilities for their planning efforts. The TPQ was developed by assigning each EHS an index that accounts for the potential of the chemical to become air-borne and for the toxicity of the substance. Each index then corresponded to a TPQ level. The TPQ for any EHS can be found on the list in 40 CFR 355, Appendices A and B. It is the TPQ that determines whether or not a facility is subject to Section 302 of EPCRA.

When doing a threshold determination, the EHS amount must be aggregated for all sources of the EHS at the facility (every container, drum, etc.) regardless of the method of storage or the number of containers. There are no exemptions given in the regulations in 40 CFR 355 for uses or storage of EHSs and, therefore, if an EHS is present at the facility, it must be included in the threshold determination. When doing threshold calculations, a facility owner/operator must consider the issues discussed below:

Mixtures And Solutions

If the EHS in question is present at the facility in a mixture or solution, the TPQ is calculated based on the weight percent of the EHS in the mixture or solution.
Substances With Two TPQs

Some substances on the EHS list have two TPQ values: a low TPQ and a 10,000 pound TPQ. These double thresholds were developed to account for solid substances which, when they exist in different physical states, represent different hazards.

EHS List Issues

Two substances appear on the EHS list with qualifiers. These substances are hydrogen chloride (gas only) and hydrogen peroxide (concentration > 52%). These qualifiers indicate the only conditions under which the substance is extremely hazardous. Therefore, hydrogen chloride is an EHS only when it exists as a gas and is subject to a threshold determination under Section 302 of EPCRA only when it is in a gaseous state. Similarly, only if hydrogen peroxide is present in concentrations above 52% by weight is it an EHS and subject to a threshold determination under Section 302 of EPCRA.

What To Submit

Once a facility becomes subject to the emergency planning requirements of EPCRA Section 302, the owner/operator must notify the SERC and LEPC that the facility is subject to emergency planning. This notice originally was required to be given by May 17, 1987, and since then is required within 60 days after the facility first becomes subject to Section 302 of EPCRA (40 CFR 355.30(b)). This notification can be verbal, but is strongly preferred in writing. The notice must specify the name and an accurate and current address of the facility (April 22, 1987; 52 FR 13379). The facility owner/ operator also must provide the name of a facility emergency coordinator who will assist the SERC and LEPC when developing a plan for their facility (40 CFR 355.30(c)).

This initial notice is not required to include information on what substances are present or what amounts are present. If the SERC or LEPC needs additional information, they will request it using their authority under Section 303(d)(3) of EPCRA. This section stipulates that if a SERC or LEPC requests any information that it feels is necessary to the development of its emergency plan, the facility owner/operator must provide the information and is subject to penalties if he does not.

Therefore, if a facility has an EHS present at any one time in an amount equal to or exceeding the TPQ (40 CFR 355.30 (a)) or has been designated by the SERC as a facility subject to emergency planning (40 CFR 355.30(a)), then the owner/operator must notify his/her SERC and LEPC that his/her facility is subject to emergency planning, provide the name of a facility emergency coordinator (40 CFR 355.30(b) and (c)) and provide any information to the SERC or LEPC that it requests under Section 303(d)(3) of EPCRA.

SECTION 304: EMERGENCY RELEASE NOTIFICATION

Under EPCRA, the SERC and LEPC are responsible for developing an emergency plan to be used when responding to emergencies in their district. In order to provide a mechanism for notifying the SERC and LEPC about emergencies needing response, Congress enacted EPCRA Section 304, the emergency release notification requirements. Unlike most other release reporting requirements, Section 304 of EPCRA requires notification to be given to the state and local authorities. These are the persons most likely to respond to and be affected by a release and are the persons with knowledge of the emergency plan and how it works.

Who Is Subject

The emergency release notification provisions of Section 304 of EPCRA apply to any facility "at which a hazardous chemical is produced, used or stored" (40 CFR 355.40(a)(1)(i)). A hazardous chemical is defined by OSHA as any substance that presents a physical or health hazard (29 CFR 1910.1200). Since a facility must produce, use or store a hazardous chemical to be subject to Section 304 of EPCRA, very few facilities will be excluded from its scope. Any facility that has any hazardous chemical in any amount is included in the scope of Section 304 of EPCRA.

An important difference between Section 304 and the rest of the EPCRA regulations is the definition of "facility." The definition of "facility" usually includes "all buildings, equipment, structures, and other stationary items which are located on a single site or on contiguous or adjacent sites and which are owned or operated by the same person..." (40 CFR 355.20). However, for Section 304 of EPCRA, the definition of "facility" is expanded to include "motor vehicles, rolling stock, and aircraft." Although the definition of "facility" was modified to encompass the majority of transportation related releases, it still does not include vessels or Federal facilities.

Substances Covered

There are two lists of chemicals covered under Section 304 of EPCRA. They are the Extremely Hazardous Substances (EHS) found in 40 CFR 355, Appendices A and B and the CERCLA Hazardous Substances found in 40 CFR Table 302.4. The EHS list was developed under the voluntary Chemical Emergency Preparedness Program (CEPP) as a list of substances that when released, could cause serious, irreversible health effects. The CERCLA hazardous substances were identified based on other environmental statutes. Section 101(14) of CERCLA designates hazardous substances pursuant to Sections 307(a) and 311(b)(2)(A) of the Clean Water Act, Section 3001 of the Resource Conservation and Recovery Act, Section 112 of the Clean Air Act and Section 7 of the Toxic Substance Control Act. If the substance in question does not appear on either list, then regardless of the amount released, it is not a reportable event under Section 304 of EPCRA.

Reportable Quantities

For each chemical that appears on either the EHS or CERCLA hazardous substance lists, an amount has been determined (based on the chemical's individual properties) which when released triggers the Section 304 notification requirements. This amount is known as the Reportable Quantity. An RQ is established under the authority of Section 102(b) of CERCLA which states that the RQ shall be equivalent to the RQ established under Section 311 of the Clean Water Act, or one pound, until such time as the U.S. EPA establishes a final RQ for the substance.

The final RQ is determined by evaluating the substance for six "primary criteria" (50 FR 13466). These criteria are: aquatic toxicity, mammalian toxicity, ignitability, reactivity, chronic toxicity and potential carcinogenicity. Each property is ranked on a scale of 1, 10, 100, 1000 or 5000 pound RQs. The lowest RQ becomes the primary criteria RQ. The primary criteria RQ is then evaluated against the following "secondary criteria" (50 FR 13468): biodegradability, hydrolysis and photolysis. The primary criteria RQ is then raised one level (to the next higher RQ) if the secondary criteria shows that the substance will degrade relatively rapidly to a less harmful compound when released.

The authority for establishing an RQ is under CERCLA Section 102(b). The U.S. EPA only has the authority to establish an RQ for substances on the CERCLA hazardous substances list (no such authority was written in EPCRA). Any EHS that is also on the CERCLA hazardous substances list was required by EPCRA to have the RQ that was established under CERCLA. Any EHS that does not appear on the CERCLA hazardous substances list was given a statutory one pound RQ under EPCRA Section 304(a)(2).

As of February 1990, there were 134 EHSs that also appeared on the CERCLA hazardous substances list. As a result, if an RQ of one of these substances is released, two notification requirements potentially must be fulfilled: one under EPCRA Section 304 and one under CERCLA Section 103(a).

In order to simplify release reporting requirements, the U.S. EPA had proposed to add the remaining 232 EHSs not listed on the CERCLA hazardous substances list to the CERCLA list (January 23, 1989, 54 FR 3388). On August 30, 1989 (54 FR 35988), the U.S. EPA then proposed to establish final RQs using CERCLA Section 102 (b) authority for these EHSs. On February 15, 1990 (55 FR 5544), the U.S. EPA took final action to delete six of the EHSs from 40 CFR 355, Appendices A and B. Therefore, the final rule to add the EHSs to the CERCLA hazardous substance list will only include the 226 remaining chemicals. These EHSs are expected to be added to the CERCLA list with their final RQs sometime during 1990 in a final rule encompassing both proposed rules mentioned above. When the final rule is published, all the substances on both lists will be subject to both release reporting requirements.

Mixtures

For Section 304 of EPCRA, the U.S. EPA is concerned only with the actual amount of EHS released when a mixture is released. Since that is the case, a mixture calculation is made in the same manner as in any other section of EPCRA, by using the weight percent of the EHS present in the mixture (April 22, 1987; 52 FR 13392). For CERCLA Section 103 (a), the Clean Water Act mixture rule is applied. If the concentrations of the constituents are known, a weight percent calculation may be made. If the concentrations are unknown, the weight of the entire mixture spilled is compared to the lowest component RQ (April 14, 1985; 50 FR 13463).

De Minimis

Unlike the rest of EPCRA, there is no de minimis exemption for Section 304. The de minimis, the minimum amount of concern, is the RQ. Therefore, no matter how low the component concentration is in a mixture, a weight percent calculation must be made.

Release

The definition of "release" is very broad to encompass all possible actions, both intentional or accidental. "Release means any spilling,

leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles) of any hazardous chemical, extremely hazardous substance, or CERCLA hazardous substance." (40 CFR 355.20).

Both the EPCRA Conference Report and the EPCRA statute stipulate that a release is to be reported under EPCRA in the same manner as under CERCLA Section 103(a). This has been interpreted by the U.S. EPA to include the 24-hour RQ time frame for reportable release amounts. Therefore, if a facility has a release of an EHS or CERCLA hazardous substance in an amount equal to or in excess of its RQ in a 24-hour period, the release is potentially subject to the reporting requirements of EPCRA Section 304 and CERCLA Section 103(a).

Exemptions

Even though there may have been a release from the facility, it still must be determined if it is a reportable release. Title 40 CFR 355.40(2) specifically exempts six types of releases from the reporting requirements of Section 304 of EPCRA. These release are: (1) any release which results in exposure to persons solely within the boundaries of the facility, (2) any release which is a "federally permitted release" as defined in Section 101(10) of CERCLA, (3) any release which is "continuous" as defined under Section 103(f) of CERCLA, (4) any release of a pesticide product exempt from Section 103(e) of CERCLA, (5) any release not meeting the definition of release under Section 101(22) of CERCLA, and therefore exempt from Section 103(a) reporting and (6) any radionuclide release which occurs: (A) naturally in soil from land holdings such as parks, golf courses, or other large tracts of land; (B) naturally from the disturbance of the land for agricultural or construction activities; (C) from the dumping of coal and coal ash at utility and industrial facilities with coal-fired boilers; and (D) from coal and coal ash piles at utility and industrial facilities with coal-fired boilers.

The preamble to the April 22, 1987 final rule (52 FR 13384) discusses three releases not included in the scope of Section 304 reporting. Although they are not spelled out in the regulations, these releases are exempted because they do not meet the definition of a release under Section 101(22) of CERCLA. They are: releases from engine exhaust, normal application of fertilizer and releases of source, byproduct or special nuclear material from a nuclear incident at a nuclear power plant. If the release is covered by one of the above exemptions, there is no reporting requirement under Section 304 of EPCRA, even if a listed substance is released in an amount equal to or in excess of its RQ.

Reporting Requirements Under EPCRA Section 304

Under Section 304 of EPCRA, if an EHS or CERCLA hazardous substance is released in an amount equal to or in excess of its RQ in a 24-hour period, it is a potentially reportable release. If the release is not exempted from the requirements, it is a reportable release and the owner/operator of the facility must immediately notify the SERCs and the community emergency coordinators for the LEPCs for all areas likely to be affected by the release. The time period for a facility owner/operator to immediately notify is intentionally not defined in the regulations to encourage prompt reporting.

The information that must be included in the initial notification is listed in the regulations at 40 CFR 355.40(b)(2) and includes the following information: the chemical name or identity of any substance involved in the release; an indication of whether the substance is an EHS; the time and duration of the release; the medium or media into which the release occurred; any known or anticipated acute or chronic health risks associated with the emergency (and, where appropriate, advice regarding medical attention necessary for exposed individuals); precautions to take as a result of the release, including evacuation (unless such information is readily available to the community emergency coordination pursuant to the emergency plan); and the names and telephone numbers of the persons to be contacted for further information. The U.S. EPA strongly recommends that the location of the release also be included in the initial notification.

Unlike CERCLA, as soon as practicable after a reportable event has

occurred, a written follow-up notice must be submitted to all EPCRA entities which received the initial verbal notice. The time frame involved is not specified in the regulation to encourage prompt submissions. The information that must be included in the written follow-up is set forth in 40 CFR 355.40 (b)(3). The written follow-up must set forth and update the information given in the initial notice as well as include additional information regarding: actions taken to respond to and contain the release, any known or anticipated acute or chronic health risks associated with the release and, where appropriate, advice regarding medical attention necessary for exposed individuals. Additionally, the U.S. EPA recommends that the cause of the incident be included in the written follow-up notice as well.

Transportation-Related Release

For purposes of EPCRA Section 304, the definition of facility includes motor vehicles, rolling stock and aircraft. If the release is a transportation-related release, the transportation vehicle is a facility and it is the responsibility of the owner/operator of the transportation vehicle to report the release.

In the case of a transportation-related release, the owner/operator of the vehicle may meet the requirements of EPCRA Section 304 by providing the required information to the 911 emergency service or, in the absence of a 911 emergency service, to the telephone operator. Also, no written follow-up report is necessary for a transportation-related release (40 CFR Section 355.40(b)(4)(ii)).

Reporting Requirements Under CERCLA Section 103(a)

Under CERCLA Section 103(a), if a CERCLA hazardous substance is released in an amount equal to or in excesses of its RQ in a 24-hour period, it is a potentially reportable release. The exemptions from the CERCLA 103(a) reporting requirements are found in Section 101 (22) of CERCLA.

If the event is reportable, any person or persons in charge of a facility or vessel with knowledge of the reportable release must notify the National Response Center (NRC) immediately. The notice information is not specified in the CERCLA regulations. It is up to the NRC to ask the procedural questions about the event and to evaluate if the event warrants federal intervention.

Differences Between EPCRA Section 304 and CERCLA Section 103(a)

Along with the obvious difference between the EPCRA Section 304 and CERCLA Section 103(a) reporting requirements, there are three other important differences which are: (1) CERCLA Section 103(a) requirements include vessels in the definition of facility and EPCRA Section 304 does not; EPCRA Section 304 only covers releases that have the potential to migrate beyond the facility boundaries (40 CFR 355.40 (a)(2)(i)); CERCLA Section 103(a) only requires that a release go into the environment to be reportable, and (3) Petroleum products are exempted from the notification requirements of CERCLA Section 103 (a) because they are not included in the definition of "Hazardous Substances" found in CERCLA Section 101(14); no such exemption exists under EPCRA Section 304. Therefore, if a petroleum product containing an EHS is spilled and an RQ of that EHS is released, it is potentially reportable under EPCRA, Section 304.

Overlap Between the Two Laws

Regardless of the differences, the potential for having to report a release under both authorities does exist. Assuming no exemptions have been met for the event, there are three possible scenarios to consider:

Release of an EHS That Is Not a CERCLA Hazardous Substance

Since the substance is listed on the EHS list only, the release is only subject to EPCRA Section 304 requirements. Therefore, a notification (and subsequent written follow-up) must be given immediately to the SERCs and LEPCs for all areas likely to be affected by the release.

Release of an EHS That Is Also a CERCLA Hazardous Substance

Since the substance is on both the EHS list and the CERCLA hazar-

dous substances list, the release is subject to both the EPCRA Section 304 and CERCLA Section 103 (a) requirements, respectively. This is because even though the CERCLA Section 103(a) requirements apply only to the CERCLA Hazardous Substance list, the EPCRA Section 304 requirements apply to both the EHSs and CERCLA hazardous substances (40 CFR 355.40(a)(1)(ii)). Therefore, a notification (and subsequent written follow-up) must be given immediately to the SERCs and LEPCs for all areas likely to be affected by the release (EPCRA Section 304) and a notification must be made to the National Response Center (NRC) (CERCLA Section 103(a)).

Release of a CERCLA Hazardous Substance That Is Not an EHS

Since the requirements of EPCRA Section 304 apply to both the EHSs and CERCLA hazardous substances, this scenario would be reportable in the same manner as Scenario number 2.

The U.S. EPA has proposed to add all the EHSs not currently on the CERCLA hazardous substances list to that list. When that occurs, Scenario number 1 will no longer exist and all releases will be reported in the same manner as Scenario number 2. Until that time, releases are reported as stated above.

SECTIONS 311 AND 312: COMMUNITY RIGHT-TO-KNOW

Sections 311 and 312 of EPCRA were designed to provide the public with important information about the types and quantities of hazardous chemicals present in their communities. This information can enhance community awareness of chemical hazards and facilitate development of state and local emergency response plans.

Sections 311 and 312 of EPCRA require facilities to make public their MSDSs or lists of their hazardous chemicals and Tier I or Tier II inventory forms which detail the quantities, hazards and storage information about these chemicals. OSHA's Worker Right-to-Know law requires employers to communicate chemical hazards to persons within the facility. Sections 311 and 312 of EPCRA expand this concept of right-to-know to the communities surrounding the facility.

The LEPCs and SERCs receive the information on hazardous chemicals from the facilities and then make it available to the public upon request. Facility owner/operators must also submit the EPCRA Section 311 and 312 information to the local fire department, but the fire department has no obligation to provide this information to the public.

Who Is Subject

Any facility which is required to prepare or have available an MSDS under the Federal OSHA Hazard Communication Standard (HCS) is regulated by EPCRA Sections 311 and 312 (40 CFR 370.20(a)). Originally, the OSHA HCS only applied to manufacturers in Standard Industrial Classification (SIC) codes 20-39. OSHA expanded its HCS to cover all non-manufacturers other than the construction industry on June 24, 1988 (53 FR 27679). It was expanded again to include the construction industry as well on January 30, 1989 (54 FR 6886). The HCS now covers all employers who handle hazardous chemicals, unless those employers are exempted.

Substances Covered

OSHA's definition of "Hazardous Chemical" is broader than many people expect. OSHA does not have an inclusive list of all hazardous chemicals, rather, they have a performance criterion: "Hazardous Chemical" means any chemical which is a physical hazard or a health hazard as defined at 29 CFR 1910.1200(b). Any of over 500,000 products may meet this criterion.

The easiest way to determine which chemicals are hazardous chemicals is to take an inventory of the facility MSDSs. OSHA requires that manufacturers and importers ensure that distributors and employers are provided with an appropriate MSDS with their initial shipment of a hazardous chemical (29 CFR 1910.1200(g)(7)). There is a good chance that every hazardous chemical on the site will be represented by an MSDS in the MSDS file which the facility owner/operator must maintain under the OSHA regulations.

It is possible that a manufacturer or supplier has been negligent in

supplying copies of MSDSs. If a chemical comes on-site without an MSDS, but that chemical has been labeled as a hazardous chemical, the facility owner/operator has an obligation to obtain an MSDS from the chemical manufacturer, importer or distributer as soon as possible (29 CFR 1910.1200(g)(7)). As the facility owner/operator goes through his/her MSDSs, he/she should take note of hazardous chemicals which contain EHSs because he/she must give them special treatment when calculating thresholds. There are certain exemptions from OSHA's MSDS requirement and from the definition of "Hazardous Chemical" under Section 311 and 312 of EPCRA. These shall be addressed later.

Thresholds

OSHA requires that an establishment maintain MSDSs for all hazardous chemicals present at the establishment, regardless of the quantity of chemical present. Under SARA, Title III, the U.S. EPA only regulates those chemicals which are present in quantities capable of significantly effecting the surrounding community. The only hazardous chemicals which need to be reported under Sections 311 and 312 of EPCRA are those present in a quantity of 10,000 pounds or more, unless the hazardous chemical is (or contains) an EHS. An EHS needs to be reported if it is present in a quantity of 500 pounds or its TPQ, whichever is lower. These thresholds apply to the amount of the hazardous chemical present at the facility at any one time. They do not apply to the amount of chemical purchased or used throughout the year.

Many hazardous chemicals are contained within mixtures. A mixture is a combination of two or more different chemicals, each retaining its own chemical identity. Under Sections 311 and 312 of SARA, the owner/operator of a facility can choose to provide the required information on each hazardous chemical component in the mixture or to provide the required information on the mixture as a whole. The decision should be made by the facility owner/operator on the basis of the situation at the facility.

The choice of how to report determines how the owner/operator must calculate his/her thresholds. If the reporting is on each hazardous component of the mixture, then the concentration of the hazardous chemical is multiplied by the total weight of the mixture to determine the quantity of hazardous chemical in the mixture. If the reporting is on the mixture itself, the total quantity of the mixture shall be reported. The owner/operator must be careful to determine if the mixture contains an EHS, because in these cases the U.S. EPA does not allow a choice in the threshold calculation. If mixtures at a facility contain EHSs, the mixture(s) or the EHS components must be reported when the TPQ or 500 pounds, whichever is less for that EHS, is reached. Quantities of each EHS must be considered individually and then aggregated to determine if the quantity at the facility exceeds the reporting threshold.

Exemptions

Certain facilities are exempt from OSHA's MSDS requirements, certain uses of chemicals are exempt from OSHA's MSDS requirements and other chemicals and uses are exempt from Section 311 and 312 of EPCRA even though they might require an MSDS. OSHA's coverage is very broad, but there are three main categories of employers which are outside of OSHA's jurisdiction. The first is state and local governments. Because OSHA excludes states and political subdivisions of states from its definition of "employer" (29 USC 652(4)), the OSHA HCS cannot apply to state or local agencies. States and local governments may be required to have available MSDSs under a state-approved plan; however, since they are exempt from federal OSHA, they are exempt from Sections 311 and 312 of EPCRA. State agencies may, however, subject their state and local governments to state community right-to-know laws under their own authority.

The next group of facilities which are not covered by OSHA are those covered by some other federal safety act, in lieu of OSHA. This situation occurs at mining facilities. Mining extraction operations are covered by the Mining Safety and Health Act (MSHA) rather than OSHA. Even though they must have MSDSs under MSHA, mining facilities would not be covered by Sections 311 and 312 of EPCRA because they are exempt from OSHA.

Special loopholes in the law exempt a final group of facilities from OSHA. A special congressional rider exempts farmers with fewer than 10 employees from OSHA. This is a special case and does not apply to any other industry. Because farmers with fewer than 10 employees are exempt from OSHA, they would be exempt from Sections 311 and 312 of EPCRA.

The U.S. EPA's EPCRA regulations have some facility exemptions as well. Federally-owned and operated facilities are exempt from EPCRA since the federal government is not included in EPCRA's definition of person. Federal facilities, therefore, would be exempt from Sections 311 and 312 since they are exempt from all sections of EPCRA.

Section 327 of SARA states that EPCRA does not apply to the transportation, including the storage incident to such transportation, of any substance, except for Section 304 reporting. Therefore, materials being distributed or stored incident to transportation would not be included in a facility threshold determination for any portion of SARA, Title III except Section 304. This exemption may apply to chemicals in a warehouse, provided the chemicals are still under active shipping papers (SARA Conference Report, October 3, 1986, p.311).

Another U.S. EPA exemption is the de minimis concentration level. This exemption is for hazardous chemicals in mixtures or solutions where the concentration of the hazardous chemical is so low that the mixture or solution does not present a significant physical or health hazard at the facility.

For mixtures which contain hazardous chemicals in amounts below the de minimis concentration, the amount of the hazardous chemical is not counted toward the threshold for reporting that substance. The de minimis for reporting hazardous chemicals is the same as the de minimis used by OSHA. OSHA states at 29 CFR 1910.1200 that the de minimis concentration is 1% by weight unless the chemical is a carcinogen or a suspected carcinogen, in which case the de minimis cut off would be 0.1 percent by weight.

In addition to the exemptions noted above, OSHA's HCS contains eight exemptions from MSDS requirements. These are defined at 29 CFR 1910.1200(b)(6) as: (1) any hazardous waste as such term is defined by the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery act of 1976, as amended (42 U.S.C. 6901 et seq.) when subject to regulations issued under that Act, (2) tobacco or tobacco products, (3) wood or wood products, (4) articles as defined under 29 CFR Section 1910.1200(b), (5) food, drugs, cosmetic or alcoholic beverages in a retail establishment which are packaged for sale to consumers, (6) foods, drugs or cosmetics intended for personal consumption by employees while in the workplace, (7) any consumer product or hazardous substance, as those terms are defined in the Consumer Product Safety Act (15 U.S.C. 2051 et seq.) and Federal Hazardous Substances Act (15 U.S.C. 1261 et seq., respectively, where the employer can demonstrate it is used in the workplace in the same manner as normal consumer use, and which use results in a duration and frequency of exposure which is not greater than exposures experienced by consumers and (8) any drug, as that term is defined in the Federal Food, Drug and Cosmetic Act (21 U.S.C. 302 et seq.), when it is in solid final form for direct administration to the patient (e.g., tablets). If the chemical meets one of these exemptions, then the facility owner/operator does not need to maintain an MSDS for it. Therefore, the chemical would be exempt from Sections 311 and 312 of EPCRA.

Section 311(e) of EPCRA contains five additional exemptions from the definition of "Hazardous Chemical." These exemptions apply above and beyond the previously listed eight OSHA exemptions, so these chemicals are exempt from Sections 311 and 312 of EPCRA even if an MSDS is required for them under federal OSHA. The definition of a hazardous chemical under Title III of SARA specifically excludes the following substances: (1) any food, food additive, color additive, drug or cosmetic regulated by the Food and Drug Administration (FDA), (2) any substance present as a solid in any manufactured item to the extent exposure to the substance does not occur under normal conditions of use, (3) any substance to the extent it is used for personal, family or household purposes, or is present in the same form and concentra-

tion as a product packaged for distribution and use by the general public, (4) any substance to the extent it is used in a research laboratory or a hospital or other medical facility under the direct supervision of a technically qualified individual and (5) any substance to the extent it is used in routine agricultural operations or is a fertilizer held for sale by a retailer to the ultimate customer. These exemptions do not exclude all amounts of the chemical on-site, but only the amount which is used in a manner consistent with the exemptions. Also, the exemptions do not take a chemical off the EHS list, they only exempt it from the definition of a "Hazardous Chemical."

Section 311 of EPCRA requires the submission of MSDSs or a list of each hazardous chemical present at the facility in quantities equal to or greater than their threshold. If a list is submitted, the chemicals must be "grouped by hazard category," meaning the facility owner/operator must indicate which of the U.S. EPA's five hazard characteristics the chemical exhibits. The U.S. EPA's five categories are based on the 23 OSHA HCS categories for physical and health hazards (29 CFR 1910.1200(c)). MSDSs usually will be standardized according to the 23 OSHA categories.

The U.S. EPA hazard category definitions (40 CFR 370.2) that follow may be used to convert the OSHA categories to the U.S. EPA categories. "Fire hazard" means any chemical defined by OSHA as a flammable, combustible liquid, pyrophoric or oxidizer. "Sudden release of pressure" means any chemical defined by OSHA as an explosive or compressed gas. "Reactive" means any chemical defined by OSHA as an unstable reactive, organic peroxide or water reactive. "Acute health hazard" means any chemical defined by OSHA as a highly toxic, toxic, irritant, sensitizer, corrosive and any other hazardous chemical with an adverse effect on a target organ that generally occurs rapidly as a result of short-term exposure and with a short duration. "Chronic health hazard" means any chemical defined by OSHA as a carcinogen and any other hazardous chemical with an adverse effect on a target organ that occurs as a result of long-term exposure and with a long duration.

Although the regulations do not require a set format for the list submission, the U.S. EPA has recommended a method of organizing the list. The facility owner/operator may list the reportable chemicals in a column on the left-hand side of a sheet of paper. Make five more columns and label each with one of the hazard categories. Then put check marks in the appropriate columns beside the chemicals which exhibit the characteristics.

It is up to the facility owner/operator to decide whether to submit MSDSs or a list of chemicals. He/she must consider the following points when choosing between the list versus the MSDS submission for Section 311 of EPCRA. The list usually is preferred by the LEPC, fire department and SERC because it reduces their information burden. The production of a list may require some additional analyses of the MSDS to determine the appropriate hazard categories of each chemical. This analysis, however, would need to be done to complete the EPCRA Section 312 requirements anyway, so sending MSDSs would only postpone this burden. Submission of MSDSs requires copying, in triplicate, all required MSDSs. Any MSDS submitted under EPCRA Section 311 must be updated if any significant new information concerning the chemical is discovered. Some states charge a higher reporting fee for MSDS submissions than they do for list submissions.

Whichever method of reporting is chosen, the report must be sent to the LEPC, SERC and local fire department. The original EPCRA Section 311 submission is due within three months after the facility owner/operator first becomes subject to OSHA's MSDS requirements. After that, the owner/operator must update the list or submit a new MSDS within three months after a new hazardous chemical requiring an MSDS becomes present in an amount exceeding the threshold (40 CFR 370.21(c)).

Section 312 of EPCRA requires the submission of a Tier I or Tier II inventory form. Copies of these forms and instructions for completing them appear in the July 26, 1987, final rule in the *Federal Register* on pages 30632 through 30656. To determine which hazardous chemicals to include on the Tier I or Tier II form, the facility owner/operator must first calculate the maximum amount of each chemical that was on-site during the reporting year. The reporting year is the calendar year preceding the year of the submission of the form. Any chemical which met or exceeded the threshold at any time during the year would be reported.

Although the Tier I form is less detailed than the Tier II form, the Tier II form can be used as a worksheet for the Tier I form. Discussion will therefore begin with the Tier II form before addressing the Tier I form.

Completing the Tier II Form

Most of the information requested on the Tier II form is self-explanatory. For questions such as the average daily amount, an educated approximation of the average amount of the chemical stored at the site is usually accurate enough for the form. Generally, the facility owner/operator can simplify the average daily amount calculation by comparing the most a facility would have with the least they would have. The average falls somewhere in between these figures. Often this observation is enough to determine the appropriate range code to enter on the Tier II form.

The storage code has three parts. The first part describes the storage type. The second part indicates the temperature and the third part indicates the pressure. The appropriate codes are found in Table II and III of the instructions.

The U.S. EPA has not mandated specific requirements for the method of expressing storage locations. Simply provide a brief description of the precise location of the chemical, so that emergency responders can locate it easily. Providing an optional site plan or site coordinates may be advantageous. A narrative form or a map with appropriate site coordinates or abbreviations also may be used.

If for some reason, revealing the locations of the chemicals would put a company at a competitive disadvantage, the owner/operator may include the confidential location sheet with the submission. Using this option, the facility owner/operator also must submit the nonconfidential form but in the location section write the word "confidential."

The easiest way to fill out a Tier I form, in most cases, is to fill out the first three rows of the Tier II form as discussed above. Then for each hazard type of physical and health hazard, add the maximum weights of all chemicals indicated as the particular hazard type, find the appropriate range value code and enter this code as the maximum amount. Finally, in the general location section, record the locations of all applicable chemicals for each hazard class. The general locations should include the names or identifications of buildings, tank fields, lots, sheds or other such areas.

The owner/operator or an authorized representative of the owner/operator must sign the certification at the bottom of the form. The form sent to the SERC should have an original signature. The forms sent to the LEPC and the fire department can be photocopied.

There are advantages and disadvantages to using each type of form. Although only the facility owner/operator can determine which form best suits his/her needs, the Tier II form is generally both easier and more useful.

SECTION 313 OF SARA:
TOXIC CHEMICAL RELEASE INVENTORY

Section 313 of SARA is a release reporting requirement which applies to certain owners/operators of manufacturing facilities. The covered owners/operators are required to report annual releases of certain toxic chemicals to the U.S. EPA and to their designated state contact. If the facility does not meet the basic applicability requirements, then they are not required to report their releases of these toxic chemicals under Section 313 of SARA, regardless of the amount released. If the applicability is met for one or more of the toxic chemicals, then the filing of release information is required for each chemical which was used at or above an applicable threshold.

Who Is Subject

Owners or operators of facilities are subject to the EPCRA Section 313 reporting requirements if their facility meets all of the following

criteria: (1) The facility is in Standard Industrial Classification (SIC) major group 20 through 39 (a facility would fall into an SIC major group 20 through 39 if the facility is primarily engaged in manufacturing operations); (2) the facility has 10 or more full-time employees or the hourly equivalents (because the U.S. EPA defines a full-time employee as someone who works 2,000 hours per year, a facility would meet this second criterion if 20,000 hours or more were worked at the facility during the reporting year); and (3) the facility meets or exceeds an applicable threshold for usage of a Section 313 toxic chemical during a calendar year.

Thresholds

The thresholds were established by Congress under Section 313 of EPCRA to be: 75,000 pounds for calendar year 1987, 50,000 pounds for calendar year 1988 and 25,000 pounds for calendar year 1989 and every year thereafter for any toxic chemical which is manufactured or processed at the facility or 10,000 pounds for calendar year 1987 and every year thereafter for any toxic chemical which is otherwise used at the facility. A Form R is required to be submitted for each toxic chemical manufactured, processed or otherwise used at a covered facility at or above an applicable threshold.

What Substances Are Covered

The toxic chemicals subject to the reporting requirements of Section 313 of SARA are those chemicals on the list in Committee Print Number 99-169 of the Senate Committee on Environmental and Public Works. The list was codified at 40 CFR 372.65 on February 16, 1988. The toxic chemical list contains more than 300 specifically listed chemicals as well as 20 chemical categories. This list is a combination of lists from the state implemented community right-to-know laws of Maryland and New Jersey. When EPCRA was enacted on October 17, 1986, Congress provided this list to the U.S. EPA. The list then contained 308 chemicals plus 20 chemical categories with a provision that the list could change based on the criteria given in the law. As of August 1990, six chemicals had been removed from the list, several more were pending or proposed for deletion and 16 had been added to the list bringing the total to 318 chemicals plus 20 chemical categories.

Threshold Determinations

The thresholds for reporting are based upon the amount of the Section 313 toxic chemical that was manufactured, processed or otherwise used during the calendar year. These thresholds were discussed previously. The amount of the toxic chemical that was released during the calendar year has no effect on the determination of whether or not the facility met or exceeded the applicable threshold for reporting. A facility owner/operator needs to do three separate threshold determinations for each toxic chemical based on the activity of the toxic chemical at the facility. The three types of activities are defined at 40 CFR 372.3 as:

* Manufacture: to produce, prepare, import, or compound a toxic chemical. This would include any activity which creates the toxic chemical or causes the toxic chemical to enter the United States (Imported)
* Process: the preparation of a toxic chemical, after its manufacture, for distribution in commerce. If the intent is to incorporate the toxic chemical in whole or in part into the final product, it is considered processed for EPCRA Section 313 purposes.
* Otherwise use: use of a toxic chemical not covered by the definitions of manufacture or process. This catch-all phrase includes any active use of a toxic chemical that would not fit the definition of manufacture or process. Toxic chemicals in storage are not counted for EPCRA Section 313 threshold determinations until they are used in some manner. The storage itself is not considered manufacture, process or otherwise use.

The following special circumstances are considered when doing a threshold calculation are discussed below.

Mixtures And Solutions

For mixtures and solutions containing the EPCRA Section 313 toxic chemicals, threshold determinations are based on the weight percent attributable to the toxic chemical, not the entire weight of the mixture or solution.

Metal Compounds

There are several metal compounds listed under the chemical category section of the toxic chemical list. For metal compounds, the entire weight of the compound is used in making the threshold determination for reporting the compound; however, release estimates are based only on the amount of the compound attributable to the parent metal.

Qualifier

Certain chemicals are only subject to reporting if they are used in the specific form listed parenthetically next to their entry. These qualifiers, with the exception of fibrous, were on the toxic chemical list when it was given to the U.S. EPA. On February 14, 1990, (55 FR 5220) the U.S. EPA added the qualifier "fibrous" to the entry for aluminum oxide. The qualifiers are: (1) fume or dust, (2) solution, (3) manufacturing by the strong acid process, (4) manufacturing, (5) friable and (6) fibrous.

Exemptions

Section 313 of SARA contains several exemptions for toxic chemicals used at a facility. Toxic chemicals that meet these exemptions do not have to be considered for either threshold determinations or release reporting requirements. These exemptions are outlined below:

* De Minimis: If a toxic chemical is present in a mixture at a covered facility and the concentration of the toxic chemical is below the de minimis, a person is not required to factor the amount of the toxic chemical in that mixture into either threshold determinations or release reporting. The de minimis levels for the Section 313 toxic chemicals are 0.1% for carcinogens or suspected carcinogens and 1% for all other toxic chemicals. There are a couple of exceptions to this exemption. First, the U.S. EPA has indicated that while the de minimis applies to unintentional impurities, it does not apply to byproducts of the manufacturing process. Also, the de minimis would not apply in the case where a toxic chemical is discharged into a waste stream where it becomes diluted to below the cutoff level.
* Article: If a toxic chemical is present in an article at a covered facility, a person is not required to consider the quantity of the toxic chemical present in such an article for threshold determination and release reporting. An article is defined at 40 CFR Section 372.3 as a manufactured item: (1) Which is formed to a specific shape or design during manufacture, (2) Which has end use functions dependent in whole or in part upon its shape or design during end use, and (3) Which does not release a toxic chemical under normal conditions of processing or use of that item at the facility or establishments.
* Laboratory: If a toxic chemical is manufactured, processed or otherwise used in a laboratory at a covered facility under the direct supervision of a technically qualified individual (defined in 40 CFR 720.3(ee)), the facility owner/operator is not required to factor that amount of the toxic chemical into threshold determination and release reporting. However, if the laboratory is engaged in specialty chemical production or operates on a pilot-plant scale, the exemption does not apply, and any toxic chemicals used at the laboratory must be included in threshold and release determinations.
* Owners Of Leased Property: The owner of a covered facility is not subject to the EPCRA Section 313 reporting requirements if the owner's only interest in the facility is the ownership of the real estate upon which the facility is operated.
* Multi-Establishment Facilities: The owner or operator of an establishment at a multi-establishment facility would not have to report for a particular toxic chemical if his/her establishment does not manufacture, process or otherwise use that toxic chemical. However, if the establishment does use a toxic chemical, then the establishment owner/operator must determine if the entire facility has exceeded an applicable threshold. If this is the case, the entire facility may report or each establishment may report, accounting for their releases of the toxic chemical.

- Specified Uses: For certain uses of a toxic chemical, the particular amount used which is consistent with one of the following exemptions is not included for threshold determinations or release reporting. These exempt uses are: (1) use as a structural component of the facility, (2) use of products for routine janitorial or facility grounds maintenance, (3) personal use by employees or other persons at the facility, (4) use of products containing toxic chemicals for the purposes of maintaining motor vehicles operated by the facility and (5) use of toxic chemicals present in process water and noncontact cooling water as drawn from the environment or from municipal sources or toxic chemicals present in air used either as compressed air or as part of combustion.

What To Submit

Each owner or operator of a covered facility must complete and submit a Form R (Toxic Chemical Release Inventory Form) to the U.S. EPA (Reporting Center) and the designated SARA, Section 313 contact for the state. A Form R is required for each toxic chemical which is manufactured, processed or otherwise used at the facility above an applicable threshold during a reportable calendar year. All Form Rs are due by July 1 of each year and cover activities at the facility that occurred during the previous calendar year. A complete Form R submission will include at least five pages of information for each toxic chemical being reported.

Filling Out The Form

After completing threshold determinations and deciding which toxic chemicals require reporting, the next step is the completion of a Form R for each toxic chemical used at or above an applicable threshold. A complete Form R must contain at least five pages of information.

Page 1 of the form contains facility identification information. Page 2 lists the names and addresses of off-site locations to which toxic chemicals are transferred in wastes. Most of the information requested on page 1 and on page 2 is self-explanatory.

Page 3 requires the following information: (1) chemical identity: the name of the chemical being reported, (2) activities and uses of the chemical: how the chemical is used at the facility and (3) estimates of release of the toxic chemical into the environment. This is where the amount of the chemical released (in pounds per year) is reported on the form. The chemical identity is simply the name and the associated CAS number of the toxic chemical being reported. For the reporting of one of the 20 chemical categories, the chemical identification would be the category name and the CAS number would be "NA." The second section of page 3 which requires information on how much of the chemical is released requires more detail and more time to complete. Fugitive and point air emissions usually are obtained from monitoring data or from general industry guidelines specific to certain manufacturing processes. Generally, these figures will be expressed as the release of so many pounds per ton of material processed. Barring any more specific information on release estimates, a facility owner/operator would multiply this number by the amount of the toxic chemical processed to arrive at an estimate that could be used when completing the Form R. Water discharges usually are monitored because of NPDES permit requirements under the Clean Water Act (CWA), and the amount of material sent to a landfill also usually is very carefully monitored.

Page 4 of the Form R requires the following information: amounts of the toxic chemical in waste sent to off-site locations, waste treatment methods and the associated efficiencies for treating the toxic chemical on-site and optional information on waste minimization.

Page 5 provides additional space if necessary to complete sections on: discharges to receiving streams or water bodies, transfers of the chemical in water to off-site locations, and waste treatment methods and efficiencies. This page must be included as part of a complete Form R submission even if blank.

SECTION 322: TRADE SECRETS

When Congress enacted EPCRA, they realized the importance of proprietary information to the regulated community. At the same time, Congress realized the importance of ensuring that the intent of EPCRA, providing information to the community, was not hindered in any way. As a result, provisions for claiming a trade secret were included in EPCRA. These provisions, found in EPCRA Section 322, ensure the protection of proprietary information and specify what information can be claimed as a trade secret.

What May Be Claimed As Trade Secret

Section 322(a)(1)(A) of EPCRA specifies that a person may withhold as trade secret only the "specific chemical identity (including the chemical name and other specific identification)." Therefore, when filing a report under EPCRA, the only information that is allowed to be withheld is the chemical identity and the corresponding CAS number. All other information must be provided.

Sections Of EPCRA For Which A Claim May Be Filed

Section 322 (a)(1)(A) of EPCRA also specifies that a trade secrecy claim may only be filed for a submittal under Sections 303 (d)(2), 303(d)(3), 311, 312 or 313 of EPCRA. It is important to realize that when reporting an emergency release under EPCRA, Section 304, no trade secrets claims can be made.

How To File A Claim

In order to claim a trade secret under EPCRA, a person must submit a trade secrecy claim package to the U.S. EPA. This claim package will provide the necessary information to substantiate the person's claim. The claim is then reviewed by the U.S. EPA and must be approved before it is considered valid.

The trade secret package that must be submitted to the U.S. EPA contains the following four documents: (1) an unsanitized version of the report, (2) a sanitized version of the report, (3) an unsanitized version of the trade secret substantiation and (4) a sanitized version of the trade secret substantiation.

Unsanitized Reports

An "unsanitized" report is the version of the reporting form that contains the trade secret chemical identity. This version of the form is sent only to the U.S. EPA, is viewed only by U.S. EPA personnel with trade secrecy clearance, is kept under lock and key and is used to evaluate the claim.

Sanitized Reports

A "sanitized" report is the version of the reporting form that does not contain the trade secret identity; in other words, it has been wiped clean. Instead of filling in the trade secret identity, the person must provide a generic class or category. This generic class or category must be one that adequately protects the trade secret identity and also provides enough information to assess the chemicals risks and hazards. The rest of the report is filled out in the same manner as if no claim has been filed.

Unsanitized Substantiation

In order to substantiate a claim of trade secrecy, a person must supply supporting information to the U.S. EPA using U.S. EPA form 9510-1, "Substantiation To Accompany Claims of Trade Secrecy Under the Emergency Planning and Community Right-to-Know Act of 1986." This substantiation form was published, with the final rules and regulations, in the *Federal Register* on July 29, 1988 (53 *FR* 28772). The substantiation form requires information regarding what steps the person has taken to guard the trade secret identity from competitors. This information includes: if the identity has ever been disclosed; the use of the substance at the facility; and what harm could come to the company if the identity of the substance is disclosed.

In order to support a trade secrecy claim, many companies are prepared to disclose confidential business information (CBI) to substantiate their claim. To protect the CBI from disclosure, the U.S. EPA will allow companies to claim supporting information confidential. When completing a trade secrecy substantiation, to claim CBI as confidential, the submitter must clearly mark the CBI contained therein. This

mark can be a stamp of "confidential" across the paragraph or any other clear indication of what is to be held confidential by the U.S. EPA.

Just as the unsanitized reporting form contains the chemical identity, the unsanitized substantiation also contains the trade secret identity. The unsanitized substantiation also contains the company's supporting CBI. This unsanitized version is submitted only to the U.S. EPA, is viewed only by U.S. EPA personnel with trade secret clearance, is kept under lock and key and is used to evaluate the claim.

Sanitized Substantiation

In order to submit the sanitized version of the trade secret substantiation, a person would again use U.S. EPA form 9510-1. Just as with a sanitized report, the sanitized substantiation would only include the generic class or category and not the trade secret identity.

As stated above, CBI that is clearly marked on the unsanitized substantiation will be held strictly confidential by the U.S. EPA. This is accomplished by allowing the submitter to delete any clearly marked CBI from the sanitized version of the substantiation form (40 CFR 350.7(d)).

The complete trade secrecy claim package includes: (1) the unsanitized version of the reporting form which contains specific chemical identity and other specific identification, (2) the sanitized version of the reporting form which contains a generic class or category in place of the specific chemical identity and does not include other specific identification, (3) the unsanitized version of the substantiation form which contains specific chemical identity and other specific identification and may contain CBI, clearly marked as confidential according to 40 CFR 350.77(d) and (4) the sanitized version of the substantiation form which contains the generic class or category in place of the specific chemical identity, does not include other specific identification and does not include any CBI that was marked as confidential in the unsanitized substantiation.

Submitting a SARA Title III Report Which Contains Trade Secret Information

When submitting a report form which the submitter has claimed the chemical identity trade secret, the submitter is only required under Federal law to submit the sanitized reporting form and the sanitized substantiation to the appropriate state and local agencies. The unsanitized versions of any form containing the trade secret identity or CBI is sent to the U.S. EPA only.

Valid And Invalid Claims

If the claim has been reviewed and it was found to be a valid claim, the U.S. EPA will notify the submitter. If the claim is found to be insufficient, the U.S. EPA will contact the submitter, inform them of the U.S. EPA's intent to deny the claim and ask if they want to submit more information or withdraw the trade secrecy claim.

Disclosure Of Trade Secret Information

Section 323 of EPCRA allows the trade secret identity to be released to health professionals only, in the following circumstances. The information will be released if it is needed for diagnosis or treatment in both emergency and non-emergency situations, for purposes of conducting preventative research studies or for providing medical treatment by a health professional who is a local government employee (53 FR 28797, July 29, 1988).

For more information, the regulations found in 40 CFR 350.5(b) through (e) explain how to file a trade secrecy claim under each applicable section of EPCRA.

SECTION 324: PUBLIC AVAILABILITY

The second part of the Emergency Planning and Community Right to Know Act provides, as the name implies, the vehicle by which the community can exercise their "right-to-know" about the hazardous chemicals being used, stored and released all around them. Most of the rules governing the public availability of data are contained in Section 324 of SARA. Essentially, the LEPC, SERC and the U.S. EPA must make available to the general public, during normal working hours

at some location, all of the EPCRA information which they have received.

The LEPCs must make available the emergency response plan, MSDSs, lists, inventory forms and followup emergency notices. The LEPC also must publish a notice of public availability concerning this information at least once each year. The SERCs must make available MSDSs, lists, inventory forms, follow-up emergency notices and Toxic Chemical Release Inventory forms (the Form R).

Typically the SERCs and LEPCs will have a room which contains all of the information they have collected. They allow visitors to examine the records and often provide a photocopy machine for duplication. The LEPC or SERC usually responds to written requests for information, and a number of LEPCs and SERCs have computerized their data, making them even more accessible.

In certain cases, the public can request and receive information above and beyond what was submitted by industry to the LEPC and SERC. The regulations at 40 CFR 370.30(a) state that if a person requests an MSDS for a facility's hazardous chemical and the LEPC does not have it, the LEPC shall request the MSDS from the facility. The regulations at 40 CFR 370.30(b) state that the LEPC must obtain the Tier II form for any facility if a person asks for it. Generally, the request is limited to chemicals present above 10,000 pounds. However, if the LEPC decides that the person's need is justified, or if the person is a state or local official acting in his or her official capacity, the LEPC can request Tier II information for all hazardous chemicals present at a facility, regardless of quantity on-site.

The Toxic Release Inventory information is available from the U.S. EPA, as well as from the state contact in several ways. To obtain TRI data, persons can access the TRI Database through the National Library of Medicine. Additionally, persons can request individual forms from the SARA, Title III Reporting Center or the state contact. Also, state data are on microcomputer diskettes and a magnetic tape containing the national data are available from the National Technical Information Service. Finally, CD-Rom disks and COMfiche will be placed in certain government depositories and county libraries.

CONCLUSION

The Emergency Planning and Community Right-to-Know Act (EPCRA or Title III of SARA) is a law which requires various facility owner/operators to report their chemical inventory and releases. The information is collected by various state and local entities and is made available to the public through different media. The information is used to enhance emergency planning and to increase community awareness of the presence of hazards in their area. Because the information is made available to the public, the law allows certain information to be withheld and claimed as trade secret by the reporting facility. In this case, the community is given information concerning the physical and chemical properties of the substance, but the chemical identity is withheld.

A summary of the EPCRA reporting requirements follows. Section 302 requires the reporting of Extremely Hazardous Substances (EHSs) at or above their Threshold Planning Quantity (TPQ). Most facilities will be subject to the reporting requirements of Section 302. Section 304 requires the reporting of releases of EHSs and CERCLA hazardous substances at or above their Reportable Quantity (RQ). Any facility that produces, uses or stores a hazardous chemical is covered by Section 304 reporting. Sections 311 and 312 require the reporting of the presence of any hazardous chemical at or above 10,000 pounds or hazardous chemicals that are EHSs present at or above 500 pounds or their TPQ, whichever is less. The Section 311 and 312 requirements apply to any facility that is covered by the Occupational Safety and Health Act (OSHA). Section 313 requires the reporting of annual emissions of toxic chemicals used by manufacturing facilities with 10 or more full-time equivalent employees. These reports are filed if the amount of any toxic chemical manufactured or processed at a covered facility exceeds 75,000 pounds for calendar year 1987, 50,000 pounds for calendar year 1988 or 25,000 pounds for calendar year 1989 and beyond. Reports also are filed for any toxic chemical otherwise used at or above

10,000 pounds for calendar year 1987 and beyond.

There are a multitude of exemptions from the requirements. Some of the exemptions were designed to reduce the burden on reporting facility owners and operators without significantly impacting the community awareness of the hazards present in their local area. The second reason for some of the exemptions is that the materials and activities are already regulated under some other act or by some other agency and additional regulation under EPCRA would not be necessary.

Additional sections of EPCRA apply to specific situations. For example, Section 322 establishes mechanisms for the claiming of trade secret information, and Section 324 provides a mechanism for public availability to any and all of the information (with the exception of trade secret information) collected under the EPCRA program.

The requirements of EPCRA are very broad in scope and may encompass a multitude of facilities. The information that is collected under EPCRA, however, may be used for a multitude of purposes, including emergency planning which, if properly used, could be of vital importance to the community.

Total Quality Management in the Site Assessment Program

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ABSTRACT

The Superfund program has developed an innovative management strategy that will help address the staggering cleanup challenges of the 1990s. The U.S. EPA believes this renewed emphasis on quality and efficiency, known as Total Quality Management (TQM), will quicken the process of evaluating and addressing the nation's worst hazardous waste sites.

The objective of this paper is to describe the application of TQM principles to one part of the Superfund program - the process for placing sites on the National Priorities List (NPL). The paper analyzes past problems in the NPL process from a TQM perspective and discusses measures taken to resolve these problems.

INTRODUCTION

This paper discusses a Superfund program initiative to improve the process for placing sites on the National Priorities List (NPL) through the use of Total Quality Management (TQM) principles. The paper begins with a brief explanation of TQM principles and tools and a description of the NPL process. Next, we discuss our analysis of problems in the NPL process and some of our initial findings. Finally, we address improvements we have begun to make to the NPL process and our plans for future improvements.

BACKGROUND

Total Quality Management is a collection of management theories and principles that emphasizes the need to build quality into a work process from the very start. Based on the writings of W. Edwards Demming, Joseph Juran and others, the TQM philosophy was adopted by the Japanese after World War II and is believed to be one of the significant factors leading to Japan's remarkable economic revitalization. The teachings of Demming and others were largely ignored by most American corporations until the late 1970s, when several companies such as Ford Motor Company began to experiment with some of the changes advocated by TQM.

TQM and Superfund

In 1988, the Office of Management and Budget issued a draft order encouraging Federal government agencies to adopt TQM. The U.S. EPA has enthusiastically embraced this suggestion and is beginning to apply TQM principles in all of its environmental programs. In the Superfund program, a number of activities are underway, including TQM training for all Headquarters management and staff and several pilot projects. One of these pilots is the application of TQM to the process of placing sites on the NPL.

The Fundamentals of Total Quality Management

Fundamental Principles

TQM stresses many general principles. Those of particular importance to improving the NPL process are:

- **Continuous improvement in the work process.** TQM theory holds that the best way to improve a work product is to focus on the process by which that product is produced. TQM emphasizes that small and continual increments of process improvement often buy more than one time "great changes."
- **Customer orientation.** Demming and other quality management theorists repeatedly argue that each part of an organization must identify and understand its customers and their needs. This process includes both customers outside the organization as well as internal customers, i.e., other parts of the organization that depend upon it for resources, information or intermediate inputs to a final product.
- **Statistical analysis of data.** Advocates of TQM note that team-work and group problem solving alone are not enough. Solutions to quality problems must be based upon a thorough analysis of data rather than anecdotes and opinions.
- **Built-in quality.** One of Demming's most important teachings is to stop reliance on inspection "after the fact" to achieve quality. Demming argues that quality must be built into a process from the very first step.

Analytical Tools

TQM emphasizes that collection and analysis of data, rather than reliance on "conventional wisdom," is necessary to understand how a process is working and where it needs to be improved. Although a variety of analytical tools are used in a TQM analysis, the Superfund Site Assessment Branch (SAB) has found these the most useful:

- **Flow charts:** A flow chart is a picture that describes all of the players and steps in a process. Detailed flow charts help to identify steps that do not add any value to a process.
- **Pareto Charts:** Pareto charts are simple bar graphs that present the frequency with which problems arise in a work process. Based on the principle that 80% of the trouble comes from 20% of the problems, these charts help managers rank present problems and future opportunities for improvement.
- **Time Management Analysis:** With this type of analysis, data are

collected on the proportions of staff time spent on different activities. Activities are then analyzed to determine whether they add value to a final work product. Once unproductive activities (e.g., the continual reworking of products) are cataloged, efforts can begin to identify ways to reduce the amount of staff time spent on these activities.

USING TQM TO IMPROVE THE NPL PROCESS

The NPL Process

The process for screening and subsequently placing the most serious hazardous waste sites on the NPL is probably less well known than other parts of the Superfund program. The following description outlines the major steps that have characterized the process in the past.

Based on a variety of factors, the Headquarters NPL staff decides that an appropriate time to propose additional sites to the NPL has arrived. Headquarters announces the expected date of the rulemaking and issues a "call for packages" to the Regions. Regional Offices have the primary responsibility for prioritizing and then nominating sites to the NPL. To nominate a site, a Region must determine its preliminary Hazard Ranking System (HRS) score and submit an "HRS package" that documents the basis for the site's score. HRS packages usually are compiled by the Field Investigation Team (FIT) - the Regions' site assessment contractors - or by a State and are based on the technical and historical information found in Preliminary Assessments and Site Inspections. Regional Offices conduct varying degrees of quality control (QC) on the packages, depending on the technical expertise of the individuals involved, the number of sites the Region wishes to propose and the amount of time before packages must be received at Headquarters to begin Quality Assurance (QA). Once packages are received at Headquarters, U.S. EPA Headquarters NPL staff and QA contractors conduct a QA review to ensure accurate and consistent application of the HRS model. After site packages are judged acceptable, the U.S. EPA publishes a list of sites proposed to be added to the NPL in the Federal Register. These proposals are called "Updates." Public comment is accepted for 60 days, followed by technical evaluation of the comments and eventual placement on the final NPL of all sites that continue to score above the HRS cutoff for listing.

Why Apply TQM to the NPL Process?

The Superfund program has been criticized for the speed at which the nation's hazardous waste sites are being cleaned up. Although significant strides have been made in streamlining the process over the last few years, the process remains complex and time-consuming. The site assessment phase alone is extremely lengthy. Table 1 shows the range of time from discovery to listing for 71 sites added to the NPL in February 1990 and the one site dropped. Approximately 43% of these sites took more than 10 years to go from discovery to final listing on the NPL. Approximately two-thirds of these sites took 2 years or more between completion of the SI and proposal to the NPL, and approximately 87% took 2 years or more between proposed and final listing.

The length of the site assessment process is of concern because the quicker sites are assessed, the sooner those with significant hazards can be addressed. In some cases, quick assessment may lead to earlier actions which can limit the migration of contamination and reduce the cost and difficulty of site cleanup. Congress recognized this problem in Section 116(b) of the Superfund Amendments and Reauthorization Act of 1986 (SARA), which requires the U.S. EPA to create an assessment process that requires no more than 4 years to go from discovery to listing.

In addition to the general need to speed up the NPL process, there are two other important reasons to apply TQM:
• The new HRS, about to be revised as required by SARA, is a more comprehensive and complex model for ranking sites than the

original HRS. A new soil exposure pathway and a number of new subpathways and factors have been introduced, each with additional data collection requirements and QA concerns.
• After all sites in CERCLIS are assessed, a substantial universe of undiscovered sites still may require the Agency's assessment. Although estimates of the size of this universe vary, there is agreement that its screening will require significant time and resources.

Table 1
Sites Added to the NPL in February 1990

Discovery to Promulgation		Discovery to SI		SI to Proposal		Proposal to Promulgation	
Years	No. Sites	Years	No. Sites	Years	No. Sites	Years	No. Sites
0-4	8	0-1	13	0-1	23	1	9
5	10	2-3	18	2-3	28	2	47
6-8	9	4-5	16	4-5	7	3-4	13
9	14	6+	18	6+	4	5+	1
10+	31	Not Known	7*	Not Known	10*	Not Known	2*
Total	72		72		72		72

* Insufficient data in CERCLIS to permit analysis.

ANALYSIS OF THE LISTING PROCESS

Data Collection

To obtain a complete picture of the NPL process and to identify problem areas, data were collected on how the process works and participants in the listing process were asked to suggest improvements. Interviews were conducted in six Regional Offices, and files and the CERCLIS data base were reviewed for sites within those Regions. In addition, Headquarters NPL staff and staff of Mitre Corporation, the U.S. EPA's primary QA contractor, were interviewed.

Detailed flow charts were constructed for the six Regions visited and for the Headquarters portion of the process. In addition, information was collected on the time spent by Headquarters staff on activities related to NPL Update 10 and final rules promulgated in 1990. Finally, data were collected and arrayed on Pareto charts on the technical and procedural issues raised in QA for Updates 7, 8 and 10.

Summary of Findings

Our initial efforts at data collection and analysis turned up three major findings:
• Insufficient communication led to inconsistent understanding of the responsibilities of all participants and wide variation in what various participants considered to be "quality products." It also led to suspicion and mistrust between Headquarters and the Regions. Regions felt that once packages were sent to Headquarters they "disappeared"; i.e., they were not informed on either progress or problems, while Headquarters felt that some Regions generally submitted incomplete or inadequate packages.
• The NPL process was characterized by substantial variation, complexity and general unreliability. Perhaps the most important aspect of this variability was the irregular scheduling of Updates, which undermined attempts to rationalize the NPL process.
• The NPL process has been overly dependent on inspection, i.e.,

QA after packages are submitted, to achieve quality, rather than building it into the process from the start.

The TQM Response

In response to these problems, TQM theory offers several general approaches:
- Break down barriers between groups and improve communication
- Regularize processes and reduce variation
- Reduce dependence on inspection to achieve quality by building quality into the process from the start

The specific application of these approaches to the NPL listing process follows.

Finding #1: Inadequate Communication Hampers the Process

Our most important finding was that communication between the different groups involved in the process has been inadequate. In the past, neither SAB nor the QA contractor clearly identified the Regional offices as the their prime "customer," and little time or effort was spent on keeping the Regions informed. Regions complained that they were unaware of the status of packages for sites in their Regions and that no comprehensive tracking system was in place. In addition, roles and responsibilities of the Regional offices were unclear and no explicit, standard process for Regional QC of packages existed.

Regions felt that with the complexity of the NPL process and with relatively high staff turnover rates, they often had to struggle to decipher the rules of the listing process. Moreover, there was considerable confusion of the Regional staff over where their activities fit into the overall NPL process. This confusion is understand-able given the huge numbers of steps and participants in the process. For example, Figure 1 shows the numerous steps and participants involved in the three week period between OMB review and publication in the Federal Register for NPL Update #10. A complete flow chart of the NPL process would take 6 to 7 pages to present!

TQM Approach

The TQM approach to these problems is to break down the barriers between the groups involved in the NPL process and to build communication into the process. TQM emphasizes collegial problem solving from all levels of the organization and establishes clear roles and expectations for all participants.

Changes Underway

SAB has introduced several new measures to improve communication for Update 11, the first update under the revised HRS:
- **QA visits:** SAB and Mitre staff are conducting large portions of HRS package review and QA in the Regional offices. With this new system, all the players involved in the production of an HRS package (the Region, FIT, States, Mitre and SAB) sit around the same table and work through any issues raised. The Regions receive immediate feedback on emerging technical and policy issues, and Headquarters and Mitre staff are directly exposed to a field perspective on sampling and other HRS requirements.
- **Regional Coordinators:** SAB has assigned one staff person to coordinate QA for each Regional Office. This person will be the point of contact for the Region and will be familiar with all of the candidate NPL sites for that Region. Mitre has also designated a single QA contact for each Region. These three individuals are expected to stay in communication throughout the year on all sites
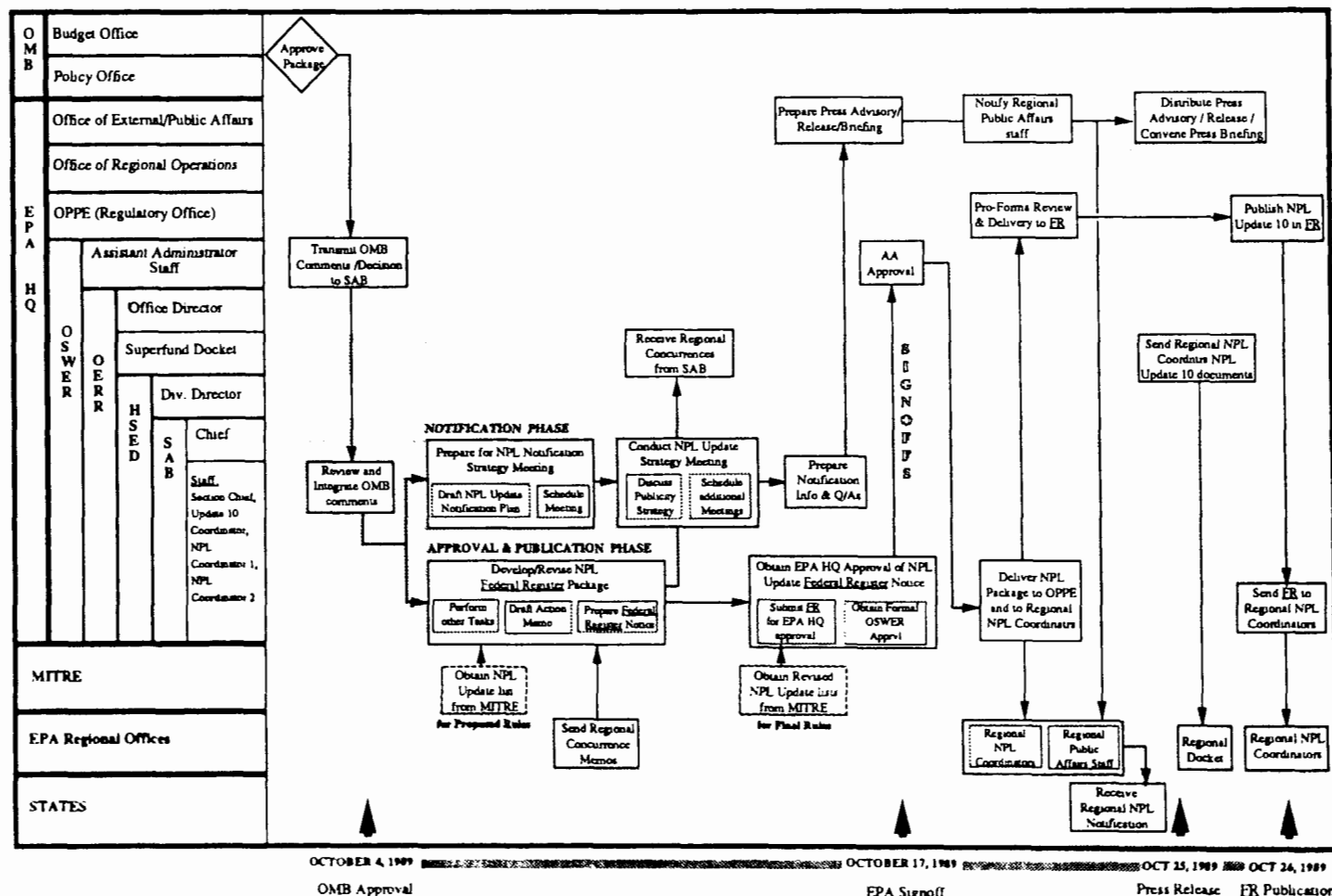
Figure 1
Proposed Update 10

under consideration for the NPL. The 10 SAB Regional Coordinators meet weekly to compare notes on emerging areas of Regional concern, QA problems and common communication needs.

- **Tracking system**: SAB has instituted a new computer based tracking system for NPL sites, which will allow us to accurately convey the status of packages as they move through the approval process.
- **Regional Quality Control Check-Off List:** To assure that Regions understand their role in providing quality HRS packages, a workgroup, made up of Headquarters and Regional staff, has created a check-off list of steps necessary for a complete HRS package. This list and a signature must accompany all NPL packages.

A number of additional measures are planned for the near future including:
- **A Guidance/Policy Hotline for Regions and States**
- **Guidance on the NPL process** - a complete description of the NPL process with flow charts illustrating the different steps.
- **Regional QC Guidance** an expansion on the QC checklist mentioned above that will elaborate upon the Regions' role in providing quality HRS packages. This guidance document is being written by Regional site assessment staff.

Finding #2: Variations in Scheduling Led to Inefficiencies

Unpredictability in the scheduling of NPL Updates has affected the quality of HRS packages produced by the Regions and the efficiency of the entire site screening process. The time intervals between NPL proposals have been sporadic over the history of Superfund, ranging from 2 to 13 months (Figure 2). Not knowing if Updates will be months or a year apart sets up numerous responses that substantially alter the site assessment process. Some Regions have responded to this irregularity by "clearing the shelves"; i.e., sending in everything that could remotely be called an NPL package no matter how incomplete, just to get it in the queue before the deadline. Other Regions stopped all other site assessment work, no matter how important, to work on scoring sites. The process has also suffered from the "hurry up and wait" syndrome where tight deadlines were imposed for the submission of packages, but were repeatedly changed, leading to a lack of trust in Headquarters schedules and to a general casualness about the process in the Regional offices. Finally, the lack of a predictable schedule for Updates sometimes led Regions to plead for delays so that they could add "just one more site" before the door was closed. In some cases, Regions were justifiably concerned that they would have a considerable wait before they received another chance at proposing the site to the NPL.

Meanwhile, back at Headquarters, the entire NPL staff (three people) was struggling to see over the stacks of dozens of packages that had all arrived on the same day! It is not hard to understand why Regional queries on the status of individual sites went unanswered for long periods of time. Moreover, where Regions had sent in incomplete or poor quality HRS packages, it was necessary to go back and correct mistakes, thereby creating additional delays.

Changes Planned or Underway

SAB is committed to making NPL Updates and final rules regular, predictable events. In the future, Updates to the NPL will be submitted to the Office of Management and Budget (OMB) every 6 months, no matter how many sites are ready. In addition, there will no longer be a "call for packages" before each Update. Regions will submit HRS packages on a rolling basis as they are completed (i.e., QC signed by Regions).

Finding #3: Dependence on Inspection

Demming's concern about dependence upon inspection to achieve

quality was particularly relevant for the QA process. In the past, QA focused on spotting mistakes in HRS packages so that these packages could be returned to the Regional offices for correction. Although the "final products" (HRS documentation packages) were of good quality (i.e., sites were scoring above the HRS cutoff and packages were well-documented and legally defensible), the process was time-consuming and inefficient. It was not uncommon for Regional offices to prepare and send to HQ three, four or even more versions of a documentation package before it was considered acceptable.

Number of Months
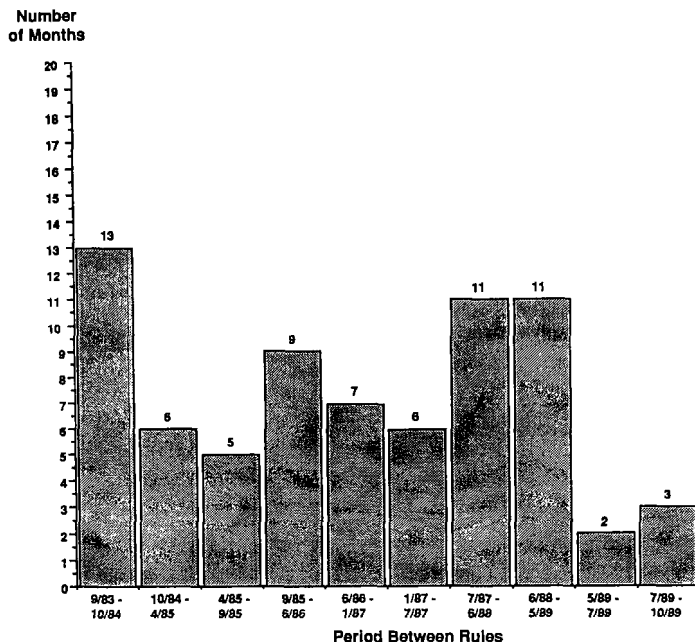
Figure 2
Lapsed Time Between Proposed Rules
September 1983 through October 1989

Figures 3 and 4 are Pareto charts that portray some of the recurring problems caught during QA review of HRS packages. Figures 3 illustrates the most common QC problems identified during reviews of 125 sites from several NPL Updates. Figure 4 breaks down the largest category from Figure 3, "Documentation," into smaller subcategories. Many of the problems identified in this chart could have been avoided had there been adequate written standards for HRS packages.
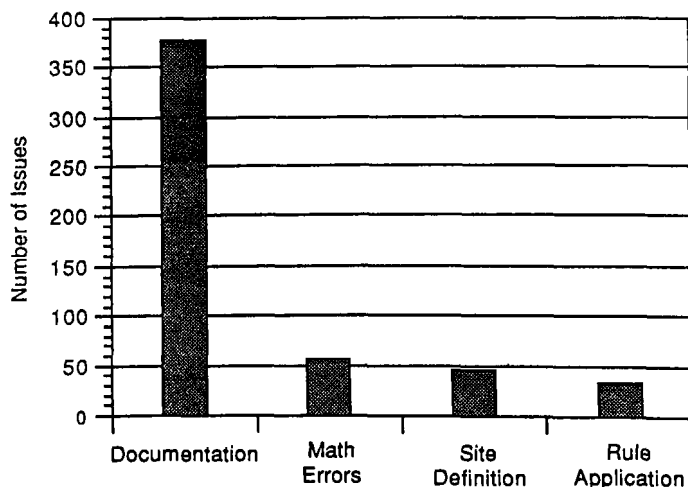
Figure 3
Quality Control Issues
125 Sites
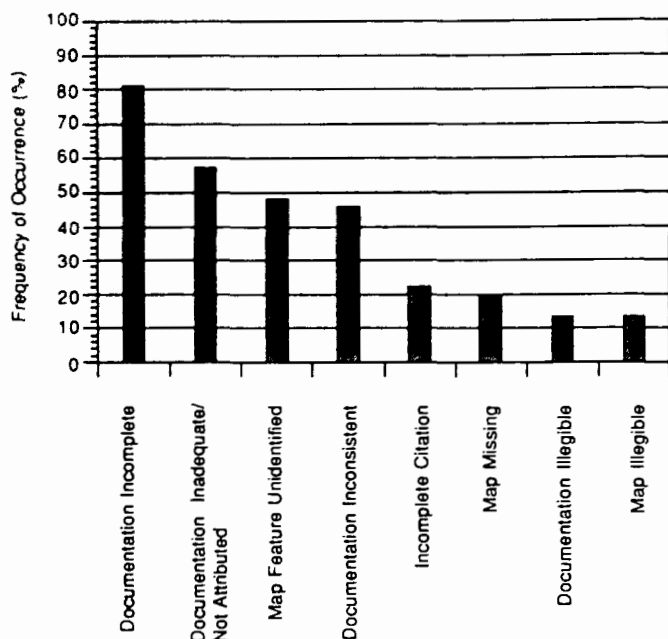
Figure 4
Documentation Issues
125 Sites

TQM Approach

TQM theorists argue that relying solely upon this "last chance" inspection of products wastes time and effort. The need for rework that results from this type of QA is wasteful and is, as one TQM expert notes, "like scraping burnt toast." Rather than relying solely upon inspection, TQM advocates providing participants a process with written standards and other tools that allow them to avoid errors in the first place. In addition, TQM theory encourages all groups involved in a process to be responsible for quality, not just the QA staff. By involving representatives from different groups in the collection and analysis of data, an organization can create a system that provides for continuous improvement in a process.

Changes Planned or Underway

SAB is initiating a number of measures intended to wean us from our dependence upon inspection to achieve quality. These measures can be divided into two categories. The first is guidance documents and other tools that will help guarantee high quality HRS packages, among them:

- **Regional Quality Control guidance** QC guidance is being developed that will provide explicit written standards for the quality of HRS packages.
- **HRS "Rules-of-Thumb" scoring manual** - This document will be a users manual for those who are scoring sites with the HRS.
- **Short sheets and guidance updates** - SAB is planning to issue guidance short sheets on a variety of policy and technical issues involved in HRS scoring. In addition, application of the revised HRS probably will require updating or changing the guidance.
- **Training** - SAB is developing HRS training sessions for State,

Regional, FIT and Federal Facility personnel.
- **Prescore** - A computerized HRS scoring package is being developed that will greatly reduce the time needed to calculate HRS scores and will eliminate math errors. In addition, the program will help field staff develop sampling plans by allowing them to test how different scenarios might affect a site's HRS score.
- **Chemical data base keyed to the revised HRS** - This computerized data base is designed to provide easy access to toxicity and mobility information for 330 chemicals.

The second category is a data collection and analysis system that helps monitor the vital signs of the process and spot problems. Although a certain amount of "last chance" QA will continue to be necessary, SAB has begun to institute a new role for its contractor QA staff. Rather than looking solely at changes to the HRS package required for a final product, the QA staff will also collect data on the types of problems that arise and recur in HRS packages. For example, Figures 3 and 4 provide an example of information on documentation problems to be collected on a continuous basis as QA proceeds on HRS packages. SAB also expects to be able to analyze problems in implementing other aspects of the HRS such as analytical data quality issues, aquifer issues and pathway- or factor-specific issues. In this way, SAB will "monitor the pulse" of the process. Pareto charts and other tools will help identify the most significant problems, both systemwide and in specific Regions. Once problems are identified and priorities are set, guidance or training can be targeted to specific areas or to specific Regional Offices.

Our prime customers, the Regions, will be actively involved in this effort to analyze data and resolve problems through their involvement in project teams and data collection. Several changes have already been made for Update 11 to facilitate this involvement:

- **Analysis of technical and procedural issues:** SAB is cataloging and analyzing technical and policy issues that arise in this first update to identify guidance needs. A project team consisting of Headquarters and Regional staff is meeting after each Regional visit to coordinate the resolution of guidance questions.
- **Evaluation of the NPL process after visits**: After each Regional visit, interviews are conducted with Regional and contractor staff to identify aspects of the new QA process that need improvement.

Ultimately, a Headquarters/Regional project team will analyze data collected by the QA staff after every update to answer questions such as:

- Which procedures worked and which did not?
- What technical issues are consistently causing confusion or need to be resolved?
- Are the worst sites being listed first, in less time, with less wasted effort?

NEXT STEPS

SAB has only just begun to reexamine the process for placing sites on the NPL. TQM is a long-term strategy, and the U.S. EPA plans to continue to make improvements to the NPL process. Thus far, we have focused our efforts on the process for proposing sites to the NPL. In the future, we plan to reexamine and revise the next phase of the process, i.e., responding to public comments on proposed sites and placing these sites on the final NPL.

Overview of the Revised Hazard Ranking System (HRS)

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ABSTRACT

The Comprehensive Environmental Response Compensation, and Liability Act of 1980 (CERCLA) required the Federal government to establish criteria for setting priorities among releases of hazardous substances, pollutants and contaminants. The U.S. Environmental Protection Agency (U.S. EPA) responded by developing the Hazard Ranking System (HRS), which is a scoring system used to establish the National Priorities List (NPL). The Superfund Amendments and Reauthorization Act of 1986 required the U.S. EPA to amend the HRS so it will more accurately assess relative risks and take into account certain specific elements of risk, e.g., potential air releases of hazardous substances and contamination of the human food chain. On December 23, 1988, a proposed rule to revise the HRS was published in the Federal Register by the U.S. EPA. After reviewing public comments, U.S. EPA published the final rule. This paper describes the major revisions made from the original to the revised HRS.

The HRS revisions change the way the U.S. EPA evaluates potential and actual threats to public health and the environment from hazardous waste sites, and may affect the types of sites to be included on the NPL.

BACKGROUND

In 1980, Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund") to establish a Federal program to respond to the risks posed by uncontrolled releases of hazardous substances, pollutants and contaminants (hereafter referred to as "hazardous substances").[1] Section 105(8)(A) of CERCLA required the U.S. Environmental Protection Agency (U.S. EPA) to establish criteria for determining priorities for response actions among releases or threatened releases.

CERCLA Section 105(8)(B) specified that those criteria be used to establish the National Priorities List (NPL), a list of at least 400 releases and potential releases. To meet these requirements, on July 16, 1982, the U.S. EPA revised the National Contingency Plan (NCP) to include the Hazard Ranking System (HRS) as the primary criterion for establishing the NPL.[2] Only sites that are on the NPL are eligible for Superfund-financed remedial action.[3]

The HRS is a scoring system which evaluates the relative threat to public health and the environment from releases (including potential releases) of hazardous substances. In the 1982 version of the HRS (hereafter referred to as the "original HRS"), the score for a site was developed by evaluating a set of "factors" for three pathways: groundwater, surface water and air, that are related to risks to public health, welfare and the environment. Within each pathway, those factors were combined into factor "categories" that evaluate the potential for a site to release into the pathway, the inherent hazards of the site or release (e.g., toxicity, persistence, quantity of the hazardous substances present at the site), and the presence or proximity of targets (e.g., drinking water wells, wetlands, or residential areas) that could be affected by a release in the pathway being evaluated. The individual pathway scores were calculated by multiplying the category values and normalizing the results to a 100-point scale. The three pathway scores were then combined using a root mean square, and the resulting value was normalized to a 100-point scale. The U.S. EPA has used this value, the "HRS score," to establish the NPL. Sites receiving scores of 28.50 or greater under the original HRS were eligible for the NPL.

The original HRS also included an evaluation of direct contact and fire/explosion hazards. Those scores, although not used in determining NPL eligibility, were intended to help identify candidates for short-term response under the removal authorities of CERCLA.

Since 1982, the U.S. EPA and the States have applied the original HRS to thousands of sites posing threats due to hazardous substance releases. Of those, as of September 1990, 1,187 sites are on the final NPL.

SARA REQUIREMENTS

Section 105 of the Superfund Amendments and Reauthorization Act of 1986 (SARA) required U.S. EPA to amend the HRS to assess, to the maximum extent feasible, the relative degree of risk to human health and the environment posed by facilities under review. SARA specified several areas that must be addressed in developing the revised HRS:
- Damage to natural resources that may affect the human food chain
- Contamination or potential contamination of ambient air associated with a release or threatened release
- Contamination or potential contamination of surface waters used for recreation or as drinking water supplies

In addition, SARA Section 118 specified that the revised HRS should assign a high priority to facilities where the release of hazardous substances from a site results in closing of drinking water wells, or contaminates a principal drinking water supply. SARA Section 125 required revisions to the HRS to address facilities that contain substantial volumes of wastes, as defined in Section 3001 (b)(3)(A)(i) of the Solid Waste Disposal Act (Resource Conservation

and Recovery Act), i.e., fly ash and other wastes from coal-fired power plants.

While SARA required that the HRS accurately assess relative risk to the maximum extent feasible, the Conference Committee Report on SARA clarified that the degree of accuracy required is to be consistent with the data collected during preliminary assessments and site inspections. In other words, Congress did not expect the Agency to undertake long-term monitoring or studies to determine the full nature and extent of contamination at the time of HRS scoring. Also, Congress did not expect the HRS to achieve the level of accuracy of risk assessments performed in support of remedial actions. As stated in the Conference Committee Report, the HRS should perform "with a degree of accuracy appropriate to its role in expeditiously identifying candidates for response actions."[4]

ROLE OF THE HRS

The role of the HRS is to serve as the primary decision tool for determining which sites are appropriate for remedial investigations based on information developed during preliminary assessments and site inspections (Figure 1). The HRS functions primarily as a screening tool and provides useful information for meeting the Superfund program's strategic goal of addressing the highest priority releases first.
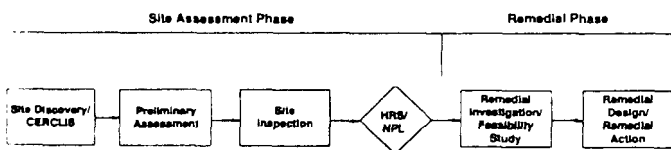
Figure 1
Typical Phases of the Superfund Process

The need to base the HRS on data available from preliminary assessments and site inspections places constraints on the factors that can be used and, consequently, on the degree of accuracy that can be expected at the site assessment stage of analysis. This places certain limits on the types of models or approaches that can be used. However, in order to fulfill its role within the Superfund program, the HRS need not establish an absolute ranking of NPL sites for remedial investigations based on risks. This approach is consistent with the Conference Committee Report[4] and the need to consider other factors besides risks (e.g., urgency, availability of State matching funds) in scheduling remedial actions.

MAJOR CHANGES BETWEEN ORIGINAL AND REVISED HRS

In developing the revisions to the HRS, the Agency undertook a comprehensive review and analysis of various sources of information. Comments to the Advance Notice of Proposed Rulemaking (52 FR 11513, April 9, 1987) and Proposed Rule Notice (53 FR 51962, December 23, 1988) were reviewed and considered while developing the final revised HRS. In addition, the U.S. EPA conducted a field test for the proposed revisions to assess the cost and implementation concerns associated with the modifications. The U.S. EPA announced the availability of the field test report and requested public comments, which were also considered (54 FR 37949, September 14, 1989).

The original and revised HRS differ substantially (Figures 2 through 5). The revised HRS is more flexible than the original HRS in that it can address a broader range of problem types and can accept a wider variety of types of data. While the factors have undergone wholesale revision, the structure of the model has largely been retained. Some of the more important changes are described briefly in the following paragraphs; more detailed descriptions and the underlying rationale are presented in the revised HRS preamble and final rule.

Likelihood of Release	X	Waste Characteristics	X	Targets

Observed Release
or
Route Characteristics
  Depth to Aquifer of
    Concern
  Net Precipitation
  Permeability of
    Unsaturated Zone
  Physical State
  Containment
		Toxicity/Persistence
		Hazardous Waste Quantity
				Ground Water Use
				Distance to Nearest Well/
				  Population Served

Revised HRS

Likelihood of Release	X	Waste Characteristics	X	Targets

Observed Release
or
Potential to Release
  Depth to Aquifer
  Travel Time
  Net Precipitation
  Containment
		Toxicity/Mobility
		Hazardous Waste Quantity
				Resources
				Population
				Nearest Well
				Wellhead Protection Area

Figure 2
Groundwater Migration Pathway

Soil Exposure Pathway

The revised HRS adds a new pathway, the soil exposure pathway which is similar to the direct contact pathway of the original HRS. This pathway, named on-site exposure in the proposed HRS, evaluates the possibility that people or sensitive environments will have direct physical contact with hazardous wastes or contaminated soil. The Agency's experience at sites such as Love Canal in Niagara Falls, New York, and Times Beach, Missouri, suggests that contaminated residential or school properties need to be addressed as special situations. The soil exposure pathway considers two groups potentially at risk, those living, working or attending school on property with hazardous wastes or contaminated soils, and those living nearby with access to the property. The pathway is evaluated only on the presence of contamination and not on release potential, as in the other pathways, because contaminants do not have to migrate off-site for exposure to occur (Figure 4).

Food Chain Threat

To address the requirements of SARA Section 105 and to more accurately evaluate relative risks, the U.S. EPA developed the food chain threat within the surface water pathway. This threat addresses human exposure to contaminated fish and shellfish resulting from hazardous substance releases. Most notable in the methodology are the use of a bioaccumulation factor (BCF) and a food production factor to estimate relative population exposure levels. BCF is based on bioconcentration values reported in the U.S. EPA's water quality criteria documents, where available, or peer-reviewed literature. Where bioconcentration studies are insufficient to calculate BCFs, the logarithm of the n-octanol-water partition coefficient can be used. Food chain production is based on fish catch or commercial landing data, where available. The approach allows an estimate of relative exposures from fish consumption, which is calibrated to values developed in the drinking water threat of the surface water pathway.

Distance/Dilution Weights

The original HRS assigned values to potentially affected populations, based on the number of people using wells, or drinking water intakes within the target distance limits - 3-mile radius for groundwater or 3 miles downstream for surface waters. Only in the air

pathway was there some further adjustment of target population values based on distance from the site. The revised HRS weights potentially-exposed targets on the amount of dilution expected in the exposure medium. In surface waters, dilution weights are based on mean annual stream flow at the point of potential exposure. For the groundwater and air pathways, dilution weights were established for various distances from sites using analytical models with relatively conservative input parameters. General dilution values were developed for concentric rings around sites (e.g., 0 to 0.25 mile, 0.25 to 0.5 mile). Applying those weights in scoring a site requires counting the number of residents residing or using wells within a given ring and multiplying that number by the distance weights for the ring.

Documented Human Exposures

While the original HRS did not differentiate between potential exposures and actual exposures, the revised HRS assigns a higher value to target populations where actual exposures can be documented. Where data indicate that promulgated health benchmarks (e.g., drinking water standards) have been exceeded, the revised HRS assigns higher values to targets than where contamination is observed, but below benchmarks, or where contamination is only potential. These changes respond to SARA Section 118(a), which requires that releases causing the closing of drinking water wells, or

contamination of a principal drinking water supply, be given a high priority. A similar approach of taking into account environmental benchmarks has been developed to evaluate sensitive environments.

Sensitive Environments

In revising the HRS, one of the U.S. EPA's goals was to improve the evaluation of sensitive environments by addressing a broader range of sensitive ecosystems and to afford a higher weight for sensitive environment factors. The original HRS addressed threats to sensitive environments through air and surface water releases, but the weights were assigned such that even a worst case problem (e.g., a release that contaminates the habitat of an endangered species or harms a National Park) could not score high enough to be placed on the NPL on that basis alone. In addition, only a limited number of sensitive environments were considered. The revised HRS substantially increases the number of sensitive environments evaluated to include all specifically identified under Federal and State statutes and regulations as requiring legal protection. The revised HRS assigns sensitive environments that are seriously threatened, or affected by releases, a higher relative weight than the original HRS. The intent of the changes is that serious environmental threats can score above the NPL cutoff. The relative weights for sensitive environments versus human health factors were established based on

Figure 3
Surface Water Migration Pathway

consensus within the U.S. EPA workgroup developing the revised HRS; U.S. EPA solicited public comment on those relative weights in the preamble to the proposed rule.

Revised HRS

Resident Population Threat

Likelihood of Exposure	X	Waste Characteristics	X	Targets
Observed Contamination		Toxicity		Resident Individual
		Hazardous Waste Quantity		Resident Population
				Workers
				Resources
				Terrestrial Sensitive
				Environments

+

Nearby Population Threat

Likelihood of Exposure	X	Waste Characteristics	X	Targets
Attractiveness/Accessibility		Toxicity		Population Within 1 Mile
Area of Contamination		Hazardous Waste Quantity		Nearest Individual

* New pathway

Figure 4
Surface Water Migration Pathway

ORIGINAL HRS

Likelihood of Release	X	Waste Characteristics	X	Targets
Observed Release		Toxicity		Land Use
		Reactivity and Incompaubility		Population Within 4-Mile
		Hazardous Waste Quantity		Radius
				Distance to Sensitive
				Environment

Revised HRS

Likelihood of Release	X	Waste Characteristics	X	Targets
Observed Release		Toxicity/Mobility		Resources
or		Hazardous Waste Quantity		Population
Potential to Release				Nearest Individual
				Sensitive Environments
Gas				
Gas Source Type				
Gas Migration Potential				
Gas Containment				
Particulate				
Particulate Containment				
Particulate Source Type				
Particulate Migration				
Potential				

Figure 5
Soil Exposure Pathway

Waste Quantity

In the original HRS, hazardous waste quantity was the amount of waste containing hazardous substances present at the site, because it is generally easier to estimate than hazardous constituent quantity, which may require extensive concentration measurements. In cases where hazardous waste quantity could not be determined, a default value of 1 was assigned.

The revised HRS substitutes a tiered approach for the hazardous waste quantity factor. The tiered approach arrives at a single hazardous waste quantity value based, in order of preference, on:

- Hazardous constituent quantity, which represents the actual quantity of hazardous substances deposited on the site
- Site wastestream quantity, which is similar to the original HRS

hazardous waste quantity factor, and represents the quantity of hazardous wastes deposited on the site
- Site disposal capacity, which represents an estimate of the quantity of hazardous substances the site could have received as indicated by the sizes of the sources identified

The tiered approach allows the scorer the flexibility to move within the tiers depending on data availability. This approach permits a more accurate evaluation at many types of sites without imposing significant new costs.

Finally, in response to public comments, the hazardous waste quantity is now multiplied by toxicity and other factors, instead of being added as they were in the original HRS. This is one of several changes that make the revised HRS more consistent with risk assessment principles.

Toxicity

The original HRS scored the toxicity factor based primarily on acute toxicity of the hazardous substance, evaluated by either of two rating systems: Dangerous Properties of Industrial Materials or the National Fire Protection Association guidelines.[3] Factor values were developed for each substance in each migration pathway and combined with persistence factor values. The substance with the highest combined toxicity/persistence value for a pathway was used to assign that pathway's toxicity/persistence factor value.

However, based on risks identified at NPL sites, it is likely that most risks at these sites result from chronic exposures to hazardous substances. To consider such risks in the revised HRS, the toxicity factor evaluates the hazardous substance and assign scores for three kinds of toxicity: (1) acute toxicity, (2) carcinogenicity, and (3) chronic noncarcinogenic toxicity. The highest of the three scores for a hazardous substance becomes the toxicity factor value assigned to that substance. The score is based on the Reference Dose for chronic noncarcinogenic toxicity; cancer potency factors combined with a qualitative weight-of-evidence for carcinogenicity; or, when these factors are not available, the ED_{10} and LD_{50} or LC_{50} values for acute toxicity. Aquatic toxicity is also considered when assessing potential risks to aquatic ecosystems.

Mobility

The original HRS did not directly consider properties of substances that affect their ability to be released and migrate through environmental media. The revised HRS adds mobility factors to both groundwater and air pathways and modifies the persistence factor in the surface water pathway to consider a greater number of potential degradation mechanisms. The groundwater mobility factor is intended to reflect the fraction of a hazardous substance expected to be released from the source, migrate through the porous media, and contaminate aquifers and drinking water wells that draw from them. Mobility in the groundwater pathway involves both release and transport concerns, and is evaluated based on solubility and distribution coefficient values for the hazardous substances present at the site. The air pathway evaluates gaseous mobility (on the bases of vapor pressure) and particulate mobility (on the basis of the Thornthwaite P-E Index).

Radionuclides

The revised HRS includes a special section on scoring radionuclides. Essentially, radionuclides are treated in a parallel manner to hazardous substances with certain special characteristics that are accounted for by separate scoring rules for some HRS factors. The revised HRS evaluates radionuclides within the same basic structure, and the evaluation of many individual HRS factors is the same whether radionuclides are present or not.

CUTOFF SCORE

One of the more challenging tasks in revising the HRS was selecting the cutoff score. The Agency has used the cutoff score as

a management tool to identify the top priority sites in the nation. In 1982, when the first sites were being considered for the NPL, approximately 700 sites had been scored. The cutoff score of 28.50 under the original HRS was chosen because it yielded an initial NPL of at least 400 sites, as suggested by CERCLA Section 105(8)(B) (now CERCLA Section 105(a)(8)(B)). Out of the approximately 700 sites, 418 were actually proposed to the NPL. The cutoff score was not chosen because it represented a threshold of unacceptable risk posed by the sites.

In the Conference Committee Report on SARA[4], Congress asked the U.S. EPA to address the relationship between risks at NPL sites and the cutoff score. The U.S. EPA performed several studies on the cutoff score.[5] While the studies were limited in scope, and definitive conclusions were not possible, they supported the continued use of cutoff score as a useful management tool in identifying priority sites. However, the studies indicated sites with scores below the 28.50 cutoff could also pose potential dangers to human health and the environment.

The U.S. EPA believes the cutoff score, under the original HRS, has served its purpose as a management tool. In general, NPL sites that scored greater than 28.50, under the original HRS, present significant risks to public health and the environment, and have necessitated some form of response.

Because the cutoff of 28.50 served as a useful management tool, the Agency proposed that the cutoff score for the revised HRS be functionally equivalent to the 28.50 cutoff under the original HRS. The Agency proposed the following approaches for determining functional equivalency:

* **Statistical equivalence** - determine what revised HRS score best correlates to 28.50, i.e., score a sample of sites with the original and revised HRS, and adjust the revised HRS cutoff score to reflect changes in values so that the original and revised HRS scores would be equivalent.
* **Numerical equivalence** - determine what percentage of CER-CLIS sites score above 28.50 under the original HRS, and set a cutoff that yields the same percentage under the revised HRS.
* **Risk equivalence** - determine the quantitative risk level that, on average, corresponds to a HRS score of 28.50 under the original HRS, and then determine what revised HRS score best corresponds to that risk level.

To perform the above analyses, the Agency scored 110 sites with both the original and revised HRS. These 110 sites were composed of:

* **Phase I Field Test Sites (30 sites)** - sites selected to test specific features of the proposed revised HRS. The field investigation on these sites was relatively complete, and generally all pathways were scored.
* **Phase II Field Test Sites (40 sites)** - these sites were scheduled to have preliminary assessments performed on them. The field investigation on these sites was less complete than for the Phase I field test sites, but still all pathways were generally scored.
* **Region IV Sites (40 sites)** - sites generally expected to be likely candidates for the NPL. A number of these sites were thought to have either groundwater or surface water contamination.

The Agency's analysis on the 110 sites indicated:

* **Statistical equivalence** - the average site score dropped from about 32 on the original HRS to 30 on the revised HRS, the median site scores dropped from 31 to 26, and the variance associated with site scores increased (Figure 6).
* **Numerical equivalence** - 72 sites scored at or above 28.50 on the original HRS versus 54 on the revised HRS. The cutoff would have to have been lowered to 13.5 in order to get 72 sites above the cutoff under the revised HRS (Figure 7).
* **Risk equivalence** - because quantitative risk information was not available for the 110 sites, the Agency looked at the qualitative risks of the revised HRS scores, particularly at theoretical sites scoring around 28.50.
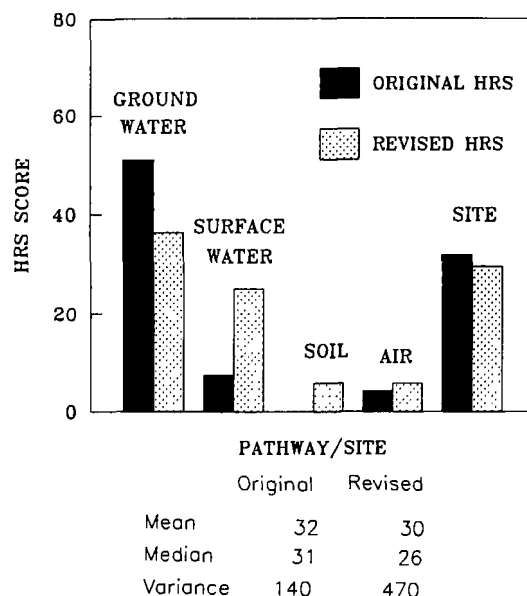
Figure 6
Pathway and Site Score Comparison
for the Original and Revised HRS

	Original	Revised
Mean	32	30
Median	31	26
Variance	140	470
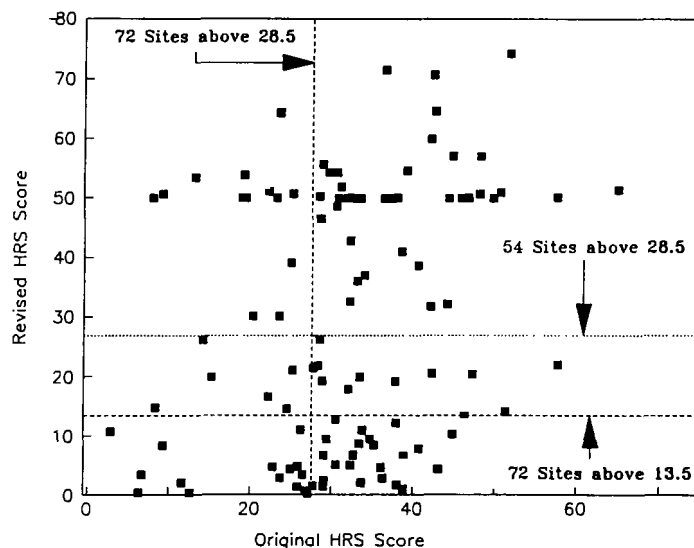
Figure 7
Scatter Plot of Site Scores for the
Original and Revised HRS

In general, the U.S. EPA found:
* Of sites that scored between 40 and 60:
  -90% had observed releases and 10% had potential releases, moderate to large amounts of waste, and large target populations
* Of sites scoring between 30 and 40:
  -70% had observed releases and 30% had potential releases, moderate to large amounts of waste, and moderate target populations.

Around 28.50, several scenarios were examined. A site with these characteristics scored 28.80:
* Observed contamination in a drinking water well above a health-based benchmark, a substance with a toxicity value of 10,000 and a waste quantity value of 100, and 22 people served by the well.

Another site with these characteristics scored 33.70:
* Observed release in a monitoring well on the site, a substance with a toxicity value of 1,000 and a waste quantity value of 100, and a distance weighted population between 10,000 and 30,000 people.

Because of the large number of changes between the original and revised HRS, it was difficult to infer a correlation between how sites scored. The statistical and numerical approaches to determining equivalency suggested that, if anything, the cutoff score should be lowered, but did not indicate a specific number. The risk analysis indicated that the types of sites scoring above 25 to 30 pose the types of risks that warrant designation as a national priority, recognizing that the cutoff score does not reflect a point below which no risk is present.

Because the statistical and numerical analyses did not point to a specific number, and because the qualitative risk analysis indicated that sites scoring around 28.50 appear to pose significant risks, the Agency decided to retain 28.50 as the cutoff score under the revised HRS.

ANTICIPATED EFFECTS ON THE NPL

The revisions made to the original HRS are likely to place new types of sites on the NPL. For example, since the revised HRS considers contamination of natural resources that can affect the aquatic human food chain, some sites that discharge substances that bioaccumulate in aquatic organisms will be listed. Also, the addition of the soil exposure pathway makes it likely that certain soil contamination problems, especially those involving contamination of residential or school property, will be listed. Because the revised HRS expands the types of sensitive environments considered and increases their weighting, some sites causing serious environmental impacts are likely to score above the cutoff score. The addition of distance weighting in the groundwater pathway is expected to lower groundwater pathway scores, and result in fewer sites being placed on the NPL on the basis of groundwater impacts. Finally, because of the addition of health-based benchmarks, sites that result in high levels of known exposure, even if only small populations are involved, will score relatively higher on the revised HRS.

ACKNOWLEDGMENT

REFERENCES

1. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C., Sections 9601-9675, as amended by the Superfund Amendments and Reauthorization Act of 1980 (SARA).
2. National Oil and Hazardous Substances Pollution Contingency Plan, Appendix A, Final Rule, 40 CFR Part 300, July 16, 1982, 47 FR 31180.
3. National Oil and Hazardous Substances Pollution Contingency Plan, Final Rule, 40 CFR Part 300, November 20, 1985, 50 FR 47912.
4. H.R. Rep. No. 962, 99th Cong., 2nd Sess. at 199-200 (1986).
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The Superfund Site Assessment Process: A Status Report

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ABSTRACT

The Agency's evaluation list (CERCLIS) now contains about 32,000 sites. The decision process for determining which of these are among the nation's most seriously contaminated sites, and therefore warrant the expenditure of the Fund for long-term remediation, is managed by the U.S. EPA's Site Assessment Program. The U.S. EPA's goal for this program is to expeditiously identify the worst sites at each step of the evaluation process and move them on to the next stage, ultimately to the National Priorities List (NPL), or to the decision that they will not be cleaned up by Superfund. This year marks a major transition time for the program. Publication of the revised Hazard Ranking System, finalization of all proposed NPL sites, and the imminent completion of site inspections at all sites in CERCLIS, prior to the Superfund Amendments and Reauthorization Act (SARA) of 1986, have brought the site assessment program to a natural opportunity for evaluation and change. This paper describes the status of the program at the time of SARA enactment, its changes under SARA, and projects where the program is headed.

In addition to this programmatic discussion, the paper will explore what the Agency has learned through an extensive statistical analysis of a random sample of 2,300 CERCLIS sites and all NPL sites. Data ranges from site ownership at time of contamination to wastes and management types present to impacted populations and environments. The results of the study will be used by the Agency for a variety of policy and resource issues, the most important of which will focus on the design of discovery strategies to be instituted next year.

INTRODUCTION

Under the Superfund program, three major categories of activities take place: (1) emergency or removal actions; (2) evaluation of sites for actual or potential releases, and (3) remediation of sites. In managing this sizable program, the U.S. EPA's general philosophy is to address the worst sites first.

Prior to determining if a site will be addressed under Superfund, the Agency:
- Discovers the site
- Determines its emergency status
- Assesses its potential for contaminating the environment
- Scores the site using the Hazard Ranking System (HRS)
- Proposes it to the National Priorities List (NPL) determines that there is No Further Remedial Action Planned (NFRAP)

Once the decision is made for a site to be addressed by the Federal Superfund Program, the following steps occur:
- Final listing on the NPL
- Comprehensive site evaluation and risk assessment
- Selection of cleanup methodologies
- Initiation of cleanup actions
- Final determination of cleanup

This paper will cover the progress to date of the U.S. EPA's Site Assessment Program.

SITE ASSESSMENT PROGRAM GOALS AND FRAMEWORK

The decision process for determining which sites are among the nation's most seriously contaminated, therefore warranting the expenditure of the Fund for long-term remediation, is managed by the U.S. EPA's Site Assessment Program. The program utilizes the talents of some 800 professionals through 46 State Multi-Site Cooperative Agreements, 10 Field Investigation Teams, 10 Regional Office staffs and a U.S. EPA Headquarters branch.

The U.S. EPA's goal for this program is to expeditiously identify the worst sites at each step of the evaluation process and move them to the next stage, ultimately to the NPL or to the decision that they will not be cleaned up by Superfund. This year marks a major transition time for the program. Publication of the revised HRS, finalization of all previously proposed NPL sites and the imminent completion of site inspections at all sites under consideration, prior to the passage of the Superfund Amendments and Reauthorization Act (SARA) of 1986, have brought the site assessment program to a natural opportunity for evolution and change.

Sites are identified for evaluation through a wide variety of mechanisms, including such diverse sources as formal notification requirements and citizens' telephone calls. After the Agency is notified of a possible release, the site is entered into the Comprehensive Emergency Response, Compensation and Liability Information System (CERCLIS), Superfund's computerized data base that contains information on potential hazardous waste sites as well as information on Superfund removal, remedial, and enforcement activities. With entry into CERCLIS, the site begins an evaluation process that consists of:
- A Preliminary Assessment (PA). The PA acts as an initial screening of the site in which all available data - past industrial activity, permit history, location of drinking water wells/intakes, surface water bodies, sensitive environments, etc. is collected and

reviewed so that the U.S.EPA can decide if the site poses a potential hazard to public health or the environment.

- **If warranted by the PA, a Site Inspection (SI).** The SI involves on-site work that usually includes collection and analysis of suspected impacted soil, surface water, groundwater and air samples, as well as wastes, if feasible. In serious cases where listing is considered likely, wells may be dug and extensive historic aerial photography analyses, as well as more extensive investigation activities, may be conducted, as well as other, more extensive investigation activities.

- **If warranted by the SI, an HRS scoring.** The HRS is the evaluation framework for the entire site assessment program, and all sites are assessed with the key factors of the model as a template. The model is not a risk assessment, but serves to give relative indications of risk posed by individual sites to surface and groundwater, air and, under the revised version of the model, soil. Informal scores are generated throughout the process; formal scores are generated prior to proposal to the NPL.

SITE ASSESSMENT PROGRAM IN 1986

In October 1986, when SARA was signed by the President, the Site Assessment universe consisted of approximately 25,000 sites (Figure 1). The Agency had:

- Completed PAs on more than 19,800 of the sites in CERCLIS
- Conducted SIs on approximately 6,500 sites
- Made decisions on about 6,000 sites; 5,100 had received a NFRAP decision, 703 were on the final NPL, and another 185 were proposed
- A backlog of about 4,400 sites that had not received any evaluation, with another approximately 12,400 sites that had had a PA, but no SI or NFRAP decision

	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989
Sites in CERCLIS	8,000	10,500	13,366	16,309	18,864	22,621	25,194	27,571	30,013	31,904
PA Completed	2,204	1,072	1,209	1,809	4,447	5,181	4,262	4,001	2,884	2,228
Total to Date	2,204	3,276	4,485	6,294	10,741	15,922	20,184	24,185	27,069	29,297
SI Completed	613	428	586	642	1,308	1,618	1,267	1,343	1,237	1,732
Total to Date	613	1041	1,607	2,249	3,557	6,175	6,442	7,785	9,022	10,754

NOTE: The graph represents the number of PAs and SIs completed during each fiscal year, and depicts the increase in the number of sites in the CERCLIS inventory as of the end of each fiscal year.

Figure 1
Historical Pre-Remedial Accomplishments
by Fiscal Year

MAJOR SARA REQUIREMENTS AND MESSAGES - OCTOBER 1986

Four major SARA requirements directly impacted the Site Assessment Program: (1) all pre-SARA PAs were to be completed by January 1, 1988; (2) all necessary pre-SARA SIs were to be completed by January 1, 1989; (3) the site assessment process was to be redesigned so that sites would have an NPL decision in no more than 4 years from the time they were entered in CERCLIS, and (4) the Agency was to revise the HRS to give higher priority to actually contaminated drinking water supplies; assess hazards to surface water used for recreation or drinking; assess food chain impacts;

assess potential air contamination, and give special considerations to fly ash wastes.

These Congressional requirements were sending the Superfund program two specific messages for the operation of its site assessment activities: (1) Get rid of the backlog and speed up the process of finding "worst sites", and (2) Make the HRS more comprehensive in addressing a variety of hazardous waste release problems, and more accurate in assessing relative risk (without making it a risk assessment).

SARA SITE ASSESSMENT IMPLEMENTATION PLAN

In order to comply with the SARA message to clean up the backlog of sites and speed up the evaluation process, the Site Assessment Branch, in the Hazardous Site Evaluation Division, developed a 5-year implementation plan. The goal of this plan was to implement basic programmatic changes that would escalate the rate at which decisions were made regarding the disposition of sites, while simultaneously expanding the HRS through the normal Agency rulemaking procedures.

In summary, the plan created the following schedule:

- **FY 1987:** Define problems for all parts of the program; achieve the PA goal for all pre-SARA sites; obtain Science Advisory Board approval of the revised HRS approach
- **FY 1988:** Reassess all PAs that did not have decisions; institute a policy of completing all PAs within 1 year of CERCLIS entry; propose the revised HRS
- **FY 1989:** Work at addressing the SI goal; reassess all SIs that were without decisions; complete public comment, issue analysis for revised HRS
- **FY 1990:** Achieve the SI goal; publish the revised HRS as a final rule; conduct training for all participants
- **FY 1991:** Achieve full-scale revised HRS implementation; institute 4-year, CERCLIS entry to NPL listing process

In order to have any chance of achieving this ambitious undertaking, U.S. EPA Headquarters realized that coordination, consultation and overall communication with the 10 Regional offices involved with the program would have to be substantially improved. The Regions needed Headquarters guidance to carry out a nationally consistent program; Headquarters needed Regional guidance to create a process that would work in the real world. To a very substantial degree, this partnership has produced the results outlined below.

SITE ASSESSMENT PROGRAM ACCOMPLISHMENTS

Clearing out the Backlog

As of September 21, 1990, CERCLIS contained 32,755 sites (Figure 2). To date, 93% of those sites have been evaluated through the PA stage. Because all sites now receive PAs within 1 year of CERCLIS entry, there is no backlog at this crucial first step. SIs have been conducted at almost 12,800 sites; Regions 6 and 10 met the actual SARA SI goal date of January 1989. All other Regions have made substantial progress at this difficult job over the last 4 years. Regions 3, 7, 8 and 9 are within a few sites of finishing. The Regions with large backlogs (1, 2, 4 and 5), expect to take another year. As Regions finish their pre-SARA SI work, their focus moves to determining which of the remaining sites need to be placed on the NPL and to instituting discovery projects to determine if all sites have been found.

It is expected that, by the time of publication of this paper, no sites will remain proposed on the NPL (at writing, 20 sites out of 1207 remained proposed). Since SARA passage, almost 400 sites have been proposed in 6 rulemakings, and 500 sites have been finalized or dropped for technical or policy reasons in 8 rulemakings. In FY90 alone, five final rules were published, as many as had been published in the previous nine years of the program combined.

Figure 2 — Chart Labels

NPL
1207

Awaiting Assessment
2233

Site Inspection - No Further Remedial Action Planned
5252

16%

Site Inspection Completed - Decision Pending
6304

19%

PA - No Further Remedial Action Planned
13428
41%

13%

Site Inspection Needed
4331

30,522 of 32,755 (93%) Total Sites In The Inventory Have Been Assessed

Figure 2
Status of CERCLIS Inventory - 9/21/90 - All Regions

Promulgating the Revised HRS

In response to SARA, the Agency undertook a comprehensive review and analysis of ways to improve the HRS. The paper "Overview of the Revised Hazard Ranking System" discusses the differences between the original and revised HRS. While the factors have undergone wholesale revision, the structure of the model has largely been retained. The revised HRS is more flexible than the original HRS in that it can address a broader range of problem types and can accept a wider variety of types of data.

NEW PROGRAM FACETS

At the same time, spurred on by the concept of Total Quality Management (TQM), the Site Assessment Program has begun to look at ways to improve the technical decision-making process and reduce the time-consuming facets of actually placing sites on the NPL. In the past, the decision on whether a site should continue on for HRS scoring or receive a NFRAP decision may have been delayed for some time after the completion of each evaluation step.

Currently, the thrust of the program is to improve both the quality and timeliness of all steps within the site assessment process. Our paper on TQM improvements, entitled "Total Quality Management in the Site Assessment Program", outlines many of the problems that our studies have identified and some of the approaches that are being tried to address them.

The PA has been tripled in scope to include numerous factors that had formerly been acquired in the SI, such as the identification of human and environmental targets, and establishes potential pathways of concern. New PA guidance, based on the most important factors of the revised HRS, will provide the Regions, States and contractors with a standardized and effective approach for conducting PAs, and continue to include the requirement for a site reconnaissance. This approach will continue to result in more efficient screening decisions earlier in the process, more site information available to conduct any subsequent SI and contribute to an overall streamlining of the decision-making process.

Standard operating guidance is being developed, and training packages to guarantee rapid and consistent application of the revised HRS will be published. The computer will play a large role in increasing the efficiency of the program. The HRS is being automated. The HRS has numerous technical factors which must be taken into account when developing the data collection plan. The Site Assessment Program has developed the "PreScore" computer program which performs the calculations required by the HRS. This allows quick sensitivity analysis to focus SI sampling on the most important HRS factors, resulting in more nationally consistent, focused, and better-quality decisions. In another of today's papers, the PreScore program for keeping site records, postulating scoring scenarios, and calculating scores will be explained, along with the recently completed Chemical Database program that will automatically supply all HRS factor data for 330 chemicals to PreScore.

CONCLUSION

The Agency believes that the expressed will of Congress to have Superfund carry out high quality, comprehensive, but expeditious, site assessment is an ambitious, but achievable, goal. Since SARA articulated this goal, the Agency has devoted substantial resources, both monetary and human, to achieving it. We expect that the next few years will be challenging and difficult, but in the end, successful.

Automation of Revised Hazard Ranking System Scoring

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ABSTRACT

The Hazard Ranking System (HRS) has been revised to reflect the requirements of the Superfund Amendments and Reauthorization Act of 1986 (SARA), to address public comments on the HRS and to improve the overall Superfund process. These changes increased both the number of calculations needed to score sites, and the requirements for chemical data to support site specific scoring. This paper describes three "user-friendly" computer programs that can aid in scoring sites using the revised HRS:
- PreScore, a program to calculate revised HRS scores from "raw" data supplied by the user
- Superfund Chemical Data Matrix (SCDM), a source of chemical data to support the revised HRS, as well as other environmental assessments
- Chemical Scoring Matrix (CSM), a module within SCDM, to output revised HRS chemical factor values to PreScore

The purpose and design of the computer program, as well as the process for compilation of chemical data, are also described in this paper.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) recently revised the HRS to reflect the requirements of the Superfund Amendments and Reauthorization Act of 1986 (SARA), to address public comments received after proposal of the revised HRS and to improve linkages in the Superfund process between site assessment and remedial activities. Under the original HRS, calculations were performed using pocket calculators and were generally a paper exercise. With the revised HRS, it was necessary to develop an automated system to assist users in performing HRS calculations. Similarly, few chemical-specific data were required with the original HRS. The revised HRS uses substantially more chemical data. Public comment on the proposed revised HRS recommended that the U.S. EPA adopt a single source of chemical data in order to implement the model consistently. The Agency agreed that compilation of a single source of chemical data was needed to ensure consistency and improve site scoring efficiency.

The proposed revised HRS was field tested. The field test results reported that significant scoring errors, generally computational in nature, could result. These scoring errors confirmed the need for a standard, automated form of HRS scoring. The U.S. EPA anticipates that proper use of PreScore, the SCDM and the CSM by the large user community of States and contractors will significantly decrease or eliminate the vast majority of computational errors.

PRESCORE OBJECTIVES/USER NEEDS

The Site Assessment program objectives for PreScore were:
- Reduce the time involved in calculating scores
- Increase consistency of supporting information used in scoring

PreScore meets these objectives. The field test results showed that PreScore can calculate a score in half the time it takes a site reviewer using a pocket calculator, thus reducing the time needed to document supporting information. The use of PreScore is also expected to greatly enhance the consistency with which sites are evaluated and users will be able to immediately document data within the program itself. The program found that PreScore filled yet another regional need. It allowed users to improve the quality of decision-making by allowing the testing of multiple scoring scenarios easily and quickly and made more efficient sampling decisions based on the expected contribution of data to overall scores.

PreScore users can test how assumed (or judgment) values will affect a pathway or overall score. A specific factor's contribution to the overall score can be tested with PreScore prior to planning what data will be gathered at the site inspection phase. If certain data will not contribute significantly to the overall score, site investigators will not pursue those data as part of the sampling effort.

PROGRAM SPECIFICATIONS

Considering the varying computer equipment in the Regional, State and Field Investigation Team (FIT) offices involved in the Site Assessment process, the U.S. EPA decided to develop a system that would meet the following specifications in order to account for the equipment differences:
- IBM PC, PC-XT, PC-AT, PS/2, or compatible
- One 5.25 inch or 3.5 inch double sided disk drive (double or high density)
- Parallel or serial printer (necessary for output functions)

In addition, the C language was chosen as the program language for three primary reasons:
- Speed - C produces a "fast" program for this application
- Efficient memory use - C allows PreScore to run on computers with as little as 384 KB of RAM
- Small size - C produces a compact code, allowing PreScore to be installed on hard disks with limited free space

OPERATION

PreScore uses an innovative menu-driven approach to allow users to enter data quickly and efficiently in any sequence. A hierarchy of menu screens accessed through a Summary Screen (Figure 1) reveals progressively greater detail on a selected HRS factor, showing intermediate scores and the raw data on which the overall score is based. The Summary Screen depicts the four HRS pathways vertically on the left portion of the screen, while the three factor categories are displayed horizontally across the top of the page. Cursor keys (left, right, up, down) are used to move around the screens and access different factor categories. The 'Status line' at the bottom appears on each screen and displays key-stroke options available to the user. The F8 key, for instance, accesses the file system, which enables the user to create, select, save, delete or copy PreScore data files in any directory or drive (Figure 2). Another important feature displayed on all factor screens is a constant display of the current site score. PreScore uses a combination of spreadsheet-like forms for easy data entry.

| | Tutorial Test Site | TUTORIAL.HRS | Site Score 26.61 |

Tutorial Test Site   TUTORIAL.HRS   Site Score 26.61

Summary Screen				
Pathway	Likelihood of Release Value	Waste Characteristics Value	Targets Value	Pathway Score
Air	360	127	■ 20 ■	4.32
Ground Water	380	127	132	31.85
Drinking Water	80	127	67	14.18
Food Chain	80	117	48	9.36
Recreation	80	87	25	3.62
Environmental	80	117	76	14.82
Surface Water				41.99
Resident	0	0	0	0.00
Nearby	10	5	60	6.00
Onsite				6.00

ENTER-Select   F8-Files F9-Info F10-Help End-EXIT   <- STATUS LINE

Figure 1
PreScore Summary Screen*
*Note - Summary Screen reflects Proposed Hazard Ranking System

Tutorial Test Site   TUTORIAL.HRS   Site Score 26.61

PreScore Data Files -> C:\PRESCORE\					
Name	Date	Time	Size	Site Name	Score
TUTORIAL	04/09/90	12:00	5130	Tutorial Test Site	26.61
SITE8	08/23/89	11:20	16602	Joe's Dump	20.81
SITE12	12/11/89	10:43	4694	Barney's Rubble and Waste Pit	7.68
SITE98	10/30/89	17:30	29827	Archie's Acres of Drums	51.68
Site329	11/30/89	10:34	3385	Edith's World of Waste	28.05

ENTER-Select F2-Chdir F3-New File F4-Copy F5-Passwd F6-Delete End-Previous

Figure 2
PreScore File System Screen

The Summary Screen is the 'main menu' for PreScore. Each progressive level of screen information gives greater detail regarding a particular factor. In Figure 3, for example, the 'Location Line' near the top indicates this particular screen is in the Air Pathway, in the Targets factor category and asks for population information in the distance rings the HRS requires to document potentially-affected population.

This screen also exhibits a valuable property of PreScore: the ability to accept raw data values to calculate scores. Without this property, users would need to calculate these HRS factor values using a pocket calculator and then input this information into the program. PreScore simplifies HRS scoring by taking the raw data (e.g., population figures) and performing the appropriate factor

calculation internally. In the 'Status line' at the bottom, the F10 key is a Help function that provides basic information about each factor including the applicable section number of the HRS (Figure 4).

Tutorial Test Site   TUTORIAL.HRS   Site Score 26.61

Air Pathway -> Targets			
Factor Categories and Factors	Max	Value	Type
Maximally Exposed Individual / Distance (miles)	50	0 /5.000	
Population	235	■ 8 ■	H
Land Use	10	10	
Sensitive Environments	100	2	
Air Pathway Targets	235	20	

ENTER-Select   F10-Help End-Previous

Tutorial Test Site   TUTORIAL.HRS   Site Score 26.61

Air Pathway -> Targets -> Population				← LOCATION LINE
Distance from Nearest Source	Population	Distance Weight	Value	
Onsite	0	5.2650	0	
Greater than 0 to 1/4 miles	0	1.0000	0	
Greater than 1/4 to 1/2 miles	439	0.1751	1	
Greater than 1/2 to 1 miles	628	0.0517	0	
Greater than 1 to 2 miles	3473	0.0171	1	
Greater than 2 to 3 miles	53925	0.0083	4	
Greater than 3 to 4 miles	41374	0.0054	2	
Air Pathway Population Factor Value (Max 235)			8	

Enter Data   F10-Help End-Previous

Figure 3
Example of HRS Factor Detail
Population data (bottom screen) are accessed by cursoring to the population factor value (top screen) and pressing <ENTER>.

AIR PATHWAY -> POPULATION   Section 2.3.2

The population factor value reflects the population actually or potentially exposed to air emissions from the site. For each of the distance categories listed, determine the number of people within that distance category. The distance for an individual is measured as the shortest distance from any on-site emission source to the place at which the individual is located (e.g., place of residence or work. The population count should include persons residing within the distance categories specified as well as others who would regularly be present, such as students and workers. Exclude transient populations such as customers and travelers passing through the area in autos, buses, or trains.

Use exact population counts where possible. If actual residential population figures are not available, the population for a distance category should be estimated by determining the number of residences located within the distance category and multiplying each residence by the most recent U.S. Census factor for number of persons per residence for the county in which the residence is located.

Figure 4
Example of PreScore Help Screen

An important function of the program is a "built-in" Documentation Record which allows the user to type in the reasoning for scoring a factor in a certain way. Additionally, a Print function is available to print both scoresheets and the text of the documentation. One other feature to ease user interaction is pop-up windows that allow selection of different sources (e.g., landfills, surface impoundments) and selection of various concentration units for chemical information.

CHEMICAL DATA COMPILATION--PURPOSE AND OUTPUTS

The chemical information the U.S. EPA is compiling provides consistent sources of chemical information to support implementation of the revised HRS. The Superfund Chemical Data Matrix

(SCDM) and the HRS Chemical Scoring Matrix (CSM) are the two distinct modules that contain this chemical specific information.

The CSM is designed to support PreScore. The SCDM compilation includes all the information compiled in CSM and much of the information from which the factor values in CSM are derived. Moreover, SCDM is packaged with a "user-friendly front-end" to aid users in extracting combinations of chemicals or chemical parameters. SCDM contains a module to output an ASCII file of revised HRS chemical factor values to be used by PreScore.

The U.S. EPA will also provide a user's guide to support these two compilations. At this time, data for about 300 chemicals have been compiled. Additional chemicals, as well as new data and revisions for chemicals, are expected to be added. Both CSM and SCDM are to be updated on a regular basis.

The development of both the CSM and SCDM modules has been coordinated with the development team of PreScore. The SCDM module includes a "user-friendly front-end" that has been constructed using Turbo-C, which facilitates use on an IBM-PC without any additional software. Because the CSM is derived from SCDM, the two modules will be consistent in terms of data. Whenever possible, function keys have been identified so that they would reflect similar functions in the PreScore and SCDM programs. The SCDM contains options for including "flag" markers to indicate changes in chemical values, sources or other fields, and a "notes" field to facilitate documentation of sources.

SELECTION OF CHEMICALS

The chemicals compiled to date, shown in Table 1, represent both the most likely substances found at Superfund sites, and chemicals known to be toxic to human health and the environment. This list was developed hierarchically using three sources.[1][2][3] Several additional sources were also reviewed to aid in selecting chemicals.[4][5][6]

Table 1
List of Chemicals

Acenaphthylene	208-96-8
Acenapthene	83-32-9
Acetaldehyde	75-07-0
Acetone	67-64-1
Acetonitrile	75-05-8
Acetophenone	98-86-2
Acetyl-2-thiourea, 1-	591-08-2
Acrolein	107-02-8
Acrylamide	79-06-1
Acrylic acid	79-10-7
Acrylonitrile	107-13-1
Adipic acid	124-04-9
Aldicarb	116-06-3
Aldrin	309-00-2
Allyl alcohol	107-18-6
Aluminum	7429-90-5
Aluminum phosphide	20859-73-8
Ammonia	7664-41-7
Ammonium picrate	131-74-8
Ammonium sulfamate	7773-06-0
Aniline	62-53-3
Anthracene	120-12-7
Antimony	7440-36-0
Arsenic	7440-38-2
Arsenic trioxide	1327-53-3
Arsenic trisulfide	1303-33-9
Asbestos	1332-21-4
Atrazine	1912-24-9
Azinphos-ethyl	2642-71-9
Azinphos-methyl	86-50-0
Aziridine	151-56-4
Barium	7440-39-3
Barium cyanide	542-62-1
Benz(a)anthracene	56-55-3
Benzene	71-43-2
Benzene carbonyl chloride	98-88-4
Benzidine	92-87-5
Benzo(a)pyrene	50-32-8
Benzo(j,k)fluorene	206-44-0
Benzo(k)fluoranthene	207-08-9
Benzofluoranthene, 3,4-	205-99-2
Benzoic acid	65-85-0

Benzonitrile	100-47-0
Benzothiazole, 1,2,-	95-16-9
Benzyl chloride	100-44-7
Beryllium	7440-41-7
Biphenyl, 1,1-	92-52-4
Bis (2-ethylhexyl) phthalate hylhexyl) ester, 1,2-	117-81-7
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl)ether	111-44-4
Bis(chloromethyl)ether	542-88-1
Boron	7440-42-8
Bromodichloromethane	75-27-4
Bromomethane	74-83-9
Bromoxynil	1689-84-5
Butadiene, 1,3-	71-36-3
Butylbenzyl phthalate	85-68-7
Butyric acid, 4-(2,4-dichlorophenoxy)	94-82-6
Cadmium	7440-43-9
Calcium chromate	13765-19-0
Calcium hypochlorite	7778-54-3
Captan	133-06-2
Carbaryl	63-25-2
Carbofuran	1563-66-2
Carbon Tetrachloride	56-23-5
Carbon disulfide	75-15-0
Carbophenothion	786-19-6
Chloral	75-87-6
Chlordane	57-74-9
Chlorine cyanide	506-77-4
Chloro-3-methylphenol, 4-	59-50-7
Chloroaniline, p-	106-47-8
Chlorobenzene	108-90-7
Chloroform	67-66-3
Chloromethane	74-87-3
Chloromethyl methyl ether	107-30-2
Chloromethyloxirane, 2-	106-89-8
Chloronaphthalene, 2-	91-58-7
Chlorophenol, 2-	95-57-8
Chlorpyrifos	2921-88-2
Chromic acid	11115-74-5
Chromium	7440-47-3
Chromium(III)	16065-83-1
Chromium(VI)	18540-29-9
Chrysene	218-01-9
Cobalt	7440-48-4
Copper	7440-50-8
Copper cyanide	544-92-3
Coumaphos	56-72-4
Creosote	8001-58-9
Cresol, m-	108-39-4
Cresol, p-	106-44-5
Cumene	98-82-8
Cyanazine	21725-46-2
Cyanide	57-12-5
Cyanogen	460-19-5
Cyanogen bromide	506-68-3
Cyclohexane	110-82-7
Cyclohexanone	108-94-1
Cyclotrimethylenetrinitriamine	121-82-4
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
DEF	78-48-8
Di-n-butyl phthalate	84-74-2
Di-n-octyl phthalate	117-84-0
Diazinon	333-41-5
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibromo-3-chloropropane, 1,2-	96-12-8
Dibromochloromethane	124-48-1
Dibromoethane, 1,2-	106-93-4
Dicamba	1918-00-9
Dichlorobenzene, 1,2-	95-50-1
Dichlorobenzene, 1,3-	541-73-1
Dichlorobenzene, 1,4-	106-46-7
Dichlorobenzidine, 3,3-	91-94-1
Dichlorodifluoromethane	75-71-8
Dichloroethane, 1,1-	75-34-3
Dichloroethane, 1,2-	107-06-2
Dichloroethene, 1,1-	75-35-4
Dichloroethylene, cis-1,2-	156-59-2
Dichloroethylene, trans-1,2-	156-60-5
Dichlorophenol, 2,4-	120-83-2
Dichlorophenoxyacetic acid, 2,	94-75-7
Dichloropropane, 1,2-	78-87-5
Dichloropropene, 1,3-	542-75-6
Dichlorvos	62-73-7
Dicofol	115-32-2
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Diethylene glycol	111-46-6
Diisopropylmethyl-phosphonate	1445-75-6

Dimethoate	60-51-5
Dimethoxybenzidine, 3,3-	119-90-4
Dimethyl phenol, 2,4-	105-67-9
Dimethyl phthalate	131-11-3
Dimethyl sulfate	77-78-1
Dinitrobenzene, 1,3-	99-65-0
Dinitrophenol, 2,4-	51-28-5
Dinitrotoluene, 2,4-	121-14-2
Dinitrotoluene, 2,6-	606-20-2
Dinoseb	88-85-7
Dioxane, 1,4-	123-91-1
Oioxathion	78-34-2
Diphenylhydrazine, 1,2-	122-66-7
Diquat	85-00-7
Disulfoton	298-04-4
Diuron	330-54-1
Endosulfan	115-29-7
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endothall	145-73-3
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Ethion	563-12-2
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl chloride	75-00-3
Ethyl ether	60-29-7
Ethylene glycol	107-21-1
Ethylene glycol monoethyl ether	110-80-5
Ethylpropylthiocarbamate, s-	759-94-4
Fenethion	55-38-9
Ferrous sulfate	7720-78-7
Fluorene	86-73-7
Fluorine	7782-41-4
Formaldehyde	50-00-0
Formic acid	64-18-6
Furan	110-00-9
Furfural	98-01-1
Glycidylaldehyde	765-34-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexabromobenzene	87-82-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclohexane, alpha-	319-84-6
Hexachlorocyclohexane, beta-	319-85-7
Hexachlorocyclohexane, delta-	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachlorophene	70-30-4
Hexane	110-54-3
Hydrazine	302-01-2
Hydrochloric acid	7647-01-0
Hydrogen cyanide	74-90-8
Hydrogen sulfide	7783-06-4
Ioxynil	1689-83-4
Iron	15438-31-0
Isobutanol	78-83-1
Isophorone	78-59-1
Kepone	143-50-0
Lead	7439-92-1
Lindane	58-89-9
Malathion	121-75-5
Maleic anhydride	108-31-6
Maleic hydrazide	123-33-1
Manganese	7439-96-5
Mercury	7439-97-6
Methacrylonitrile	126-98-7
Methanol	67-56-1
Methomyl	16752-77-5
Methoxychlor	72-43-5
Methyl chlorocarbonate	79-22-1
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Methyl methacrylate	80-62-6
Methylene bis (2-chloroanilineloro-benzeneamine), 4,4'-	101-14-4
Methylene chloride	75-09-2
Methylenediphenyl diisocyanate	101-68-8
Metribuzin	21087-64-9
Mirex	2385-85-5
Naphthalene	91-20-3
Nickel	7440-02-0
Nickel chloride	7718-54-9
Nitric acid	7697-37-2
Nitric oxide	10102-43-9
Nitroaniline, p-	100-01-6
Nitrobenzene	98-95-3
Nitrogen dioxide	10102-44-0
Nitroglycerine	55-63-0
Nitrophenol, 4-	100-02-7

Nitroso-di-n-butylamine, n-	924-16-3
Nitroso-di-n-methylurethane, n ester	615-53-2
Nitrosodiethanolamine, n-	1116-54-7
Nitrosodiethylamine, n-	55-18-5
Nitrosodimethylamine, n-	62-75-9
Nitrosophenylamine, n-	86-30-6
Nitrosopyrrolidine, n-	930-55-2
Nitrotoulene, 4-	99-99-0
PCBs	1336-36-3
Parathion, ethyl-	56-38-2
Parathion, methyl-	298-00-0
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene	82-68-8
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Phenol	108-95-2
Phenyl sulfide	139-66-2
Phenylmercuric acetate	62-38-4
Phorate	298-02-2
Phosgene	75-44-5
Phosphamidon	13171-21-6
Phosphine	7803-51-2
Phosphoric acid	7664-38-2
Phosphorodithioc acid, phenyl-o-ethyl-o-(4-nitrophenyl)ester EPN	2104-64-5
Phosphorous	7723-14-0
Phthalic anhydride	85-44-9
Potassium chromate	7789-00-6
Potassium cyanide	151-50-8
Potassium silver cyanide	506-61-6
Pronamide	23950-58-5
Pyrene	129-00-0
Pyridine	110-86-1
Quinoline	91-22-5
Radium	7440-14-4
Radon	10043-92-2
Resorcinol	108-46-3
Ronnel	299-84-3
Selenious acid	7783-00-8
Selenium	7782-49-2
Selenourea	630-10-4
Silver	7440-22-4
Silver Cyanide	506-64-9
Sodium	7440-23-5
Sodium azide	26628-22-8
Sodium chloride	7647-14-5
Sodium chromate	7775-11-3
Sodium cyanide	143-33-9
Sodium hydroxide	1310-73-2
Strychnine	57-24-9
Styrene	100-42-5
Sulfuric acid	7664-93-9
TB, 2,4,5-	93-80-1
TCDD	1746-01-6
TP, 2,4,5-	93-72-1
Tetrachlorobenzene, 1,2,4,5-	95-94-3
Tetrachloroethane, 1,1,1,2-	630-20-6
Tetrachloroethane, 1,1,2,2-	79-34-5
Tetrachloroethene	127-18-4
Tetrachlorophenol, 2,3,4,6-	58-90-2
Tetraethyl lead	78-00-2
Tetraethyldithiopyrophosphate	3689-24-5
Tetrahydrofuran	109-99-9
Thallic oxide	1314-32-5
Thallium	7440-28-0
Thallium acetate	563-68-8
Thallium carbonate	6533-73-9
Thallium chloride	7791-12-0
Thallium nitrate	10102-45-1
Thallium selenite	12039-52-0
Thallium(I)sulfate	7446-18-6
Thiourea	62-56-6
Thiram	137-26-8
Thorium	7440-29-1
Toluene	108-88-3
Toluene diisocyanate	584-84-9
Toxaphene	8001-35-2
Tribromomethane	75-25-2
Trichloro-1,2,2-Trifluoroethan	76-13-1
Trichlorobenzene, 1,2,4-	120-82-1
Trichloroethane, 1,1,1-	71-55-6
Trichloroethane, 1,1,2-	79-00-5
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
Trichlorophenol, 2,3,6-	933-75-5
Trichlorophenol, 2,4,5-	95-95-4
Trichlorophenol, 2,4,6-	88-06-2
Trichlorophenol, 3,4,5-	609-19-8
Trichlorophenoxyacetic acid, 2	93-76-5

Trichloropropane, 1,2,3-	96-18-4
Trichlorphenol, 2,3,5-	933-78-8
Triethanolamine	102-71-6
Trifluralin	1582-09-8
Trinitrobenzene, 1,3,5-	99-35-4
Trinitrotoluene	118-96-7
Tris (2,3-dibromopropyl) phosphate	126-72-7
Uranium	7440-61-1
Vanadium pentoxide	1314-62-1
Vinyl acetate	108-05-4
Vinyl chloride	75-01-4
Warfarin	81-81-2
Xylene, m-	108-38-3
Xylene, o-	95-47-6
Xylene, p-	106-42-3
Zinc	7440-66-6
Zinc cyanide	557-21-1
Zinc phosphide	1314-84-7
Zinc sulfate	7733-02-0

These additional sources are commonly used by Superfund Regional field personnel to identify and classify hazardous wastes. While most of these substances appear on the CERCLA Reportable Quantities list, they are not found in the Integrated Risk Information System (IRIS). Furthermore, the next set of chemicals to be evaluated includes radionuclides that are currently included in the Health Effects Assessment Summary Tables (HEAST).[7]

Chemical Parameters

Chemical parameters were added to both the CSM and the SCDM modules to reflect the increasing data needs incorporated into the revised HRS and in health issues applications.

A list of chemical parameters and their sources is provided in Table 2. Examples of the HRS chemical parameters include water solubility and bioconcentration factors. Other chemical parameters

to assist with health issues applications include cancer potency, RfD (inhalation and oral) and LD50.

SUMMARY

Introduction of these automated components will aid in the implementation of the revised HRS in the site assessment process. This process is expected to facilitate Superfund's evaluation of the thousands of sites that must be considered yearly for possible inclusion on the National Priorities List (NPL).

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Table 2
Reference List for Chemical Properties Data Base

Primary Reference		Secondary Reference	Other References
LD50 (oral)	CERCLA Technical Background Documents		
LD50 (dermal)	CERCLA Technical Background Documents		
LD50 (inhalation)	CERCLA Technical Background Documents		
RfD (Oral)	IRIS	Superfund Public Health Eval. Man.	
Cancer Slope Factor (SF)	IRIS	Superfund Public Health Eval. Man.	
Weight of Evidence	IRIS	Superfund Public Health Eval. Man.	
ED10			
Vapor Pressure	Peer-reviewed literature (including Chemfate)	HEAST database	CHEMEST: est. from boiling point
Henry's Law Constant	HEAST database	CHEMEST : calculated from vap. pres./solub.	"est. from Hine & Mookerjee method"
Dry Relative Soil Volatility	Calculated*		
Water Solubility	Peer-reviewed literature (including Chemfate)	HEAST database	CHEMEST: est. by Lyman reg. eqn.
Coefficient of Aqueous			
Migration	Metals only - see TSD - Sec. 3.4.3		
MCL	National Primary Drinking Water Standards		
RfD SC**	Calculated		
SF SC***	Calculated		
Hydrolysis Halflife	Peer-reviewed literature	Peer-reviewed literature	
Peer-reviewed literature			
Volatilization Halflife	Peer-reviewed literature	Peer-reviewed literature	
Biodegradation Halflife	Peer-reviewed literature		
Peer-reviewed literature			
Photolysis Halflife	Peer-reviewed literature		
Peer-reviewed literature			
Total Halflife	Peer-reviewed literature		
Peer-reviewed literature			
BCF	Ambient Water Quality Criteria Documents	Peer-reviewed literature	*HEAST database, or est. using Lyman regression eqn.
Log P	Peer-reviewed literature (including Chemfate)	HEAST database	CHEMEST: est. CLOG P3 method
Water Solubility	Peer-reviewed literature (including Chemfate)	HEAST database	CHEMEST: by Lyman regression
Biomagnification	Ambient Water Quality Criteria Documents		
FDA Action Level	FDA action level document		
Dose Adjusting Factor	Calculated****		
Chronic Freshwater Criteria		Ambient Water Quality Criteria Documents	
Chronic Saltwater Criteria	Ambient Water Quality Criteria Documents		
LC50 (fresh)	Ambient Water Quality Criteria Documents		
LC50 (salt)	Ambient Water Quality Criteria Documents		
Chronic Freshwater Benchmark		Ambient Water Quality Criteria Documents	
Chronic Saltwater Benchmark		Ambient Water Quality Criteria Documents	

* Dry Relative Soil Volatility = (Vapor Pressure at 25 °C)/(molecular weight)**1/4
** Slope Factor Screening Concentrations (air, water, soil)
*** Reference Dose Screening Concentrations (air, water, soil)
**** Dose Adjusting Factor = (0.66)(dermal permeability constant) + (0.16)(mass plus dilution factor)

Providing Technical Assistance Under the U.S. EPA's TAG Program

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ABSTRACT

SARA enabled the U.S. EPA to give technical assistance grants to citizens' groups representing populations affected by Superfund sites in their communities. This money is to be used to hire advisors to assist the citizens in understanding the technical details of site investigations and remedial actions and to help them articulate their concerns to the U.S. EPA.

One of the first grants was awarded to the Old Forge Toxic Waste Removal Committee, which represents the community in the vicinity of Pennsylvania's Lackawanna Refuse Site, a series of abandoned coal mine pits used for industrial and municipal waste disposal. A subsequent grant was obtained by the Greater New Bedford Environmental Community Work Group, neighbors of the New Bedford Harbor Superfund site in Massachusetts, an estuary and bay extensively contaminated with PCBs and heavy metals. Acknowledgement of the social, economic and emotional impacts associated with a Superfund site and addressing them in the decision-making process, is an acute challenge for today's environmental professional and an essential ingredient for a successful remedial action. The U.S. EPA's grant program is a step in that direction. Serving as technical advisor to citizens' groups provides an opportunity for environmental scientists and engineers to broaden their horizons and gain an appreciation for a different perspective on environmental issues.

INTRODUCTION

SARA provides Technical Assistance Grants (TAGs) up to $50,000 to citizens' groups to assist them in understanding the activities associated with cleaning up contamination at Superfund sites in affected communities. The U.S. EPA issued an Interim Final Rule on March 24, 1988 establishing the initial policies and procedures governing the TAG program. Additionally, Volume 40 of the *Code of Federal Regulations* (CFR) Subchapter B—"Grants and Other Federal Assistance", including 40 CFR Parts 30, 33 and 35, contains regulations applicable to the TAG program.

The U.S. EPA's Management Review of the Superfund Program, issued shortly after William Reilly was approved as its new Administrator, found that "The TAG program is not working well...Citizens are deterred from using TAGs...[and]...U.S. EPA financial managers are wary of potential risks..." When that report was published, only nineteen TAG grants had been awarded and advisors had been hired at just a fraction of those sites. The TAG program was criticized as having too much red tape and excessive matching-funds requirements. Recently, the U.S. EPA has moved to make the TAGs more accessible, and additional grants have been awarded and advisors hired.

The U.S. EPA is authorized to award grants to "...any group of individuals which may be affected by a release or threatened release at any facility which is listed on the National Priorities List..." Groups threatened by a site proposed for listing on the NPL where a response action has begun also are eligible. Some citizen groups chartered by government entities may be ineligible, as are PRPs, academic institutions, political subdivisions and corporations not incorporated for the specific purpose of representing affected individuals at the site. Once the U.S. EPA determines that a group is eligible for a TAG, the group's ability to manage a grant must be demonstrated, generally by establishing recordkeeping and financial management procedures. The group must be incorporated, or have plans to incorporate as a nonprofit organization for the purpose of representing affected individuals.

TAG funds may be used to pay technical advisors to review and interpret documents, meet with citizens' groups to explain technical information, assist in communicating the group's concerns, disseminate information to the community and perform site visits. Funds may not be used to prepare for or participate in any legal proceeding, to generate new data, to challenge final U.S. EPA decisions or for any political activity. The U.S. EPA initially required the citizens' group to contribute 35% of the total project cost, with administrative costs not to exceed 15% of the total cost. The 15% cap has been removed and in-kind services may now be used to meet the total matching funds requirements.

The TAG process consists of: (1) submission of an application for the grant to the U.S. EPA; (2) selection of procurement method if awarded (i.e., small-purchase method for grants up to $25,000 or competitive negotiation for more than $25,000; (3) selection of a technical advisor; and (4) development, approval by the U.S. EPA and ratification of a subagreement between the citizens' group and the technical advisor.

The technical advisor's role is to help the citizens in affected communities make significant contributions to the decision-making process of Superfund. The advisor's role involves interpretation of technical details so that nonscientists can understand the complex issues associated with site activities; the advisor also assists the citizens in articulating their concerns, fears and frustrations to scientists and engineers not accustomed to considering nontechnical factors in their evaluations. Activities performed on the TAG projects have included: review of site characterization data and feasibility study reports; site inspections; preparations of reports; attendance and participation at technical meetings with the U.S. EPA, responsible parties and their contractors; and presentations at public meetings. The advisor often acts as a mediator or facilitator in meetings and interpersonal communication and relation skills, as well as technical ability, are essential in these situations.

In the following pages, two case histories of TAG projects are presented and some highlights of this work are discussed.

CASE HISTORY I—LACKAWANNA REFUSE SITE, PENNSYLVANIA

According to the U.S. EPA's remedial investigation and subsequent studies, three former coal stripping cuts were used for waste disposal at the Lackawanna Refuse Site. One of these, known as Pit 5, contained numerous drums of hazardous waste. Additionally, three other features, known as the Paint Spill Area, the Access Road and the Borehole Pit, were found to contain surficial contamination which required remediation.

The proposed remediation process for the two coal stripping pits not containing hazardous waste (Pits 2 and 3) entailed construction of a cap, leachate collection and treatment systems and a gas venting system. Contaminated soil from the Paint Spill Area, the Access Road and the Borehole Pit would be removed for off-site disposal. All drums and wastes would be excavated from Pit 5. Uncontaminated material [i.e., material containing concentrations of key indicator compounds (KICs) below established threshold levels] would be used to backfill the pit, with contaminated material disposed off-site. A cap, leachate collection and treatment systems and gas vents would be installed at Pit 5. A groundwater monitoring system would be installed following remediation.

Mobilization of the remedial action contractors, establishing site facilities and the associated vehicular traffic represented a highly unusual situation for the small community. Moreover, the perceived threat of a release of hazardous or toxic contaminants into the air as a result of excavation activities was of great concern to nearby residents and to the community in general due to the relatively close proximity of a school.

A consulting firm had extensive involvement with the Lackawanna project working for the citizens' group prior to the TAG program. Beginning in 1985, a number of documents pertaining to the design, conduct and safety of the remedial action and the plans for post-closure care of the site were reviewed by the consultants at the request of the Old Forge Toxic Waste Removal Committee (Committee). The group used a variety of fundraising activities to pay for this work; however, such technical assistance is relatively expensive and funds were limited. Nevertheless, privately funded technical support of the citizens' group continued through the 90%-design phase of the remedial action project.

Remedial activities began in 1987 with cleanup of the Access Road, Paint Spill Area and Borehole Pit and the construction of haul roads to Pit 5. Excavation of wastes from Pit 5 and regrading of Pits 2 and 3 in preparation of cap placement commenced in 1988. In September 1988, at the Committee's expense, the consultant performed a site inspection, reviewed data and met with the U.S. EPA and Committee representatives concerning the status of the remedial action project. At last, in 1988 the Committee's efforts resulted in the award of one of the first $50,000 TAGs. Because of its previous involvement in the project, the Committee wanted to retain the consultant as technical advisor after the TAG was obtained. The small purchase procurement method was used to award a $24,000 one-year contract for Phase I technical assistance. The consultant then assisted the Committee in its efforts to help the local citizens understand the technical issues concerning remediation of the Lackawanna Refuse Site using U.S. EPA funds.

Numerous site inspections were performed and the advisor prepared written trip reports documenting the status of the remedial action with photographs noting the progress made in resolving outstanding items of concern to the community. Construction, waste excavation and removal activities were observed and results of waste analyses and post-excavation (i.e., after cleanup) soil sampling obtained during the inspections were reviewed for consistency with the remedial design. The Committee was kept informed on the progress of the remedial activities in a series of technical briefings.

At the end of the Phase I contract, the Committee solicited proposals from a number of prospective firms and chose the incumbent consultants to continue as their technical advisor. A fact sheet was prepared and distributed to the community as the technical advisor presented a slide show at a public meeting in Old Forge near the end of removal opera-

tions to show the progress made in cleaning up the site. Additionally, the advisor assisted the U.S. EPA's consultant with a magnetometer survey to investigate for additional buried drums; reviewed the post-closure groundwater monitoring system installed at the site; evaluated leachate and gas emission data; and continued to interpret technical details and to help the Committee articulate its concerns in several meetings with the U.S. EPA. All work was documented in quarterly progress reports to the Committee.

CASE STUDY II—NEW BEDFORD HARBOR

On June 6, 1989, the consultant entered into an agreement with the Greater New Bedford Environmental Community Work Group (Work Group) to provide technical assistance for the New Bedford Harbor Superfund site remedial action under the TAG program. The Work Group had issued a Request for Proposal (RFP) seeking interested parties for providing technical assistance after receiving a $50,000 TAG. The consultant had tracked this potential new business opportunity in a typical fashion, submitting a qualifications package to the Work Group, proposing a scope of work and cost estimate, traveling to the community to meet with the potential clients and finally winning the job after making a "best and final" offer.

New Bedford Harbor is an urban tidal estuary located at the head of Buzzards Bay in southeastern Massachusetts, approximately 55 miles south of Boston. The communities of New Bedford, Fairhaven, North Dartmouth and Acushnet border the harbor which is home port to one of the largest commercial fishing fleets in the United States. From the 1940s until the late 1970s, when use of PCBs was banned in the United States, factories along the Acushnet River discharged industrial process wastes containing PCBs into the harbor. In 1976, the U.S. EPA conducted a New England-wide PCB survey which included New Bedford Harbor. During the next five years, field studies conducted by the U.S. EPA and the Commonwealth of Massachusetts identified PCBs and heavy metals, notably cadmium, lead, copper and chromium, in the sediments and marine life throughout a 1,000-acre area of New Bedford Harbor and parts of Buzzards Bay. In 1977, testing of edible fish tissue samples revealed PCB levels in excess of the U.S. Food and Drug Administration's 5 ppm guideline (subsequently reduced to 2 ppm). As a result, the Massachusetts Department of Public Health restricted fishing by establishing fishing closure areas in New Bedford Harbor and Buzzards Bay.

The U.S. EPA estimates that the Hot Spot area (a five-acre portion of the estuary) contains approximately 10,000 yd^3 of contaminated sediment with PCB concentrations ranging from 4,000 ppm to over 100,000 ppm and heavy metal concentrations ranging from below detection to approximately 4,000 ppm.

In 1988, an Engineering Feasibility Study (EFS) being performed by the U.S. Army Corps of Engineers was expanded to include a Pilot Study at the site, allowing the Corps to conduct physical demonstrations of dredging equipment and construction and testing of disposal facilities in the estuary, while continuing to carry out site sampling, analysis and research. The Pilot Study took place in a cove in the upper estuary and involved the removal and disposal of approximately 15,000 yd^3 of sediments, including approximately 7,500 yd^3 of PCB-contaminated sediments. The shoreline disposal facility, called a Confined Disposal Facility (CDF), was used to contain 5,000 yd^3 of contaminated sediment dredged from the cove. An underwater disposal facility, known as a Confined Aquatic Disposal (CAD) cell, was constructed using the hole created when sediments were dredged for placement in the CDF. The CAD was partially filled with the remaining 2,500 yd^3 of contaminated sediments dredged from the cove and then capped with a clean layer of sediment excavated from below the level of contamination.

In May, 1989, the U.S. EPA made available to the Work Group a draft Hot Spot Feasibility Study report which presented the range of remedial alternatives considered for the Hot Spot area. The Draft Final Hot Spot Feasibility Study report was published in July 1989. Having the technical advisor under contract as these complex documents were released enabled the community to obtain a clear understanding of the remedial

alternatives and the significance of underlying assessments and evaluations made by the U.S. EPA and its contractors. The technical advisor reviewed all previous studies and reports, including the Public Health Risk Assessment, EFS reports and the Hot Spot FS report. This independent analysis helped the concerned citizens gain confidence in the U.S. EPA's risk assessment, although some technical flaws and questionable assumptions were brought to their attention.

The advisor assisted the citizens in articulating some of their concerns regarding cleanup of metals in the sediments, potential hazardous air emissions from incineration, the presence of heavy metals in residual ash, long-term stability of ash after chemical fixation and the potential for future environmental degradation and health effects from disposal of residuals in the unlined CDF. Some of these concerns were initially based on emotions and fueled by misrepresentation by interest groups or the media. The advisor's experience with these issues, however, enabled the concerns to be put forth on a technical basis.

The U.S. EPA held a public meeting at which time the proposed plan for cleaning up the Hot Spot was presented. The technical advisor accompanied members of the Work Group to the meeting and discussed the plan with the U.S. EPA and state agency representatives. The preferred alternative consists of removal of approximately 10,000 yd^3 of sediment by dredging, incineration of the dredged sediments in an on-site, mobile incinerator to destroy PCBs, possibly treating the incinerator residue to reduce the mobility of heavy metals and temporary storage of the treated sediments in the existing CDF used in the Pilot Study. This cleanup is estimated to cost approximately $14.4 million and would take approximately one year to complete.

Another meeting was held later to allow AVX, essentially the only responsible party, to discuss a plan for in-place containment of the sediments by capping the estuary from the Coggeshall Bridge upstream. The advisor was present at this meeting and interviewed the consultants for AVX in an effort to better understand their proposal. This involvement helped the Work Group to offer cogent comments into the public record concerning the U.S. EPA's and AVX's plans for remediation of the Hot Spot.

ENHANCING SUPERFUND

Based on the authors' experiences in working on these two TAG projects, providing groups of responsible and concerned citizens with financial assistance to retain technical advisors has enhanced greatly the Superfund program. First, the community gains an understanding of many technical details that were very mysterious before the advisor interpreted them in a context that could be understood by nonscientists. Many nonscientists, no doubt, do not grasp easily the significance of a risk of 3.17 E-7. Explaining what this means can ease the level of anxiety in a Superfund community; people generally are less fearful of things they understand. Moreover, a measure of trust appears when the citizens' advisor enters the picture. The public often feels they are given the "runaround" and many grow suspicious when faced with the complexities and procedures institutionalized in Superfund. The advisor must represent a readily available and unbiased source of information—someone not considered to have a "hidden agenda" for forcing a remedial action onto the community. These factors help bring the citizens on board as part of the solution and help keep them from becoming the opposition. The following anecdotes illustrate these benefits.

The citizens of Old Forge were able to learn from an impartial eyewitness of the progress made in removing hazardous waste from their community. In one instance, their advisor helped negotiate additional investigations to locate buried drums after some drums had been encountered in an area previously thought uncontaminated. The advisor was on-site during the subsequent magnetometer survey, thereby ensuring that the citizens would be comfortable with the U.S. EPA's

reported results. In another instance, the citizens were concerned that the cleanup was leaving unacceptable levels of PCBs in residual soils at the base of Pit 5. The technical advisor helped the citizens understand applicable PCB cleanup criteria, the negligible risk associated with deeply buried low-level PCB contamination and the impracticality of additional removal. Once, photographs of the newly constructed cap were offered by a disgruntled site worker, along with allegations of improper construction practices and escape of hazardous leachate from Pit 5. The advisor was consulted and his knowledge of the status of work at the site, based on a recent site visit, helped reassure the citizens.

On the New Bedford project, one area of concern to the community was the planned disposal of residual ash from incineration of Hot Spot sediments in the proposed unlined disposal cell along the shore. The feasibility studies had noted that the high concentration of metals in the ash may require chemical fixation to immobilize the metals. One of the treatability tests conducted on the sediments, however, enhanced the mobility of certain metals. The community was confused about the potential for future contamination if metals leached from the disposal cell. The advisor pointed out that Massachusetts regulations for solid waste disposal required liners and if residual ash contained metals at concentrations above hazardous waste criteria, it would have to disposed of in an appropriate manner.

During one public meeting in answering a question concerning PCB air emissions from incineration of Hot Spot sediments, a scientist referred to the incinerator's efficiency "six nines." This pronouncement resulted in many glazed-over eyes and expressions of bewilderment in the audience. The technical advisor later interpreted this to the non-scientists so that they grasped the level of destruction of the incineration process. Many individuals were concerned with dioxin and lead in emissions from incineration as well. The advisor helped the citizens understand the nature of these emissions and the technologies available to scrub incineration by-products.

In these cases, advice from the citizens' own consultant was accepted more comfortably than from the U.S. EPA. Furthermore, the advisor could be directed to perform evaluations that centered on the communities' concerns which may not have been provided by the U.S. EPA. For example, the Old Forge community was concerned about the potential release of hazardous vapors and the risk of fire or explosion from the gas vents installed through the cap at the site. The advisor commissioned a study of landfill gas emissions by a firm that specializes in landfill work. In this manner, the concerned citizens were provided with an evaluation of the quality of emissions from the Lackawanna site, a comparison of those emissions with other typical gases from municipal landfills and hazardous waste sites and an identification of applicable monitoring and pollution control regulations.

A similar study was performed by the advisor regarding the quality of leachate generated at the site. He illustrated that Lackawanna leachate was generally less contaminated than leachate from hazardous waste sites and in some cases it was more dilute than sanitary sewage. The results of this effort were taken into consideration as the community and the U.S. EPA agreed to disagree on leachate management options (i.e., construction of an on-site treatment plant or discharge through municipal sewer to the local POTW).

Regardless of whether or not communities have the financial ability to engage their own technical advisors to assist them on Superfund matters, uncertainty and apprehension will be a factor in the government's efforts to remediate hazardous waste sites. In fact, our experience has shown that even when expert technical advice is offered, emotional arguments can prevail. The technical advisor, however, can help close the gap between the risk perceived by the community and that actually presented by a Superfund site. Serving as community technical advisor offers today's environmental scientist or engineer the opportunity to expand one's horizons while helping society deal with the complex emotions associated with environmental issues.

The Pros and Cons of PRP Involvement in Superfund Community Relations

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ABSTRACT

Dealing with the public is a frightening prospect for most companies. Many would rather ignore the public—and hope it goes away. It never does; at least not until after you are out of business. This paper examines Superfund Community Relations from the perspective of a company involved in a Superfund action. It discusses some benefits and pitfalls companies face and details some strategies to increase their chance for success.

The number of "enforcement-led" Superfund sites has grown far more quickly in recent years than the number of "government-led" sites. So-called PRPs have assumed an increasing role in financing studies and cleanups. However, PRPs have not taken as much initiative in the implementation of the accompanying community relations activities required by law. In most cases, the U.S. EPA or the state performs most or all community relations.

It is generally recognized that remedy selection should be interactive. All affected parties (federal, state and local governments, residents, environmental groups, PRPs, etc.) are encouraged to voice their viewpoints and concerns so that a consensus can be reached.

When PRPs communicate only with regulators and not with other affected parties, their influence over remedy selection is severely limited. Under the Superfund law, PRPs have no more influence over remedy selection than other affected parties—even at enforcement-led sites. Despite their expertise, they can become just one of many voices trying to influence remedy selection. However, if PRPs share their expertise and viewpoints directly with other affected parties (as well as the U.S. EPA and the state) they can increase their influence over remedy selection. This process can result in an environmentally sound, economically practical, privately funded and timely cleanup. Of course no amount of communication can force acceptance of a remedy that is patently inadequate.

There are obstacles to overcome, such as the perception that PRPs are only interested in cutting costs or the potential for negative publicity. However, if handled properly, PRP involvement in community relations can be valuable in selecting appropriate remedies at Superfund sites.

INTRODUCTION

Financial liabilities related to site remediation projects are becoming one of the biggest worries facing corporate America today. For most large manufacturers, there is no way to accurately predict how many sites a company will be involved with or the extent of their liabilities.

For companies involved in Superfund projects, how well they deal with the public almost invariably has a substantial impact on the cost of the project. The U.S. EPA chooses a remedy for each site based on factors such as protection of human health and the environment, compliance with applicable laws, long-term effectiveness, permanence and public opinion. It is a political reality that public opinion is often given much greater weight than is indicated in the regulations.

In Superfund, dealing with the public consistently and effectively can make the difference between paying $10 million and $100 million for a cleanup just as surely as a marketing strategy statement can make or break efforts to reach a sales goal.

This statement does not mean that every company involved in a Superfund cleanup must have a high public profile. In some cases, this clearly is not desirable. It also does not mean that PRP community relations efforts should always urge selection of the cheapest possible remedy. This tactic is impractical, unethical and bound to be counter-productive.

The goal of most companies involved in Superfund cleanups is to control overall costs while implementing an environmentally sound remedy. In fact, implementing the cheapest remedy may not be the best way to control costs. Issues such as third-party lawsuits, future costs to correct an inappropriate remedy and damage to public image may produce costs far in excess of the actual cleanup. Many issues that can produce additional cost are related to interaction with the public.

GOVERNMENT/PRP ROLES IN COMMUNITY RELATIONS

Superfund mandates detailed community relations planning and implementation. The purpose is to involve each affected community as an important part of the decision-making process—not simply to provide information on what the government or the company is doing at the site. Many Superfund cleanup plans have been changed as a direct result of community comments.

The new NCP, the blueprint for implementation of the Superfund law, places even greater emphasis on the role of the public.

According to U.S. EPA guidelines, the U.S. EPA or the state has the lead in all community relations activities at both government-led and enforcement-led Superfund sites. This requirement means regulators have primary responsibility for informing the public about site activity and for seeking public input on all aspects of the study and cleanup process.

Without going into too much detail on Superfund Community Relations requirements, key activities generally include:

- Community Relations Plan—Outlines plans and stratgegies for gathering and providing information
- Public meetings—Held at the Workplan and RI/FS completion stages
- Briefings—Informal meetings with community residents, local officials, news media and other interested parties
- Informational material—Fact sheets and brochures to summarize ongoing events and solicit comment
- Responsiveness summary—Describes comments received on the RI/FS and responses from regulators

While regulators claim primary responsibility for implementing community relations in Superfund, they also recognize that PRP involvement in community relations can be beneficial. From the perspective of the government and the public, it allows easier access to the study and cleanup process, especially at enforcement-led sites where PRPs are performing a study or cleanup work, they may be the best source for timely and accurate information on site activities. From the perspective of the affected companies, PRP involvement in community relations can promote an effective working relationship with the public and increase the chance for completion of a site study and cleanup with minimum opposition, intervention or delay.

Specific guidelines for PRP involvement in community relations are determined by the U.S. EPA Region (or state) involved —with the regulator in as overseer. Some regions are quite restrictive, while others encourage active interaction between companies and communities.

POTENTIAL BENEFITS TO COMPANIES

The core objective of any community relations efforts should be to establish and maintain an effective working relationship with affected groups and individuals. By initiating a community relations program in cooperation with regulators, a company can actively control its own destiny at a Superfund site rather than leave its destiny solely in the hands of regulators. Regulators will generally inform and involve the community as specified under the law. But, although regulators, companies and affected communities are all working toward an environmentally sound cleanup, a community relations effort implemented by the government alone is likely to lack certain aspects that can be very important to PRPs. Some of these aspects are discussed below.

Providing a True Picture of the PRP's Role in the Site

During its community relations efforts, the U.S. EPA will generally explain the Superfund process to the community quite thoroughly. But it is not a priority for the agency to explain how each PRP contributed to the problem, or their specific roles. By communicating directly with the public, a PRP can more clearly define its role in causing the problem and its involvement in the project. These issues may be important to the PRP—particularly if it has come forward voluntarily and assumed a role in cleanup of a site in which it had little actual involvement or where it was in compliance with current regulations when the contamination occurred. These people may be moot under SARA, but they can be very important in third-party lawsuits and maintaining the company's public image.

Virginia Fly Ash Site

At a Virginia fly ash site, corporate executives for a PRP assumed a visible role in the community relations process. They assumed financial responsibility for the cleanup, but took care to emphasize that they were operating within current regulations when the problems were created. The result was an ever-improving working relationship with a powerful environmental group involved in the project and more detailed media coverage of the company's actual role in the site. Ultimately, a cost-effective, privately financed, on-site containment remedy was chosen.

Opening Direct Channels of Communication Necessary to Complete Site Work

Particularly at enforcement-led sites, it is often necessary to deal with community residents in getting access to adjacent property, sampling residential wells and other activities. This can be cumbersome if all such activity has to be conducted through regulators. Regulators should be kept fully informed of any contact with community residents, but direct communication can be invaluable in keeping a sampling program, or other necessary activity, on schedule.

Pennsylvania Industrial Facility

At a Pennsylvania industrial facility, community relations contractors for the facility operator provided nearby residents with ongoing information on site activity, the Superfund process and the company's role in the problems and the solution. Information, closely coordinated with the Regional Office, was provided through mailings and in person. This groundwork helped simplify gathering more than 100 residential well samples necessary to the RI/FS.

Influencing Remedy Selection

When the U.S. EPA considers public comments on a proposed cleanup remedy, it can give comments from PRPs no greater weight than comments from the general public. By communicating directly with the public, PRPs can share their knowledge and expertise with the general public, which may influence comments. Especially if there is disagreement between the U.S. EPA and the PRPs over which cleanup remedy is most appropriate, PRPs can only ensure that their opinions are adequately expressed to the public by communicating directly with the affected community.

Pennsylvania PRP Group

A Pennsylvania PRP group had serious concerns about a U.S. EPA proposal for on-site treatment at a site they had formerly operated. The group expressed its concerns to the U.S. EPA, but also met with state and local officials and residents to explain the group's concerns. The results were a letter from local officials to the agency and other communication expressing concern over the proposed remedy. The agency decided to reexamine its preference for an on-site treatment alternative.

A secondary but potentially valuable benefit to PRP community relations activities is the broader benefits to corporate image that can be engendered by a credible and responsive community relations effort.

POTENTIAL PROBLEM AREAS

While there are few down sides to a well orchestrated community relations effort, there are some important issues to consider during planning and implementation.

Credibility

PRPs can have an even worse credibility gap in their dealings with affected communities than regulatory agencies. There may be a perception that, because they are the parties which caused the problem at the site, the PRPs cannot be trusted to implement an appropriate solution. Another common perception is that PRPs are not interested in the quality of the cleanup—only its price tag.

Reliability and accessibility are two of the most important ingredients in establishing and maintaining a credible relationship with any community. Since most Superfund sites are abandoned properties, it is unlikely that PRPs have an ongoing relationship with communities before becoming involved in study and cleanup plans. They also may be geographically distant from the site. These factors can aggravate credibility problems.

Overcoming these problems can be the most important step in establishing working relationships with an affected community, in

conducting an effective study and in ultimately choosing a cost-efficient remedy. It is essential that PRPs or their representatives make themselves readily available to the community beginning with their initial contacts. These contacts must be factual, objective, two-way exchanges. As most PRPs realize, it would be a poor business decision to cut costs by purposely working toward a remedy that is not environmentally sound. Discussing potential economic drawbacks to the company of implementing a cheap but environmentally unsound cleanup can help the community understand the company's rationales.

While it is important that the community understand the PRP's role in past and future site activity, discussions should focus on the best ways to find solutions to problems at the site. One sure way to lose credibility is to try to "sell" a remedy to a community.

Legal Issues

The effectiveness of relationships between a company's community relations professionals and its legal counsel can determine the success or failure of community relations efforts. Full disclosure of pertinent information can damage negotiations or other aspects of the company's legal position, but withholding pertinent information can severely limit a company's ability to communicate effectively with the affected community. A balance between the two cannot be reached if lawyers and communicators cannot find common ground on which to base a community relations strategy.

Community relations during enforcement actions should be conducted much like community relations during government-led actions—almost all information generated or considered is public information. However, there will be times when limits must be placed on information released during enforcement actions. Information about ongoing negotiations, confidential business information and other potential PRPs can be particularly sensitive. While community relations staff must have latitude to discuss site-related work and issues with the public, all written material that addresses legally sensitive topics should be reviewed by counsel. In addition, it is advisable to meet with counsel prior to major public appearances to identify subjects which cannot be discussed and go over other, less severe ground rules.

Generally, any information that does not specifically and clearly threaten a company's legal or negotiating position should be made available to the public with as little delay as possible. It is likely that such information will be released under the Freedom of Information Act (FOIA) anyway. Forcing community residents to go through the cumbersome FOIA process unnecessarily can create resentment.

Just as it is important for a company's technical staff and consultants to form a cohesive team early in the Superfund process, it is important that legal and community relations representatives be an integral part of that team. This relationship allows team members to agree on general guidelines for the project and minimizes the potential for future serious philosophical disagreements.

Internal Communication

Coordinating the flow of information among different PRPs and within individual corporations can be cumbersome when planning and implementing a community relations program.

Superfund cleanups often involve groups of PRPs represented by law firms and environmental consultants that manage projects on a day-to-day basis. While the lawyers and consultants may be empowered to make most technical decisions without extensive review from all involved PRPs, such PRP groups are often very sensitive to site-specific dealings involving the press or public.

If a group consists of only two or three companies, developing a consensus on most community relations issues may not be an insurmountable task. However, if the group includes four or more

PRPs, it can become impractical to solicit frequent input from each PRP. In such cases, a meeting of key group members should be organized early in the process to reach consensus on basic community relations guidelines. A community relations strategy can then be outlined, agreed upon and implemented with frequent status reports provided to the full group. In such cases, group concurrence on all but the most crucial or unusual community relations events should be kept to a minimum. The roles of in-house staff and consultants in this process are discussed later in this paper.

Even in cases where only one PRP is involved, site-specific community relations efforts can cut across a number of internal corporate organizational systems—particularly at sites which involve both a local facility and corporate headquarters.

Generally, site-specific community relations are best handled at the most local level of a corporation's structure. If individual facilities are involved, plant managers and their staff are most likely to have an ongoing relationship with the local community. In such cases, community relations efforts should be based there. However, possible media attention and political involvement will likely engender interest from the corporate office—so corporate communications managers will have to be kept abreast of developments at the site.

The quality of this communication process may seriously affect the relationship between a facility and its corporate office—particularly if there is negative media coverage regarding the site.

BEST USE OF RESOURCES FOR PRP COMMUNITY RELATIONS EFFORTS

In-House Staff

Corporate staff should generally be active in Superfund community relations as much as possible. Serving as the key point of contact for the community and media reinforces a company's commitment to a project. It also allows closer control over statements made and information provided to the public throughout a project.

But in some cases, such direct involvement may be impractical or undesirable. It may be impractical because other demands can prevent corporate staff from spending as much time on a project as is needed. A company's credibility will be judged more by how responsive it is, than by what it says. If a key contact is not accessible to a community, and, therefore, not as responsive as he or she should be, there is a serious risk to the company's credibility. A half-hearted community relations effort can be almost as bad as no community relations effort at all. It is generally better to surrender some direct control over the nuances of public interaction than to try to run a community relations program in your spare time. Selection of an experienced consultant can be the next best thing to doing it yourself.

There may be cases where it is undesirable for a company to take a visible role in community relations efforts. When several PRPs are involved in a project, it may be difficult to single out one as the point of contact. Most companies in this situation are reluctant to draw attention to themselves and away from the other members of the group—for a variety of reasons.

Unfortunately, there also are projects which generate a lot of negative publicity and controversy. It is a fact that this happens rarely when a well-planned community relations program is established. In such cases, companies may prefer to designate a third party as the primary community and media contact. Companies cannot stay out of the picture through this approach, but they can focus attention on the contact and the project, rather than on the company.

Consultants

Three types of organization generally provide community relations services for Superfund PRPs:

- Public Relations Firms—These firms are likely to have the widest array of capabilities, ranging from fancy graphics to video production. Many large firms have offices or affiliates throughout the world. Personnel at PR firms generally have responsibilities outside the realm of environmental issues and may not have extensive practical experience with Superfund.
- Management Consulting Firms—Several of the larger companies have developed departments that deal only with environmental communication issues. Personnel at such firms may be technically proficient and have a good grasp of how Superfund community relations fits into a company's management systems. Many such firms have contracts to perform Superfund community relations for the U.S. EPA, posing a possible conflict of interest with private sector work.
- Engineering Firms—Some of these companies have developed community relations capabilities, primarily to serve clients that have already hired them for technical work at Superfund sites. These people generally have extensive technical knowledge and good communication skills. This arrangement also simplifies communication between technical and community relations staff.

Engineering firms may have to use subcontractors for fancy graphics or video presentations.

The type of company used for community relations support depends on the specific needs and preferences of the PRPs involved.

TACTICS

There are several key community relations decision points at each Superfund site. Planning an approach to these decision points can help ensure that activities are most effectively carried out.

Initial Contacts with the Public

It is essential that close coordination between regulators and PRPs begins as early as possible. Roles should be defined and responsibilities identified before community contacts are made. Such coordination shows that, although the two sides may not agree on all issues, there is a cohesive plan for involving the public in the decision-making process. Since initial community contacts may be made before the Community Relations Plan (CRP) is completed, the parties should hold an organizational meeting as soon as the PRPs become involved in site study and cleanup.

Community Relations Plan

The CRP is a blueprint for community relations activities at a Superfund site. Regulators and PRPs should work together in preparing the CRP to explain the roles of each. Community interviews, required by law, help gather pertinent information from neighbors, local officials, environmental organizations and other interested parties. PRPs should participate in community interviews to answer any questions about their involvement in the site and to assist in identifying key concerns. The U.S. EPA generally assumes responsibility for actually producing the plan.

Meetings with the Public

A variety of public and small group meetings are generally held throughout the project. These meetings provide opportunities for two-way dialogue between those involved in study and cleanup and the community. PRP participation in these meetings conveys responsiveness to the community and a willingness to work with

regulators rather than against them. PRP representatives may be best prepared to answer questions and respond to requested changes in project plans—particularly if the site is enforcement-led.

Media Interviews

A company's discomfort over dealing directly with the public can be exceeded by its disdain for dealing with the press, but good media relations is generally essential to a company's efforts to project responsiveness and credibility during its involvement at a Superfund site. A company must appoint one spokesman who is knowledgeable about the site, informed about the Superfund law, experienced in dealing with the press and accessible to reporters. Of these four qualities, experience and accessibility are the most vital.

Informational Material

All information developed specifically to inform the public should be reviewed by counsel. Production of any fact sheets, brochures, press releases or other items should be scheduled to allow time for such review. Once community relations personnel and lawyers agree on basic guidelines for public statements (as described under Legal Issues) these reviews should involve only minor changes in wording and emphasis.

Responsiveness Summary

As a required part of all RODs, a responsiveness summary can have a substantial impact on remedy selection. The government prepares all responsiveness summaries independently. PRPs must submit comments on proposed cleanup alternatives along with the general public. Comments by PRPs are given equal weight with comments from the public. If comments from PRPs and the public agree, they are likely to have more impact than if they are divergent. PRP involvement in community relations will increase the likelihood of common ground with the public at the responsiveness summary stage. (This issue is also discussed under "Influencing remedy selection.")

KEY POINTS FOR A SUCCESSFUL EFFORT

A corporation can use community relations best to complete a timely site study and implement an environmentally sound, cost effective cleanup if it takes an approach which:

- Realizes that the PRP's relationship with the community can have a direct bearing on the amount of money it spends at the site
- Recognizes the community as a key factor in study implementation and remedy selection
- Includes community relations staff as a vital part of the project team
- Plans the community relations effort to make the best use of available resources and to be most responsive to site-specific conditions
- Devotes the necessary time and resources to building a credible relationship with the community
- Implements the community relations effort with special emphasis on critical decision points

This approach can take some of the fear out of dealing with the public by helping a company to better control the amount of money it eventually sinks into a Superfund site.

Partners in Remediation:
Making a "MESS" of Community Participation

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ABSTRACT

The Milltown U.S. EPA Superfund Site (MESS) committee formed to monitor remedial progress at the Milltown Reservoir Sediments National Priorities List Site near Missoula, in western Montana. The Environmental Protection Agency remedial project manager recognized the community's need to voice their concerns as participants in the remedial process.

MESS is involved in the Milltown Endangerment Assessment Committee (MEAC). Citizen involvement at such a fundamental level is unique to the Superfund process and relies on the commitment of not only the citizens but also the U.S. EPA staff, the State of Montana and the potentially responsible parties. Early citizen involvement and acceptance is critical to successful remedy selection and implementation. The Superfund process can be, and has been, brought to a standstill by public rejection of a proposed plan or record of decision.

Still, many committee members believe there should be even more opportunity for involvement. The U.S. EPA has yet to attain the MESS committee's ideal of citizen participation in the Superfund remedial process.

INTRODUCTION

The community of Milltown lies at the confluence of the Clark Fork River and the Big Blackfoot River in western Montana. The town grew up around the William A. Clark mining company lumber mill. As the mill expanded, the rivers offered a cheap source of energy, and so Milltown Dam was constructed and went on-line in 1907. The resulting reservoir unintentionally served as a settling pond for contaminated sediments in the Clark Fork River.

The contaminated sediments entered the river starting from its headwaters in Butte, Montana, where the Anaconda Copper Mining Company and others mined and milled copper, gold, silver and other valuable minerals. More contaminants entered the river from Mill and Warm Springs creeks, which flowed past heavily contaminated areas of Anaconda, Montana, where copper was smelted into anodes for manufacturing uses. Additional hard rock mining activities throughout the Clark Fork drainage contributed to the heavy metals and metalloids sediment load in the Clark Fork River.

These contaminated sediments found a resting place in the quiet backwater of Milltown Reservoir and settled to the bottom. At last estimation (1990), approximately 6 million cubic yards of reservoir sediments are contaminated with heavy metals and metalloids.

In 1981, a 2-year old Milltown child contracted an intestinal disease of unknown origin. The Missoula City-County Health Department (MCCHD), in searching for a possible cause, tested her family's well and found elevated levels of heavy metals and arsenic. While it later was established that the disease was organic in nature and not a result

of heavy metals or arsenic ingestion, seven other wells were tested, and four showed elevated levels of arsenic. Thirty-five homes were served by these wells, and in August 1981, the residents were told to stop using their well water for drinking and cooking purposes.

The Milltown Reservoir site was put on the National Priorities List in 1983, and a citizens' advisory committee formed to provide public comment on the selection of contractors to perform the remedial action study and review progress reports. After various samples were taken at the reservoir and an abandoned riverside landfill in 1984, the source of contamination was traced to dissolution of heavy metals from mill tailings in the reservoir sediments.

For almost 3 years, affected community residents hauled their drinking and cooking water. Some families even refused to bathe in the water and went to the local school to shower. Concern among the citizens varied from very worried to not at all concerned. Most people resigned themselves to hauling water and hoped local, state and federal officials would expedite replacement of the water source.[1]

After intense pressure from public interest groups such as Missoula Peoples' Action (MPA), the Montana Public Interest Research Group (MontPIRG) and the Milltown Water Users Association (MWUA), the National Guard provided a water truck for the affected citizens. By 1985, the Montana Department of Health and Environmental Sciences (MDHES), with funding from the U.S. EPA, replaced the water source and replaced residential plumbing that showed concentrations of contaminants. However, that action ameliorated only the immediate threat to human health and the environment. The reservoir sediments awaited investigation.

The process of performing a remedial investigation and feasibility study was derailed when the State declared its contractor in default in 1987. The U.S. EPA took the lead and, under the policy of enforcement-first, began negotiations with the potentially responsible party, the Atlantic Richfield Company (ARCO). ARCO was deemed responsible for the cleanup because the U.S. EPA asserts that ARCO is the successor-in-interest to, and has assumed the liabilities incurred by, the Anaconda Copper Mining Company (which became the major operator in the Butte/Anaconda area). The U.S. EPA made plans for negotiating, with ARCO, terms of the remedial investigation and feasibility study, with the U.S. EPA retaining full oversight authority.

MILLTOWN DAM PROBLEMS

During this time, Montana Power Company (MPC), owner of the Milltown Dam since 1929, was told by the Federal Energy Regulatory Commission (FERC) to upgrade the dam. Several severe weather incidents in the past had weakened the dam structure. After consulting appropriate state and federal agencies, including the U.S. EPA, MPC had a drawdown of the reservoir, dredged some sediments and repaired

the dam. The sediments were removed to an upland disposal area that all agencies had approved. However, no official noticed the three homes directly east of the area. One resident insists that when she indicated where she lived, officials said, "No, where do you really live?"[2] Nevertheless, the residents noticed the disposal area and were told by a contractor that MPC was constructing a toxic waste dump. The residents immediately called the MCCHD and were told to call the Clark Fork Coalition (CFC), a Montana environmental watchdog group whose sole charge is protection of the Clark Fork River basin resource. The citizens did call CFC.

In turn, CFC called the U.S. EPA. The remedial project manager (RPM) at this time (August 1988) was Ken Wallace. Wallace's background was in the public interest/environmental field, and he had established a good working relationship with the Clark Fork Coalition. They, in turn, were looking at a model of citizen participation in the Superfund process that avoided the cumbersome application process for the newly instituted Technical Assistance Grant program.

After responding to the citizens near the "waste dump," and several months of discussion, Wallace proposed that a (new) citizens' advisory group meet with state and federal Superfund personnel on a regular basis, providing a forum for U.S. EPA and MDHES to present data, report on activity progress, discuss problems and solicit input. He promised monthly meetings in Milltown or Missoula (downstream approximately 5 miles). The few restrictions were that Bonner Junction and Milltown citizens be members, that it not be solely a technical group and that it not be a partisan political forum.[3]

Seldom has the U.S. EPA encouraged this level of involvement from the public. However, Wallace saw this as an opportunity to expand greatly public participation in the Superfund process and preclude incidents such as the citizen ignorance of the upland disposal area, and so he successfully lobbied the issue with the Region VIII Montana Office management and ARCO. After several memos and letters, all parties agreed on the terms of participation. Thus, in March 1989 the "MESS" Committee was born.

THE COMMITTEE

The Milltown U.S. EPA Superfund Site (MESS) Committee was the vehicle of citizens who had no great faith in the Superfund process, the agencies (U.S. EPA and MDHES) or ARCO. They had seen decisions made both slowly and with seemingly little regard for public opinion. The name they chose for themselves reflects a deep-seated cynicism with Superfund and the major players. "MESS" means what it spells: the group saw a mess at the Milltown site, as well as a mess in the way the cleanup and citizen concerns were being handled. One of the first successful gestures the U.S. EPA made to the group was to accept their name without dissent or attempt to exert any pressure to change the name, despite the overt cynicism.

MESS is comprised of the Clark Fork Coalition's staff scientist, the Montana Public Interest Research Group's executive director and chair of the board of directors, the Five Valleys Audubon Chapter, the Missoula League of Women Voters, representatives from the MCCHD and the conservation district and unaffiliated citizens from Milltown and Bonner Junction (the site of the upland disposal area). Leadership follows two lines with CFC providing exceptional technical expertise, and MontPIRG providing expertise on community organizing and citizen groups. The MESS Committee set a goal for their involvement, which is:

"The complete removal, or the equivalent, of all contaminants at the Milltown site showing metals concentrations above background or which pose a threat to public health or the environment, whichever is lower, and an equivalent level of cleanup of upstream sources which will result in the elimination of downstream transport of contaminants. Final remedies which do not involve complete removal of contaminants must not require continued societal maintenance or concern [i.e. no institutional controls (ed.)]. Contaminants which are removed must be treated such that they cannot pose a threat to human health or the environment."[4]

By September 1990, the MESS committee felt reasonably comfortable and competent in its role (although they may be no less cynical

about the agencies or potentially responsible parties). There still are areas with which the committee has difficulties. As one member metaphorically stated, "MESS is a two-year old child. It knows what it wants to ask, but the words don't always come out right. We don't have the ability yet to rephrase our question to get the right answer, so we just keep asking the same question, hoping the answer we want will appear. But, like a child, we learn fast, and we'll know how to ask the questions better!"[5]

MILLTOWN ENDANGERMENT ASSESSMENT COMMITTEE

As an outgrowth of the successful relationship between MESS, the agencies and ARCO, Wallace proposed that MESS be involved in endangerment assessment (EA) activities. Wallace stated that all meetings would be open to the general public, decisions would be consensus-based and "should the meetings become non-productive, the U.S. EPA will dissolve the committee."[6] All parties indicated approval of this idea.

In a letter from ARCO project manager Christiane Garlasco, she said, "ARCO endorses the EPA's involving potentially responsible parties and local citizens in the endangerment assessment process" and recognized that the U.S. EPA would retain the final decision-making authority and responsibility. She continued, "the proposed (endangerment assessment committee) process, while experimental, may provide a valuable forum for exchange of information. ARCO will work with EPA and the other participants to make it so."[7] Phil Tourangeau of the Clark Fork Coalition said the MESS committee saw the purpose of the committee to be "to produce...(a) workplan for the conduct of the EA" and proposed additional work groups, of which one was adopted.[8]

The Milltown Endangerment Assessment Committee (MEAC) has been working together now for over a year. There have been growing pains and disagreements involved with the process, but the citizen members have been able to influence regulators (and sometimes ARCO), and MESS is aware of most activities concerning the Milltown site. Ken Wallace believes a completely successful model would need to have been implemented earlier in the Superfund process, but given what he and Tourangeau of CFC had to work with, MESS and MEAC are effective models of citizen participation.[9]

THE IDEAL OF CITIZEN INVOLVEMENT

However successful this incarnation of citizen involvement at a Superfund sight might be, it falls short of the ideal. These shortcomings hinder competent involvement on the part of the citizens, and that causes frustration for all parties. Wallace gave one indication of an obstacle to overcome, that of starting the concerted effort to involve the public late in the process. In addition, change of agency personnel played a role in the ability of the citizens to participate.

Shortly after the formation of the endangerment assessment committee, Ken Wallace chose to leave the U.S. EPA. In doing so, he allowed enough time to introduce and integrate the new project manager, Julie DalSoglio, into both the technical and community issues that existed. Fortunately, DalSoglio shared Wallace's public interest background and desire to facilitate public involvement in the Superfund process. However, any new managerial face at a site causes a certain amount of perturbation among all remaining parties, and Milltown was no exception. Some resentment was directed at DalSoglio simply for being new and for replacing a project manager with whom MESS had established a working rapport. DalSoglio made it clear, however, that she intended to follow the lead that Wallace had set and pursue involvement at all possible points in the process.

The MDHES also has had changes in personnel; since the formation of MESS, three successive project managers have been assigned to the site. Due to the U.S. EPA lead, this turnover has had less impact than it might otherwise have had, but it still causes some procedural difficulties. At times, MESS members wryly have referred to themselves as the oldtimers on the site and the institutional memories.

Additionally, MESS has disputed their exclusion from the negotiations for the remedial investigation/feasibility study administrative order on consent and work plan. The U.S. EPA, MDHES and ARCO re-

jected the MESS committee's request to be allowed to observe or participate, citing federal rules of evidence and privacy issues. While the committee does not accept these reasons, they agreed to participate in the endangerment assessment and pursue the issue of negotiations further.

Also, there remain logistical problems with an agency or other group working with a citizen-based group; most meetings need to be conducted in the evening so that all citizen members have the opportunity to attend. Unfortunately, that limits the amount of work that agency, ARCO and other personnel can do.[10] Various permutations have been attempted, but no one group is satisfied completely and continually. Such a problem is endemic to agency-public interactions, and no truly satisfactory solution has been espoused.

Finally, the issue of an informed, competent citizenry has to be addressed. The uninformed citizen is like the stereotypical insensitive tourist in a foreign country: unable to speak the language, when the citizen asks for a hamburger and the vendor does not understand, he simply says again "I want a hamburger" loudly, as though the vendor were merely deaf. So too does the citizen; isolated from arcane technical information, he simply rails against agency decisions all the louder, never making much sense to the agencies or potentially responsible parties. Such a situation is frustrating for all involved, but especially so for the citizen, because citizens also are powerless to influence the decision-makers.

The impotence felt by a citizen up against the bureaucracy lends itself to blocking actions that impede remedial activities at Superfund sites. Sometimes that action takes the form of requesting congressional interference; at other times people will lie down in front of bulldozers. The public is not completely powerless. The agencies serve their own best interests when they actively encourage early citizen participation and work to make that participation as skilled as possible. One way to promote participation skills is to utilize workshops on Superfund early in the process.

Region VIII, in conjunction with U.S. EPA headquarters, has developed a prototype workshop for citizens. Called the "Citizens' Superfund Workshop," it leads citizens new to Superfund through the process, putting them in the place of the project manager, with exercises on site-related issues. The MESS committee made the trial run through this workshop in May 1990, long after their involvement in the Milltown site. While they were past the need for the information contained within the workshop, and resented what they perceived as an agency attempt to make them sympathetic to the plight of the project manager, they were able to look at it from the point of view they had a few years ago, and affirmed its value to the Superfund novitiate.

Yet competent participation extends beyond simply understanding what step of the process one is on and relies on project managers and others providing information that they themselves use to guide their actions. If the agency wants to avoid lengthy battles at the proposed plan stage, they must put citizens in the position where they are not expected to answer a year's worth of questions in a 30-day comment period. Such a level of knowledge requires a continuous effort to bring the public along with the process and give them some participation aids.

In the end, agencies, contractors or potentially responsible parties can either play the game and pretend to foster citizen involvement while their meetings and studies thwart this involvement, or they can take some fairly straightforward steps to actively encourage effective citizen participation.

The following steps are suggested as a means to ensure competent, effective citizen participation. While we may not be able to guarantee that the citizens will agree with our decisions at the record of decision stage, they may be able to better explain their opposition, and we may be able to better meet their needs.

FIVE SIMPLE STEPS TO COMPETENT CITIZEN INVOLVEMENT

These steps are geared to the project manager and community involvement coordinator at a site; they are applicable to the efforts a potentially responsible party makes to involve the public, also.

- Do whatever you can to help citizens establish a firm knowledge of the Superfund process. This includes setting aside time to give briefings on the particular site as well as the process. However, talk not only about the process, but also about policy debates, the politics they will face and other insider information critical to successful operation in the Superfund arena.
- Open the process itself. To do this, invite citizens to join in risk assessments, RI/FS meetings or other meetings exclusive of those to which legal convention prohibits access. Help citizens prepare for meetings by making the pertinent data available beforehand, distributing agendas beforehand and informing them on the time table.
- Encourage citizens not to rely solely on the RPM but to use other resources, including other local and national citizen groups. In addition, encourage them not to rule out going to the PRPs for information. As we use other agencies, so too can the citizen benefit from outside experts.
- Encourage citizens to research and utilize the skills of citizen involvement and organizing. This includes (at any step in the Superfund process) taking the time to meet with their own group and establish their goals, their mutual questions and a strategy for their successful involvement in the process.
- As agency personnel, make yourself available and encourage PRPs to make themselves available to citizens for one-on-one briefings or background. By opening up the process to citizens, you create a relief valve so all issues do not have to be addressed in the forum of infrequent, confrontational public meetings.

CONCLUSION

We have to ask ourselves an important, but hopefully rhetorical, question. Do we really believe in citizen involvement or is our sole purpose to mollify the concerned public and have them agree with our decisions? We are obligated to realize and accede that the local citizens are the ones who must live with any decisions we make. No matter how trustworthy we believe ourselves to be, these people have to have some ownership of the decisions that will guide their future. We are not "arming our enemies" if we follow the steps suggested above; rather, we are giving the citizens an opportunity to participate in a meaningful, competent manner in a process that often robs them of that opportunity.

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Understanding Effective Community Organizations

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ABSTRACT

Industrial firms and governmental agencies dealing with hazardous waste recognize that public information is a crucial element in the success of technical projects. Numerous articles and studies attest to the validity of this concept. However, these publications have consistently viewed the issue from a one-sided perspective: that of the industry/agency being forced to include the public in its operations. Writings are replete with suggestions on how industries and agencies can "break through public opposition" and "overcome public ignorance." The public is viewed as a forbidding presence that the industry/agency can somehow control during a project by feeding it a steady stream of information.

A steady stream of information from the industry/agency, however, does not necessarily ensure a successful community relations program. In some cases where frequent high-quality project information has been distributed, community organizations have been able to force the industry/agency to alter or abandon a technical project or decision in favor of community concerns and desires. A common response of the industry/agency is to ask, "What did we do wrong?" In this paper, we argue that it is equally, if not more, important to understand what the community organization did right.

Through an analysis of case studies, we have identified those strategies that community groups have used to successfully alter project plans. These strategies include common organizational goals; detailed knowledge of technical plans and documents; a strong legal and scientific understanding of the issues at hand; presentation of viable alternative technical plans; involvement of local and political officials; continued persistence by the group in the face of opposition; and the application of a calm, professional manner in dealings with the industry/agency.

We have studied several community groups and in this paper we present detailed descriptions of each of the strategies listed above. By doing so, we provide a thorough understanding of effective and ineffective community strategies. This understanding should contribute significantly to the formulation of community relations programs that allow technical teams to complete their work in a manner consistent with the concerns and desires of the industry/agency and the affected public.

INTRODUCTION

Daily newspapers, radio reports, television stories and magazine articles regularly feature stories of community groups interfering with, altering and even halting, technical progress at hazardous waste project sites. This constant flow of information about hazardous waste projects in the media is resulting in a public that is increasingly aware of the issues surrounding these projects, as well as a public that is educating itself to safeguard what it perceives as its current and future safety and well-being.

But incinerators must be built, hazardous waste recycling efforts must increase, landfills must be sited and hazardous waste sites must be controlled or cleaned up. In the face of increasing public knowledge and awareness of environmental issues, how can industries and agencies successfully complete these projects? How can they accomplish their goals in the face of public opposition?

In this paper, we maintain that the ultimate success of hazardous waste projects rests in understanding what makes certain community organizations successful in their campaigns against hazardous waste projects.

As consultants and strategists who establish and maintain effective community relations programs, our primary goal is to help companies and agencies complete their technical projects successfully and efficiently. As heads of families, homeowners and community members, we understand the most conservative efforts to keep all risk and health threats out of our lives and our communities. We are, therefore, "on both sides of the fence." As a result, we have concluded that there must be compromise on both sides of that fence.

Compromise often is not a popular concept with companies in position to earn millions of dollars through the successful siting of a hazardous waste landfill. Compromise is difficult for agencies responsible for investigating and making decisions about the best way to clean up a functioning or abandoned hazardous waste site. Compromise is rarely an acceptable concept with community members who view their property values at risk and their lives and their children's lives as imperiled by hazardous waste projects.

At the very least, the strategies used to successfully complete controversial projects must be responsive to real issues and threats, as well as to the political and passionate climate of a community. Even the most powerful company is not guaranteed success by the sheer weight of that power. The strongest and most valuable asset that community members have is their passion to protect and safeguard those elements of life most dear to them: property values, their health and the futures of their children and grandchildren. No amount of money or skill can equal the power and effectiveness of this passion.

Although the importance of compromise cannot be overlooked, it is not our focus in this paper. Our purpose instead is to examine those strategies used by community organizations to impose their will on that of an industry or agency attempting to complete an unpopular project in that community. By examining and understanding effective community strategies, we can assist industrial firms and governmental agencies to successfully complete controversial projects in the face of opposition. We had originally intended to examine those strategies on the basis of detailed descriptions of specific case studies. However, in examining the merit of that presentation, we have opted in favor of presenting the strategies themselves, rather than details of the case studies. We are doing this in an effort to protect the anonymity of the companies, agencies and individuals currently embroiled in heated battles.

INFORMATION GATHERING

An effective community organizational effort starts by gathering the information crucial to the issue: the technical, political and legal factors of the issue. That information is then analyzed and understood to develop effective action: action that will delay, modify or even halt an undesired project. The first vital step in a community's strategy is to gather the information necessary to determine the exact environmental threats and local implications of the proposed project. This process sometimes requires hiring technical experts or capitalizing on the technical skill of an organization member. Very often, however, information is gathered simply by going to the public library to research the issue and the applicable Freedom of Information laws. Technical knowledge can be accumulated by accessing information prepared by state and federal environmental agencies which is available as public documents, or by telephoning the public affairs offices of those agencies. Technical information also can be gained through polite and careful questioning of company officials who are attempting to do their best to be responsive and responsible to the affected community. Community organizations have long understood that the "enemy" in an issue can become the most valued "ally" when dealt with carefully and skillfully.

Successful community groups also research the legal issues involved in a project. They determine if zoning changes are necessary to complete the project or if permits and licenses are required to implement all the phases of the project. Rarely has it been necessary for a community organization to pay for legal counsel. Organizations frequently have been able to recruit competent attorneys to their cause; attorneys whose contributions are the donation of legal advice and service. However, groups which need legal representation in court may have to hire attorneys. Optimally, these attorneys are also members of their communities, who have the benefit of personal passion to the cause in addition to expertise in legal environmental issues.

Successful community organizations also recognize and use the expertise of other groups. They network heavily, eliminating the need to "reinvent the wheel." The methods used and knowledge gained by others are invaluable in determining what strategies will be most productive and effective in their particular community. One of the most widely acknowledged and successful nonprofit organizations offering advice and expertise to communities is the Citizens Clearinghouse for Hazardous Waste, formed by Lois Gibbs, a former Love Canal resident and activist. Ms. Gibbs is at the forefront of the grass-roots protest on environmental issues and has established a sophisticated network to assist other groups, based on previous successes and failures.

The other vital piece of information that groups acquire before any successful challenge begins is a thorough knowledge of the elected and appointed officials, from the local to the federal level. Not only do groups know who these individuals are, they also learn the officials' postures on environmental issues, their terms in office and when they are up for reelection. This information is one of the most vital tools a community group can have and is readily available to all citizens. The most effective groups also use political offices as key sources of information. U.S. congressmen and senators can offer citizens direct access to the resources of the Library of Congress; state representatives and senators can provide critical insights into the inner workings of the state. Also, most U.S. congressmen and senators have staff personnel knowledgeable in environmental issues who are available to personally answer questions. They can direct group members to the appropriate federal agency personnel when necessary, cutting through reams of red tape.

Successful organizations also become familiar with the form of local government prevailing in their area. The federal and state government may be fairly easy to understand, but town governments can be more complicated. It is crucial to know who the true decision-makers are.

As part of the information gathering process, the organization also determines the sentiment of the affected public. By learning this, they can determine whether education is needed regarding the issue, whether they have to "line up the troops" or if the support is already there. It is imperative to have a vocal majority on the side of the "cause" if politicians and officials are going to rally behind the community.

Also integral to group success is familiarity with the local media and a good working relationship with those reporters interested in and willing to cover news and events relevant to the group's cause.

MOVING INFORMATION INTO ACTION

We identified six strategies that have been especially effective in transforming the accumulated information into action.

Create Awareness of the Group and its Mission

Most effective groups have first successfully created an "inner" and "outer" awareness of their organization and its mission. Inner awareness is the belief among group members that "David can fight Goliath" and win. To challenge an agency or industry successfully, individual members must believe that they can win no matter how few they are in number, how small their town or community, how little they think they know or how late in the official process they have become involved. Although it is difficult to pinpoint specific strategies and techniques by which inner awareness is built, its importance must not be underestimated. Inner awareness is the cornerstone upon which successful organizations are built; it is often the sole motivator when their cause appears futile; and it is nearly impossible for an agency or industry to defeat.

The most successful groups do not rely on inner awareness alone, however. They also create an outer awareness of their membership and mission; that is, they create an awareness of the group and its purpose in the community. This has been most often and most effectively accomplished in relatively simple ways:

- Petitions. Circulating petitions requesting support for the group's mission is an inexpensive and very effective tool for spreading the word quickly over a large area. Taking petitions door-to-door, to shopping centers, to community centers and to churches, temples and synagogues helps to spread the group's message not only to a large geographic area, but also to a large number of community members.
- Fair/Festival Booths. Many groups set up booths at fairs, festivals and other neighborhood events that attract large numbers of people. This activity provides an excellent opportunity for recruiting new members because it allows for one-on-one discussion of the group and its purpose.
- Working with Other Community Organizations. As we mentioned earlier, successful groups have found it extremely useful to work with existing community organizations, even if the purpose of those organizations is not related to the group cause. Existing community organizations often are able to provide the fledgling group with valuable resources such as contact lists of possible volunteers, newsletter items publicizing the group and monthly meetings at which group members may speak.

Focus on "Service-raising" Rather Than Exclusively Fundraising

Groups challenging an agency or industry are, at heart, running a political campaign. And, like every other political campaign, a constant source of money is needed to purchase the services necessary. Because money is so important, it often is the area on which the agency or industry concentrates, and they always have the advantage. Many agencies and industries feel that they can stop a community organization by pouring funds into extensive media campaigns, supporting local schools and causes and hiring scores of lawyers, engineers and scientists. These same agencies and firms are often thrown into a quandary when this strategy fails.

Successful community groups focus more on "service-raising" than on traditional fundraising. Group leaders acknowledge that they would never be able to compete with an agency or industry in terms of dollars, so they do not try. Instead, they focus their fundraising efforts on gaining the services that money can buy. Rather than hiring a print shop to produce and copy flyers, they turn to members with home computers and easy access to copy machines. Instead of renting halls for community meetings, they turn to members who can access rooms at minimal or no charge. Rather than hiring photographers to record group

events, they turn to members with the equipment and expertise to do the job. By exploring the individual capabilities and hobbies of each member, these group leaders acquire, at a low cost, the elements they need to continue, counterbalancing many of the dollars spent by their opponents. By utilizing the abilities and services available in and through their members, they increase the feeling of involvement and worth of the members. This mode of operation translates into increased allegiance and dedication to the cause.

Gain the Attention and Enlist the Aid of Every Possible Politician

Individuals who have successfully challenged the agency or industry also have successfully gained the attention and assistance of as many politicians as possible. Communities appear to have better luck at this than do agencies or industries. This seems to be due to two main reasons. First, politicians (particularly mayors, state representatives, state senators, U.S. representatives and U.S. senators) are accountable to voters. They need public support to stay in office. Any other goals a politician may wish to accomplish while in office (such as becoming instrumentally involved in certain areas of public policy) will become impossible if that person does not remain responsive to his or her electorate.

Second, in the public's eyes, the organization represents the interests of the "people," but the agency or industry may not. For this reason, it usually is not difficult for the organization to mobilize citizen support to put effective electoral pressure on elected officials. Some strategies and techniques in this area include the following:

- Invitations. Every politician is invited to all group meetings and functions. Each presence or absence is widely publicized.
- Questions. Every politician is publicly asked his or her opinion on the issue with questions phrased to require a yes or no answer. The answers are widely publicized.
- Voter Registration. One member of the group is deputized to register voters. Groups then set up a clearly marked voter registration booth at every meeting or function so that it is visible to the politicians in attendance.
- Letter Campaigns. Letter-writing campaigns are organized to simultaneously flood a politician's office with mail.
- Telephone Campaigns. Telephone campaigns are organized to simultaneously flood a politician's office with phone calls.
- Demonstrations. Peaceful demonstrations are held outside political offices.

Gain the Attention and Enlist the Aid of the Media

Effective community organizations appoint one person as media spokesperson for the group. It is the ultimate luxury to have a group member who is skilled in media relations, has established contacts and is willing to utilize them as his/her contribution to the group efforts. However, even in the absence of this, one person is appointed to serve as spokesperson, regardless of previous experience. This person gains the skills needed "on the job." Media contacts prefer to deal consistently with the same representative. The most successful spokespeople make themselves available at all times and carry a beeper or pager so that they can be reached at a moment's notice.

The spokesperson has no problem arousing interest and procuring media coverage with a good, fresh environmental or political story. It is a different matter when there is no new or "hot" news. Effective groups create their own stories during lulls in the action to keep the story fresh in the minds of the community, the media and the politicians.

Successful organizations maintain control of the coverage of their issue in the media. Without that control, the reporters will turn to others involved in the controversy for news. When this happens, the group may find that the stories become slanted in a different light and its side is not presented fairly or correctly.

A creative mind is the only limitation on the possibilities of creating stories that gain media attention. One effective proven technique is the creation of an event, sometimes a group fundraiser. Local popular media personalities are invited to host and judge the event. This garners pre-event publicity, event coverage and post-event reports.

Remain Active Even if the Agency or Company Does Not

A common mistake made by many organizations challenging agencies or industries is to react rather than act. When the agency or industry appears to be doing nothing, the group also does nothing. The group then loses momentum, members drop out, press coverage disappears and politicians ignore the cause. It is then very easy for the agency or industry to "move in" and win the fight.

Effective organizations, therefore, have adopted a strategy of continuous action. They put particular emphasis on remaining active when the agency or industry does not appear to be active. This strategy not only allows the group to hang on to the advantages it has gained, but it also helps to maintain inner and outer awareness.

The group leaders we spoke with mentioned no specific techniques for accomplishing this strategy. Instead, they suggested carrying on "business as usual," whether through press conferences, political rallies, demonstrations or mass mailings. Their key is to always keep the group as active as possible.

Work Within the Law at All Functions

In some community fights, the agency or industry often is able to stop a group activity by finding a legal loophole that was missed, such as finding out whether there are more people in a meeting hall than the allowable limit or whether a group needs (and consequently has) a parade permit to conduct a rally. The most successful groups search out these loopholes before the agency or firm has a chance to do so. They ensure that every requirement of every applicable law has been met.

CONCLUSION

There are effective and ineffective community organizations. The effective groups accomplish their purposes through a variety of techniques, but the strategies that result in success and accomplishment of group goals are consistent. Agencies and industries need to understand those strategies thoroughly in order to most effectively respond, compromise and accomplish their end goals.

Successful groups first carefully gather information relevant to the site or issue. That information includes a thorough knowledge of the technical issues of importance, the local political structure and method of government, the elected and appointed officials from the local through the state to the federal level and the applicable legal factors. This information is then put into action in a robust, impassioned, yet rational plan of action. Effective community organizations have used the following tried and true strategies:

- Create awareness of the group and its mission
- Focus on "service-raising" rather than fundraising exclusively
- Gain the attention and enlist the aid of every possible politician
- Creatively gain the attention and enlist the aid of the media
- Remain active even if the agency or industry does not
- Work within the law at all functions

Hazardous waste projects will always generate controversy. The industrial firms and governmental agencies that develop effective methods of dealing with and responding to the controversy will be the most successful in accomplishing their goals. A flexible, thorough community relations program based on a complete understanding of successful community organizations will smooth the process and give the agency and industry the leading edge to accomplish project goals.

Communicating Risk to Communities

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INTRODUCTION

This paper will discuss the common communication problems encountered by environmental professionals when dealing with the nontechnical community. Environmental professionals need to understand the community's point of view. Once the community's viewpoint is understood, action can be taken to address their concerns.

The Federal Superfund program requires individual states to achieve the ability to dispose of hazardous wastes without depending on land disposal. This requirement has created a need for new facilities. California's Tanner Bill (AB 2945) requires each county to have the capability to dispose of its own hazardous wastes. This is a microcosmic view of what is (or will be) happening on a national level.

The siting of a new waste disposal facility depends heavily on the surrounding community's willingness to accept it. Even in states without a formal community participation plan, homeowners know they can veto the development of a new facility through political action. Who really wants a hazardous waste facility in their neighborhood?

There are several reasons for the breakdown of communications: technical language versus lack of technical knowledge and nonrecognition of age, gender, language and ethnic barriers. The project team can overcome these barriers with various techniques: the use of common images; informal interviews with residents; addressing community concerns instead of attempting to overcome objections; and recognition of local conditions (demographics, politics, etc.).

More problematic than technical communication problems is a difference in values. Each element viewed as a benefit by the environmental professional may be viewed in the opposite light by the community. Each side, and often there are more than two sides, may have a completely different perception of the potential impact of a proposed project. Community relations efforts usually focus on convincing residents to support the proposed facility. These types of efforts are generally ineffective against the risks perceived by the community.

The environmental professional needs to realize that the community is operating from a psychological response to the fear of loss of control. Perceived risk is more real to the community it affects than the statistical reassurances produced by technical experts. This predisposition to fear is what creates the grassroots movement against the proposed facility. Miscommunications energize this movement and give it its eventual political force.

The importance of understanding the community's point of view increases as effective community relations plans become more vital to the siting process. Environmental professionals will have to learn to communicate more effectively with the communities involved. Effective communication can diffuse political pressures and high levels of controversy which would result in the disapproval of a site.

COMMON COMMUNICATIONS PROBLEMS

Effective communication involves the transfer of ideas from one person to another. Simply using the same spoken language does not guarantee communication, as anyone who has ever been in a parent/child discussion knows. For example, my mother and I will stand at Point A. We will agree that we are at Point A. We will agree that we want to get to Point B. We will stand at Point A and argue about how to get to Point B. This discussion is not much different from agreeing that the site is contaminated, agreeing that it needs to be cleaned up and arguing about how it needs to be cleaned up. When two people have something at stake, it leads to communication barriers.

In risk communication, the most common communication barrier and the easiest to overcome, is the use of technical language with people who do not use technical language. There are environmental professionals who seem shocked to learn that not everyone knows that EP-CRA is a section of SARA which amended CERCLA. In fact, there probably are quite a few environmental professionals who do not know what these acronyms stand for and what they mean. In the same vein, members of the general public ordinarily have no need to understand the differences between stabilization and solidification, or bioremediation versus excavation and treatment. Translating technical information into nontechnical language is simply a matter of explaining the problem clearly. Common images are extremely useful here. The object is to get the basic functional idea across, not to train the listener in the nuances of the technology. A carbon adsorption unit is like a giant fish filter in an aquarium. Both units use carbon as the primary cleaning agent. Both may also use secondary filter material. The only functional difference is size. Once the basic idea has been understood, then technical language may be used.

Common images can be used to illustrate pieces of explanations as well. The images do not need to continue on a theme—they just need to get a picture into someone's head. As an example, when explaining asbestos affects on the lungs, several different nonrelated images can be used: the lung is like a sponge; asbestos fibers are very aerodynamic, like a spear; when asbestos fibers get down deep into the spaces in the lungs, they can do a great deal of damage; the passages into the deepest parts of the lungs are covered with cilia, which looks like wheat; when asbestos gets down into the lung, it is like a 747 landing in a wheat field; and the asbestos cuts a path in the cilia, which does not regrow, embedding itself in the side of the lung.

Certain words and phrases associated with environmental risks already create images in the public's mind. Words like cancer, asbestos, cyanide and toxic are guaranteed to get a reaction. Special care should be taken with the phrase "one in a million" when describing risk. The public perceives 10^{-6} to mean if one million people are exposed to this

substance, then one will die. In risk assessment, 10^{-6} means that daily exposure of a specific dose to a 70-kg person over the expected lifetime of 70 years would increase the chance of cancer by one person out of one million people.

Sometimes the problem with using technical language is that it may give more information than is necessary. The public may not need to know that EPCRA is a section of SARA which amended CERCLA. Communicating that the community has a right to know may be the only important information.

Environmental professionals should recognize that communities are fully capable of understanding the technical and scientific issues. "The public" includes doctors, scientists and teachers, as well as persons with less scientific background who are able to understand the intricacies of the problem.

A second barrier to effective risk communication is the communicator's lack of recognition of age, gender, language and ethnic barriers. Recognizing the demographics of the effected community may give an indication of the probable public reaction. Younger people and couples with children, especially younger children, will react the most strongly against health risks. Younger couples and families who have recently purchased their homes (less than five years) are the most likely to be financially tied to the area. This group feels that they have the most to lose financially. Long-time residents, especially those over 60, feel that they have the most invested in their homes, in memories and effort as well as money. In addition, if they depend on a fixed income, they also may be financially tied to their home. The health threat of carcinogens will have less effect on this age group, since the attitude seems to be that cancer takes 20 years to develop and they may not have 20 years of life left anyway. Women tend to be more vocal against health threats, especially when protecting young children. Many community activist movements are begun and coordinated by mothers of young children.

Overcoming these types of communication barriers can be accomplished by addressing community concerns instead of attempting to overcome objections. Too often, community communications are focused toward "selling" the community on the remedial action that has been selected. The public focuses on risk factors not found in the quantitative data. Dismissing public reactions without any attempt to understand them may lead to greater public opposition and, ultimately, a greater expenditure of resources trying to quiet the controversy. Not recognizing language differences will lead to complete miscommunication and will fuel anger in residents. In communities with large non-English speaking populations, communicating in their fluent tongue may be critical to responding to community concerns.

Another barrier that may hinder effective communication is a difference in values—that is, the difference between what is important to the community and what is important to the agencies and PRPs. An example of this barrier could be a decision to excavate and treat contaminated soils. Although this process would clean the area much more quickly than on-site treatment, the community may object to the transporting of hazardous waste through their streets. Another example could be the reverse scenario, when the community wants the soils excavated and the PRPs object and want to treat on-site. A way to overcome this barrier is through informal interviews with residents.

An interview is exactly the opposite of "public information meetings," where the idea is to give out information. In these interviews, the idea is to get information regarding any local condition which may impact the community's reaction to activity at the site. One should listen to the questions that the community asks. People ask about what will affect them. They ask, "Will I die?" not, "How many people have died from exposure to X?" They ask, "How will exposures be limited?" not, "What is the level of exposure?" Actions speak louder than words. One should focus on what is happening now.

The community needs to be considered a legitimate partner when planning the remediation of a site, especially a large Superfund site. Communities not involved during the planning stages often fight agency decisions. The lines of communication must be kept open at all times. Staff who will be interacting with the public must be trained to handle not only the questions, but also the strain of contact with an angry or upset community. All information should be filtered through one contact point, if possible, to avoid conflicting statements from different sources. All information disclosed to the community should be as honest and up-to-date as possible. Trust and credibility are the best tools in risk communication; once lost, they cannot be regained.

COMMUNITY'S POINT OF VIEW

Hazardous waste is a threat to a community. The common psychological response to a threat is fear, anger and a feeling of a loss of control.

In addition, the concept of risk is different between agencies, industry and communities. There is a kind of "chemophobia" running through society; if it is natural, it must be better than if it has chemicals. We see this concept promoted endlessly in advertisements for varying products. Industry, on the other hand, is dependent on chemicals and technical processes. Agencies are comfortable with proven cleanup technologies and certain levels of residual contamination. The public does not ordinarily have an understanding of the proposed cleanup technologies and will therefore consider them a higher risk. What is unknown is considered a higher risk than what is known. This fear of the unknown is also why risk comparisons between involuntary risks (such as living near a contaminated site) and voluntary risks (such as driving or smoking) usually are not accepted by the public. People know what cigarettes can do to them, but they choose to increase their chance of cancer by smoking. Given the choice, they would not choose to increase their chance of cancer by exposure to hazardous waste at a nearby Superfund site.

Risk perception is a learned fear. Communities have a predisposition to fear through their knowledge of other communities and their experiences with toxic contamination. Note the word **toxic**. In a community's mind, the contamination is always toxic, never just hazardous. This concept is perpetuated by the media. Toxic fits better in a headline. The environmental professional is aware that a site may be contaminated with a waste considered hazardous because of its flammability or reactivity. To the affected community, it is toxic. "It could happen here" is the true legacy of Love Canal. Risks that can be associated with other events, such as Love Canal or Bhopal, India are considered a higher risk.

As a proposed facility is publicized, the community associated with the hazard becomes stigmatized. The stigma is applied both to the hazard and to the community that contains the hazard. Many times this result is due in part to fiscal impacts and issues unrelated directly to hazardous waste. Hazardous waste facilities require more public funding and support than other types of facilities. The fiscal responsibility for closure, permits, emergency funds and training emergency response personnel takes money away from other areas of the community. In addition, the money spent on a hazardous waste facility, other than direct construction costs, is often invisible to taxpayers. So when the media relates the total amount spent (i.e., the $14,000,000 hazardous waste facility in Smalltown...) it creates a twisted perception of favoritism where the community with the hazardous waste facility has more money spent on it. As the controversy escalates, the stigmatized community has a higher stake in keeping the facility out.

The community may feel victimized by both the contamination and the system that is in charge of removing it. Once again, involving the community in the decision-making process may help to keep everyone's perception of the risk within a close range.

If a community feels that it has not been involved in a decision, its members feel a loss of power over their community and a loss of control over events in their own lives. This loss of control leads to an increase in fear and anger, which can translate into action by the formation of community activist groups. This response can create a deep sense of community, which will enable the community to focus on solving the problems important to them and making their concerns heard. The activist group serves to focus the anger and use it against the feelings of powerlessness. The greatest fears in a community surround the issue of health. To be sick is feared more than being hurt, so materials that have high probability for accidents (such as explosives

or reactives) are feared less than materials that have a high probability of causing cancer.

The community's point of view focuses on the people involved with the site and what they have to lose. When the lights go out and the flyers handed out at the public meeting litter the parking lot, the agency people can go home and try to forget about the problem. However, the community feels that a silent killer is stalking them in their own homes and they have nowhere safe to go. The community feels an invasion of home and territory, especially when the exposure pathways are through the air and the water supply. A site where the exposure pathway of concern is direct contact may generate this type of emotion against the process of cleanup, rather than the contamination itself.

THE POLITICAL FACTOR

In our democratic society we are aware that we have certain rights, among them the Freedom of Speech and the Freedom of Assembly. The community may understand the risks as they have been explained and simply not agree with that position. Although most community activist groups arise out of being ignored and the need to affect the decisions made through traditional channels, there are groups and consultants that are adept at using political strategies for issues beyond the specific site. Since the community's concern usually focuses on health issues and the agency and PRP view usually focuses on the economic issues, some legitimate disagreement is inevitable.

A primary disagreement may be over zero risk. The demand for zero risk may be made for several reasons: it may be a negotiation point for a risk that seems too high; it is what the community wants, regardless of its feasibility; it may be a symptom of the intense anger generated by the site; or it may be politically motivated. When the demand for zero risk is politically motivated, the situation presents special challenges to those attempting to communicate risks to the community. This may be the one time when the strategy in public and in private may be different. During public meetings when the emotion and rhetoric run high, the best strategy is to stay open and direct. Try to arrange private or semi-private meetings where honest discussion and negotiation might be possible.

On some occasions, there may be interference from local politicians for political gain. The agencies usually follow the traditional problem-solving approach to a site; in contrast the community usually favors a more democratic approach. In the environmental arena, majority rule may not protect the minority and this has to be made clear to the community. Community education is ordinarily aimed at convincing the community, not addressing their fears. Once again, listening to the community and searching for the qualitative factors that influence them and adapting the pattern of risk communication to address specific concerns may overcome barriers to effective communication.

CONCLUSION

The keys to effective risk communication are explaining technical jargon clearly, recognizing barriers, addressing community concerns and maintaining credibility and trust. The community is going to be concerned about risk and may reject the explanations of risk offered to them. They also are likely to have concerns that are not reflected in the quantitative risk assessment. All community concerns must be acknowledged and addressed.

It is vital to understand the community's point of view and the variables affecting the site in order to avoid political pressures and high levels of controversy which may result in the disapproval of a site. Although this concept may sound like common sense, in real-life the community's concerns are often overlooked and the resulting controversy is played out in the media. Everyone involved with a Superfund site, the community, agencies and industry, wants the same thing. They all want to know what is there and how much is there and what will be done about it. Effective risk communication can pave the way for the process to focus on correcting problems rather than how data were presented.

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The NIMBY Syndrome: Environmental Failure and the Credibility Gap

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INTRODUCTION

While environmentalists and industry disagree on many issues, one thing they are certain to agree on is the growing opposition of the Not-in-My-Backyard (NIMBY) Syndrome. Government officials and industry analysts now are suggesting that the most difficult obstacles to siting hazardous waste facilities may be sociopolitical, not technical. Public opposition to new hazardous waste sites has been stiffening in recent years as citizens in communities across the country have organized politically to block permits. Will Collette, director of the Citizen's Clearinghouse for Hazardous Waste, estimates that between 1986 and 1988 the number of groups protesting toxic disposal in the U.S. more than doubled, from 1,700 to 3,650.[1] A recent story in the *New York Times* declared the NIMBY Syndrome an emerging movement and "a potent anti-development force" leading to "a paralysis in effective corporate response to marketplace incentives."[2] One specialist recently lamented, " No major anti-pollution project in at least ten years has been able to proceed without intense public opposition."[3] Moreover, there is no indication that public opposition will abate in the near future. Most of the recent poles show that the public demands for a cleaner, safer environment have increased. For example, 1988 Gallup poll showed that 84% of Americans were "very concerned" about water pollution and 73% held similar views about air pollution. Both figures represented significant increases from polls in the 1970s when fewer than half of those interviewed expressed such concerns.[4] Ironically, the resurgence of the environmental movement has occurred during a period in which the federal government has spent billions of dollars to improve methods of hazardous waste treatment, disposal and remediation, primarily through RCRA and Superfund. The current impasse over siting raises some critically important questions about the effectiveness of these government programs, and about confidence in the new regulations and new technologies. Indeed, it even raises questions about the credibility of government agencies and industry to place public health and safety above profits and politics.

THE DAYTON SURVEY

Some of these questions were addressed specifically in a recent study of a proposed hazardous waste site near Dayton, Texas, a small community about 45 miles northeast of Houston. A Florida-based company, Hunter Industrial Facilities, Inc., has proposed storing hazardous wastes in a salt dome at that location. Salt dome storage of hazardous wastes is one of only two disposal methods approved by the EPA. Through a grant awarded by the Gulf Coast Hazardous Substance Research Center, a consortium of eight universities estab-

lished in 1986 through Superfund legislation and headquartered in Beaumont, Texas, this author was able to conduct a study of community reactions to the proposed site from the earliest stages of the project. Part of the two-year study included a public opinion poll of residents in four communities (Dayton, Liberty, Huffman and Atascoctia) adjacent to the proposed site. The affected area covers the far western portion of Liberty County and the northeastern portion of Harris County. The poll was conducted in January 1990 using a scientific sample of 439 adult residents randomly drawn from telephone listings and interviewed by a research team from Lamar University. Some of the findings culled from the survey are discussed in this paper, and should be a cause of concern to corporate and government leaders.

The Dayton survey revealed a widespread belief among area residents that the federal government legislation had not improved waste management practices in recent years. Only 32% agreed with the statement "federal government legislation in recent years has dramatically improved the safety and effectiveness of hazardous waste methods and practices." A majority, 52% of the sample, disagreed with the statement and 16% said they didn't know. Substantive comments by respondents indicated doubts about the government's ability to compel strict compliance, and about industry's lack of initiative to comply in the face of increased costs. Citizens' responses did not vary significantly with level of education or income. In effect, it appears that most of the general population in the sample area were not willing to give the government a passing grade on its record.

A similar pattern emerged with regard to the perceived viability of the technology to be utilized. Sixty-six percent of the public disagreed with the statement, "The technology to ensure safe and effective disposal of hazardous wastes in salt domes has been adequately developed." Approximately 16% agreed with the statement and 18% said they didn't know. Again there was no significant variation by education or income.

Industry representatives will argue, of course, that few respondents have the knowledge of expertise to make a technical judgement. No doubt that such an objection would be correct. What the survey suggests, however, is a paucity of confidence in those segments of industry and government responsible for safe disposal of hazardous wastes. In other words, it may be less a technical issue than one of credibility and public trust. People are not often able to separate a technology from the carriers of that technology. Though some companies have better track records than others, there is a tendency for the public to lump them all together, good/bad companies and good/bad methods. Since the average citizen does not have

the requisite specialized knowledge and training to make reliable assessments of technology, he or she must be able to trust those who do. Thus, the most salient issue is credibility, and it does not appear that industry and government officials have it. This was borne out by several other items on the survey.

To test the issue of credibility, three questions were posed to community residents essentially asking them whom they would believe regarding assurances of safe hazardous waste methods of disposal. We had to consider the possibility that the citizens might refuse to believe anyone, given the frequent complaints about radical NIMBYists. However, the findings revealed that credibility was selectively imputed to one of three groups mentioned. Most sample area residents tended to trust scientists and technical experts, while distrusting industry representatives and government officials. Sixty percent of the public said they would believe assurances given to them by scientists or technical experts, while only 26% would believe government officials and even fewer, 22%, would believe industry representatives. The exact wording of the questions and the response patterns are shown in Table 1. It is worth noting that questions are identical except for the phrase identifying the source of assurances being given (industry representatives, government officials, scientists and technical experts). It should also be mentioned that they would have to be independent - not company employees - in order to gain credibility.

Table 1
Selected Items on Credibility from 1990 Dayton Survey (N=439)

	(Response in Percent)		
	agree	disagree	don't know
If INDUSTRY REPRESENTATIVES assured me that the technology to ensure a safe and effective disposal of hazardous wastes in salt domes had been developed, I think I would believe them.	22	75	3
If GOVERNMENT OFFICIALS assured me that the technology to ensure a safe and effective disposal of hazardous wastes in salt domes had been developed, I think I would believe them.	26	71	3
If SCIENTISTS AND TECHNICAL EXPERTS assured me that the technology to ensure a safe and effective disposal of hazardous wastes in salt domes had been developed, I think I would believe them.	66	31	3

THE CREDIBILITY GAP AND THE ENVIRONMENTAL FAILURE

These data may be helpful in shedding some light on the NIMBY Syndrome. If the attitudes of the population in our survey reflect the attitudes of other communities, it would appear that refusal to accept a new waste site or facility is tied to widespread distrust of waste-related industry and government agencies to safeguard public health. A credibility gap exists that thwarts the efforts of these institutions to resolve the problems of treatment and disposal. This crisis of confidence is not entirely unwarranted. Environmental studies do not show marked improvements in the quality of air and water in the U.S. over the last decade. Furthermore, new studies that may entail

data on longstanding problems have served to heighten awareness and outrage. For example, the infamous Waxman report revealed that approximately 2.4 billion pounds of toxic waste were released into the air in 1987 causing considerable adverse reaction. However, many experts concede that emissions had probably declined from a few years earlier.

While there are some notable successes in the fight against pollution, the general public impression seems to be one of environmental failure. This is strongly evidenced in the growing apprehension of the public concerning environmental problems as measured by polls. In a 1986 CBS/*New York Times* poll, 66% agreed with the statement, "Protecting the environment is so important that requirements and standards cannot be too high, and continuing environmental improvements must be made regardless of cost." The number of people agreeing with this same statement increased to 80% in 1989. Evidence of heightened public anxiety, the growth of NIMBY groups, the increased demands for a cleaner environment, and our own finding from the Dayton survey are all indicators that the characterization of environmental failure is an accurate portrayal of public perception. The theme of environmental failure is echoed throughout the polls, the electronic media, popular books, through special features in major magazines, and wherever one finds a public forum on the environment. The affects of environmental failure have been articulated in a recent book by Barry Commoner, Director of the Center for the Biology of Natural Systems at Queens College, New York. Commoner writes in *Making Peace with the Planet*[5]:

> It hardly takes a sociological survey to determine the response to (environmental) failure. It justifies the polluter's inaction and intensifies the public's frustration. It erodes the integrity of regulation and diminishes the public faith in the meaning of environmental legislation.

A social scientific analysis of the NIMBY phenomenon suggests that future resolution of the impasse will come painfully slowly since the public demonstrates little confidence in the institutions that are most directly involved in the effective disposal of hazardous wastes. A credibility gap threatens to make any efforts by government regulators of industry laborious, protracted, conflict-ridden and ultimately ineffective. However, our data suggest that independent research scientists or technical experts may play a key role in providing the public with reliable information upon which to make decisions. While the introduction of neutral scientists does not guarantee resolution, it may help the facility siting process hurdle one very important obstacle. Industry representatives and government officials may welcome this as an opportunity to reclaim public trust if and when independent studies confirm the integrity of their own claims and statements.

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Alternative Methods for Estimating Hydraulic Conductivity

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ABSTRACT

From the early 1930s until 1982, municipal, commercial and industrial wastes were deposited at a municipally operated 15-acre landfill in Maine. Following a RI/FS, a PCP contracted for consulting services to develop and implement a Remedial Action Plan (RAP). The RAP included a three-phase hydrogeologic investigation to provide site information on which to demonstrate Alternate Concentration Limits (ACLs). ACLs were to be used to determine if aquifer remediation was needed. Soil borings, monitoring well installations and groundwater sampling and analyses were used to identify chemical flow paths from the landfill to points of discharge in an adjacent lake to the south and a brook to the north. In order to estimate chemical travel times in groundwater, several Darcy-based methods were employed to estimate hydraulic conductivity (K). These calculational methods included a chemical travel time based on landfill operational history, a water balance approach supported by seepage meter measurements and, hydraulic conductivity testing. These estimates were confirmed by the results of groundwater modeling and an aquifer pumping test.

The chemical travel time estimate of K was based on a range of distances between alleged liquid chemical disposal areas at the landfill and known locations of chemical discharge to surface water. This range of distances was divided by the range of time periods when chemicals were dumped and estimated chemical arrival at groundwater discharge points. Using a miscible, nonretarding indicator chemical, the resulting range of velocities was considered representative of the average linear groundwater velocity. When combined with porosity and a known hydraulic gradient along the flow path, a range of values for K could be calculated using Darcy's Law.

The water balance estimate was developed from a groundwater surface contour map for the site and well-defined aquifer geometry. Based on estimated precipitation recharge and regional groundwater flow into the site area, flow volumes were identified. Using known depths and widths of chemical flow paths, the cross-sectional area of flow paths was determined. Knowing the gradient, area and volumetric flow rate, K was estimated.

At the south end of the site, seepage meter measurements confirmed water balance estimates. Rising head hydraulic conductivity testing performed at selected monitoring wells provided a third estimate of K within flow paths.

Three dimensional groundwater flow (and chemical transport) was simulated at the site using the Princeton Transport Code (PTC). The resulting calibrated head distribution was obtained using K values comparable to those estimated by the above methods.

Finally, a 30-hour, 115-gpm aquifer pumping test was conducted with water levels recorded at 35 monitoring wells with Hermit Data loggers. Aquifer parameter analysis using the Hantush leaky aquitard solution confirmed estimates of K obtained with the above methods. The results of these studies indicated that, for certain site settings, simple application of Darcy's law provided estimates of K that are consistent with the more rigorous (and costly) analytical estimates provided by numerical computer modeling and aquifer pumping tests.

INTRODUCTION

This paper summarizes three simple methods used to estimate K of sand and gravel aquifer materials beneath a former municipal landfill. The three methods provide comparable results with the more rigorous analyses of a three-dimensional groundwater model and are consistent with the results of a comprehensive aquifer pumping test. While local variability in stratigraphy can cause large changes in K, no substantial layering was observed in borings located within the sand and gravel chemical flow paths.

Accurate estimates of K are necessary to assess chemical migration rates and design a groundwater extraction system capable of capturing chemicals migrating from the landfill. It is believed that the methods are applicable to sites with good geologic definition (using traditional soil boring methods) and hydrogeologic understanding of groundwater flow paths (based on groundwater contour mapping), a general understanding of chemical travel times and site area water balances.

HYDROGEOLOGIC SETTING

The geology of the site consists of a deep (greater than 150 feet below ground surface) bedrock trough filled with morainal sand and gravel. Uniform fine sand overlies the sand and gravel which, in turn, is overlain by a confining glacial marine clay silt. An extensive monitoring well network (more than 70 monitoring well and piezometer screens) provides a detailed description of both groundwater flow conditions and the chemical distribution on a quarterly basis.

Groundwater flows from areas of high groundwater potential in silty soils immediately west of the landfill to areas of lower groundwater potential in sand and gravel soils that occupy the landfill and stretch southward to the lake (southern flow path) and northward toward the brook (northern flow path) (Fig. 1). Most of the groundwater flowing through the site is believed to originate from precipitation falling on the topographic high along and east of the road. A groundwater divide exists beneath the northern portion of the landfill between MW-106 and MW-108.

Some lateral inflow from the brook drainage basin to the northern site area is expected to occur north of MW-7A through very fine sand and silt soils present along the road (western site modeling boundary). South of MW-7A, a layer of saturated silt and very fine sand, along with higher topography, is interpreted to be a (second) groundwater divide limiting the amount of lateral (i.e., west to east) groundwater

inflow through soils into the site area. Lateral inflow to the site area through the upper fractured portion of the bedrock is interpreted to occur along the entire length of the western boundary.

Landfill chemicals are consistently detected in monitoring wells along the southern and northern flow paths (Fig. 2). The flow paths follow consistent patterns of decreasing hydraulic head and are bounded on either side by higher elevation groundwater. The southern flow path discharges to the lake shore in an area approximately 300 feet by 180 feet. The northern flow path discharges to the brook along an approximate 500 foot reach where the confining clay silt is absent. Where the clay silt is present, a small portion (10%) of the northern flow path discharges upward through the clay silt to the brook.

HYDRAULIC CONDUCTIVITY ESTIMATES

Chemical Travel Times

Groundwater velocities for the southern and northern flow paths were estimated based on landfill operational history (known periods of waste disposal) and distances to known groundwater discharge areas. Tables 1 and 2 list the range of calculated groundwater velocities for the southern and northern flow paths, respectively. Based on this distribution, the most frequently calculated groundwater velocities for the southern and northern flow paths are believed to be the most representative of actual groundwater velocities. Because the predominant site chemical (dimethylformamide or DMF) is infinitely soluble, has low volatility and has a low affinity for organic carbon, no substantial attenuation of DMF is believed to be occurring at the site.

The range of travel times for the southern flow path was selected based on the following site history:

- The maximum time of chemical travel would be 30 years from the early 1950s (the earliest time chemical wastes could have been deposited based on manufacturing plant operational history) to 1980, when residents complained of occasional odors in private well water.

- The minimum time of chemical travel would be five years, based on chemical wastes allegedly disposed of at the southern end of the landfill in 1975 when the plant closed and complaints of occasional odors in private well water in 1980.

The range of distances used for the southern flow path is a minimum of 800 feet (from MW-5A at the southern edge of the landfill to the discharge area in the lake), to a maximum of 1,700 feet from an interpreted groundwater divide near Area B where chemical wastes allegedly were deposited (Fig. 1). Using these ranges with the distances shown in Table 1, the most frequently calculated groundwater velocity for the southern flow path is 60 ft/yr.

The range of travel times used for the northern flow path was based on the following site history:

- The maximum time for chemical transport from the landfill to the groundwater discharge point in the brook was 30 years (i.e., early 1950s to 1983 when chemicals were first detected in the brook).
- The minimum time for chemical travel was eight years (1975 to 1983 when chemical analyses detected waste constituents at Hoyt Brook).

The actual travel time is expected to lie within but probably not at the extremes of this range.

The range of distances over which chemical transport occurred during this period is based on the following site conditions:

- Chemical waste disposal is known to have occurred in Area H (Fig. 1), a distance of 1,400 feet from the brook discharge area. This is the minimum length of travel.
- The maximum distance for chemical transport is estimated to be 2,400 feet from Area B (Fig. 1) which is where chemicals were allegedly deposited and which is near an interpreted groundwater divide between the northern and southern flow paths.

Based on data in Table 2, the most frequently calculated groundwater velocity for the northern flow path is 80 ft/yr.
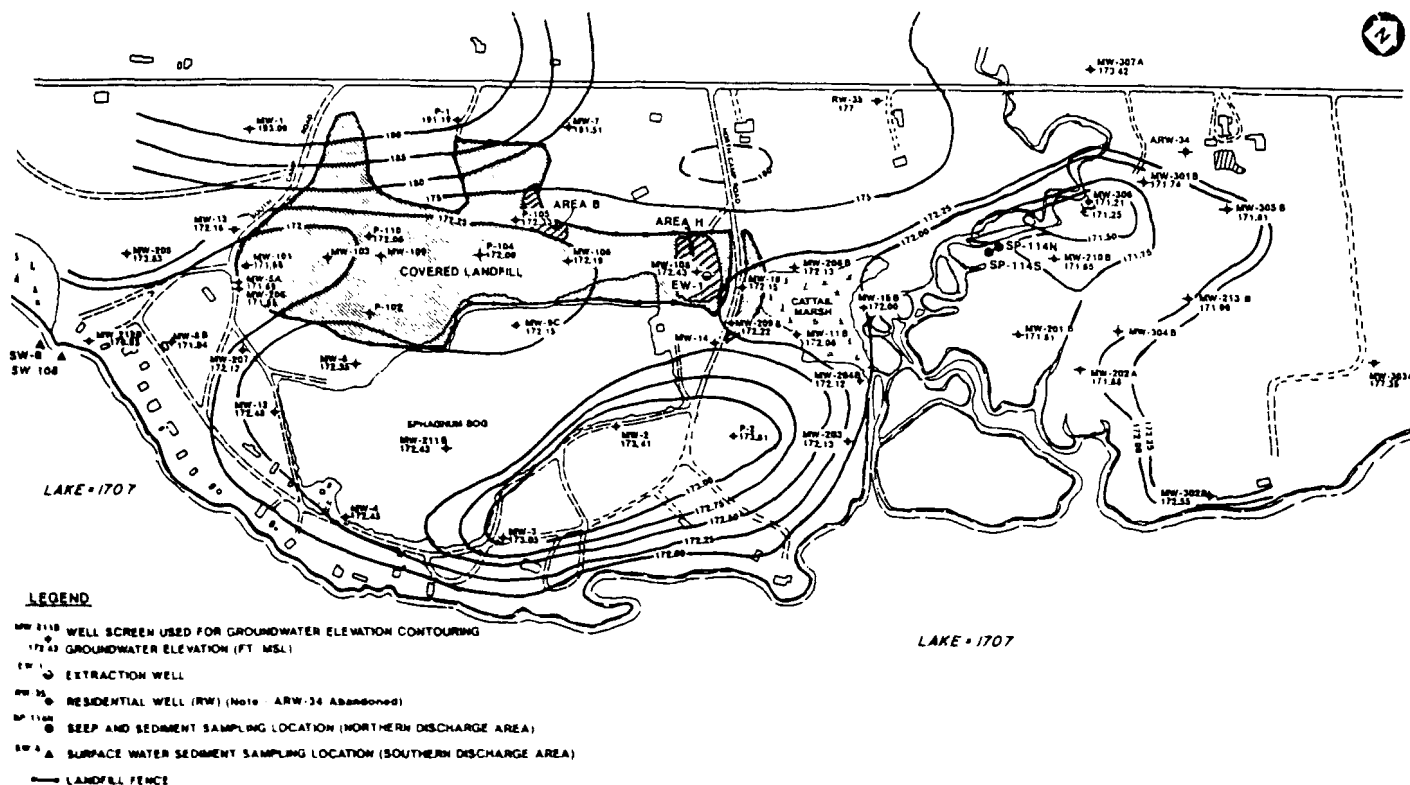

Figure 1
Interpretive Groundwater Surface

Table 1
Calculated Southern Flow Path Groundwater Velocities

DISTANCE (FEET)	TIME (YEARS)	VELOCITY (FEET/YEAR)
800	30	27
	25	32
	20	40
	15	53
	10	80
	5	160
900	30	30
	25	36
	20	45
	15	60
	10	90
	5	180
1000	30	33
	25	40
	20	50
	15	67
	10	100
	5	200
1100	30	37
	25	44
	20	55
	15	73
	10	110
	5	220
1200	30	40
	25	48
	20	60
	15	80
	10	120
	5	240
1300	30	43
	25	52
	20	65
	15	87
	10	130
	5	260
1400	30	47
	25	56
	20	70
	15	93
	10	140
	5	280
1500	30	50
	25	60
	20	75
	15	100
	10	150
	5	300
1600	30	53
	25	64
	20	80
	15	107
	10	160
	5	320
1700	30	57
	25	68
	20	85
	15	113
	10	170
	5	340

RANGES OF CALCULATED VELOCITIES (FEET/YEAR)			FREQUENCY OF CALCULATED VELOCITIES
0	to	20	0
20	to	40	9
40	to	60	16
60	to	80	10
80	to	100	6
100	to	120	4
120	to	140	2
140	to	160	3
160	to	180	2
180	to	200	1
200	to	220	1
220	to	240	1
240	to	260	1
260	to	280	1
280	to	300	1
300	to	320	1
320	to	340	1
340	to	360	0
			0

NOTES:

1. Distances are based on lengths of flow lines originating from possible locations of chemical waste disposal at the landfill and discharging to the lake at SW-8.
2. Frequency of velocity column indicates the number of calculated velocities that are equal to or less than the corresponding velocity range, but greater than the previous velocity range.

Table 2
Calculated Northern Flow Path Groundwater Velocities

DISTANCE (FEET)	TIME (YEARS)	VELOCITY (FEET/YEAR)
1400	30	47
	25	56
	20	70
	15	93
	10	140
	5	280
1600	30	53
	25	64
	20	80
	15	107
	10	160
	5	320
1800	30	60
	25	72
	20	90
	15	120
	10	180
	5	360
2000	30	67
	25	80
	20	100
	15	133
	10	200
	5	400
2200	30	73
	25	88
	20	110
	15	147
	10	220
	5	440
2400	30	80
	25	96
	20	120
	15	160
	10	240
	5	480

RANGES OF CALCULATED VELOCITIES (FEET/YEAR)			FREQUENCY OF CALCULATED VELOCITIES
0	to	20	0
20	to	40	0
40	to	60	0
60	to	80	4
80	to	100	8
100	to	120	5
120	to	140	4
140	to	160	2
160	to	180	3
180	to	200	1
200	to	220	1
220	to	240	1
240	to	260	1
260	to	280	0
280	to	300	1
300	to	320	0
320	to	340	1
340	to	360	0
360	to	380	1
380	to	400	0
400	to	420	1
420	to	440	0
440	to	460	1
460	to	480	0
480	to	500	1
			0

NOTES:

1. Distances are based on lengths of flow lines originating from possible locations of chemical waste disposal at the landfill and discharging to Hoyt Brook at SP-114.
2. Frequency of velocity column indicates the number of calculated velocities that are equal to or less than the corresponding velocity range, but greater than the previous velocity range.

The following values were used for each flow path:

South	North
$V = 60$ ft/yr $= 0.16$ ft/day	$V = 80$ ft/yr $= 0.22$ ft/day
$n = 0.25$	$n = 0.25$
$i = 0.0017$	$i = 0.0015$
$K = 24$ ft/day (8.5×10^{-3} cm/sec)	$K = 37$ ft/day (1.3×10^{-2} cm/sec)

Water Balance

The water balance method of estimating K for each flow path relies on estimates of volumetric groundwater inflow rates to the southern and northern flow paths and a knowledge of the cross-sectional areas through which groundwater flows out of each flow path. Groundwater that naturally flows into the aquifer under the landfill comes primarily from precipitation recharge and, to a much lesser extent, from groundwater inflow from the west in bedrock. The basis for calculating flow rates from each of the two inflow sources is the groundwater surface contour map for the site. The map is used to measure the land area over which precipitation would infiltrate the landfill cover system and undisturbed soil and, in turn, percolate down to the groundwater system beneath the landfill (Fig. 3). Only areas within the landfill groundwater shed were included in estimating precipitation recharge. For each flow path, the area of the landfill cover system was given a groundwater recharge rate of 3 in/yr which was based on the design specification and simulation with the Hydrologic Evaluation of Landfill Performance (HELP) model. Uncapped areas were given a recharge of 14 in/yr based on discussion with the local watershed district and water balances calculated for the site. The cross-sectional areas of each flow path were determined from geologic profiles in Figure 4.

Using these calculated velocities, the average hydraulic gradient from the landfill (MW-5A) to the discharge area at the lakeshore (SW-8, near MW-212) and from the landfill (MW-10B) to the brook (at SP-114) in the north was calculated from quarterly water level data for the period from May 1988 to May 1990. Using an effective porosity value of 0.25, a hydraulic conductivity was calculated for each flow path by rearranging Darcy's law as follows:

$$V = \frac{Ki}{n} \; ; \text{ then } K = \frac{n}{i} \qquad \text{where} \tag{1}$$

V = average linear groundwater velocity (ft/day)
K = hydraulic conductivity (ft/day)
i = hydraulic gradient in the direction of flow (ft/ft)
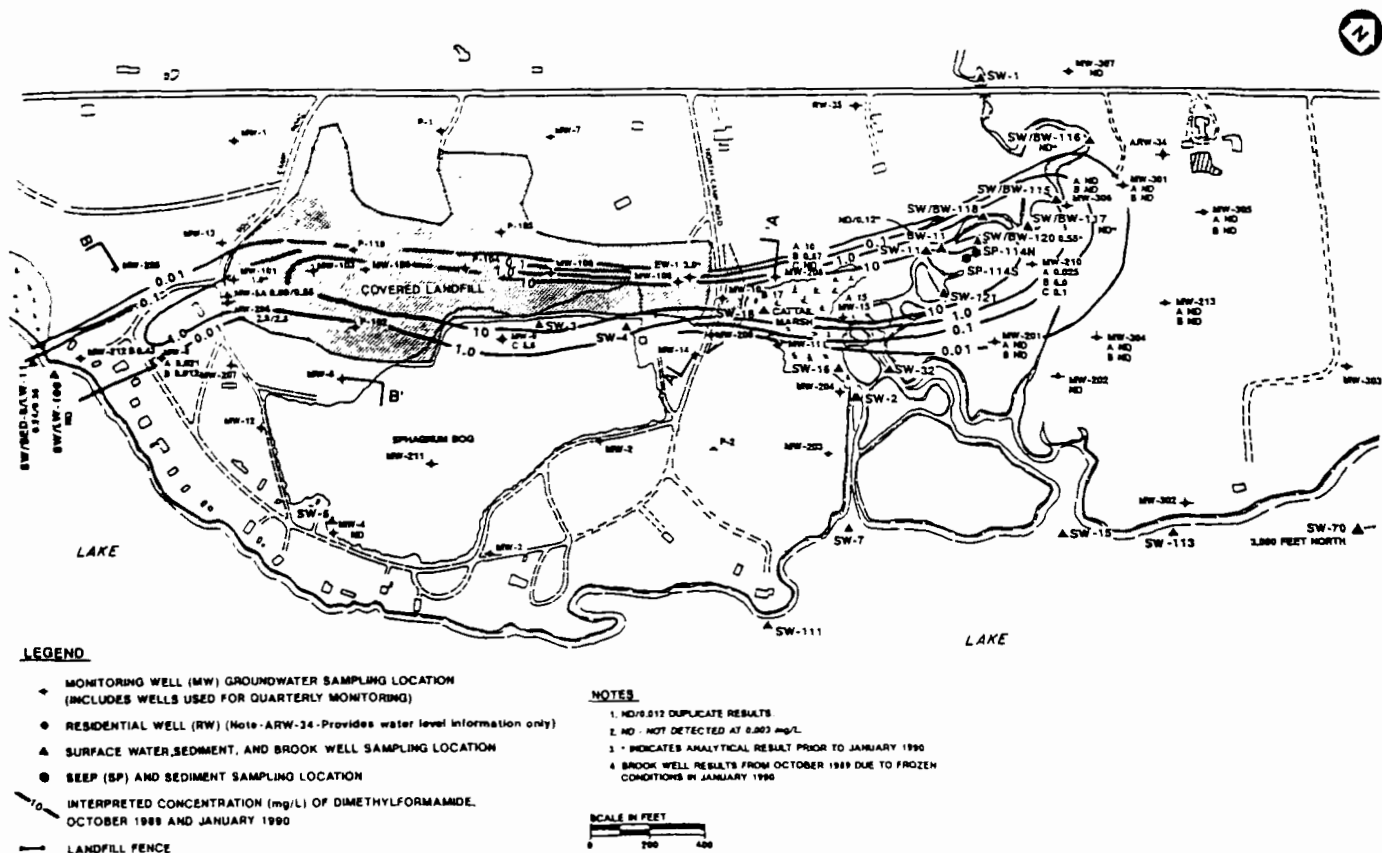n = porosity (dimensionless)

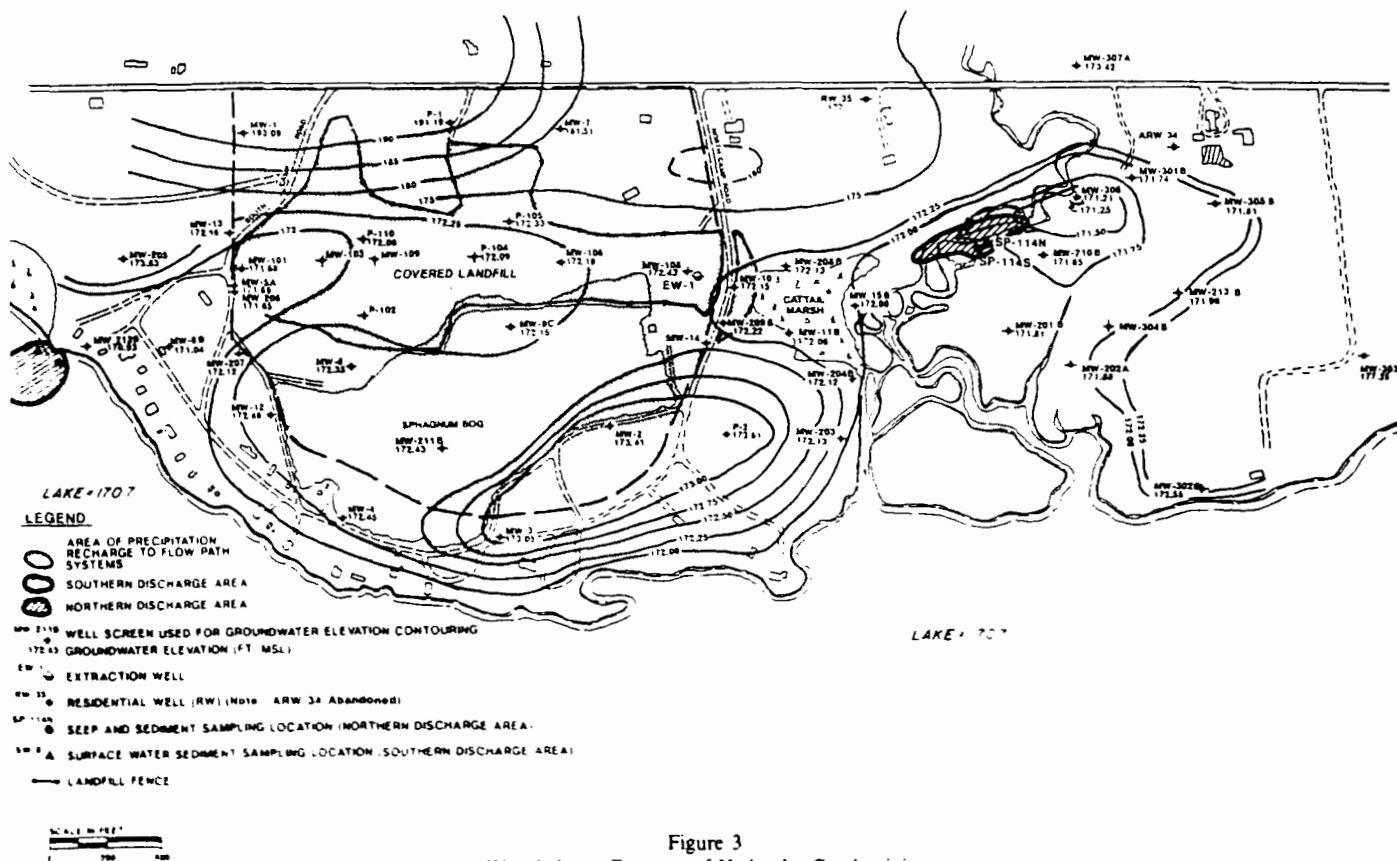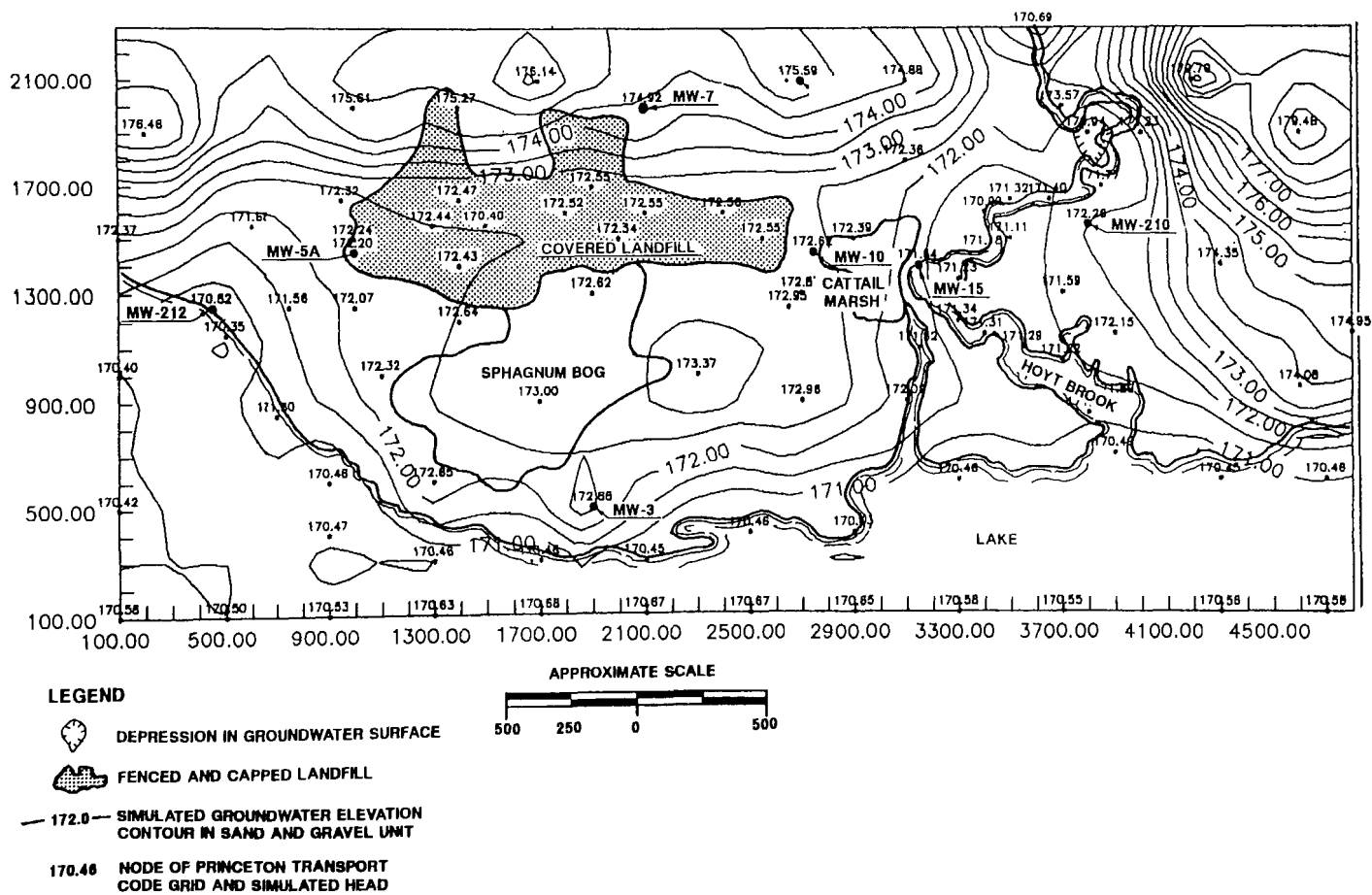Figure 2
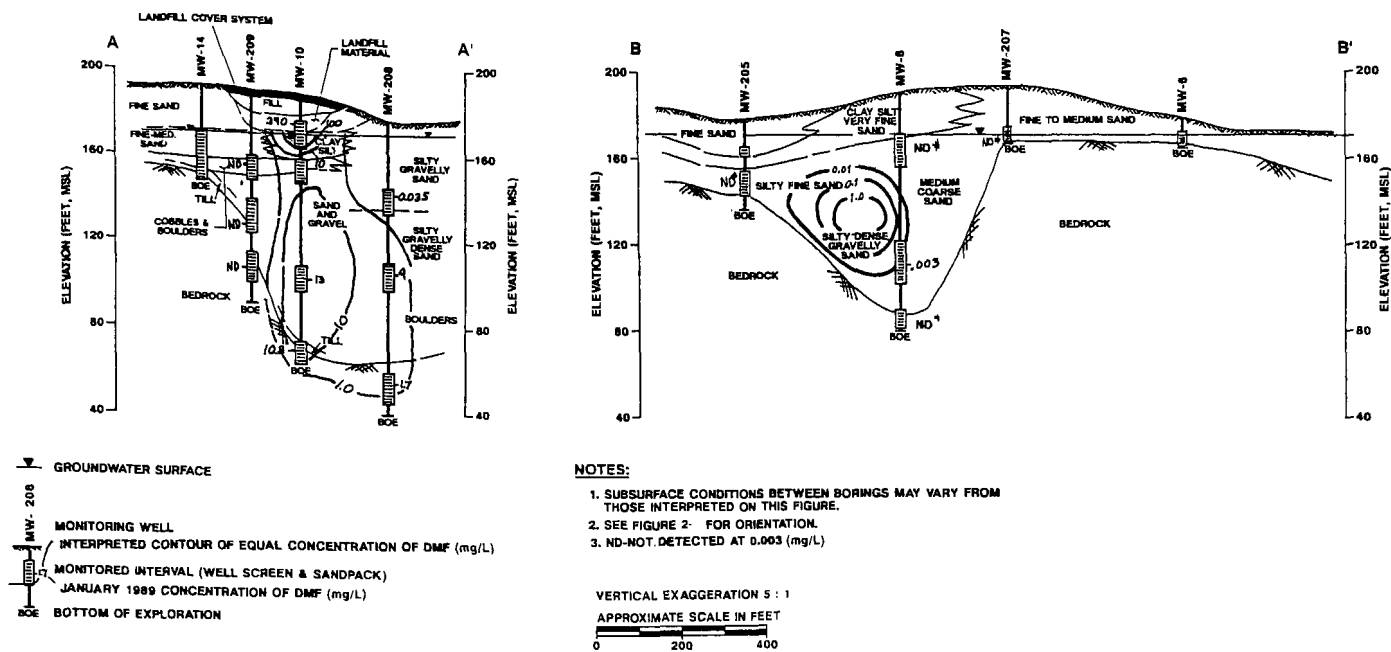Dimethylformamide Distribution in Groundwater

Figure 3
Waterbalance Estimate of Hydraulic Conductivity

Figure 4
Geological and Dimethylformamide Distribution
Profiles Across Northern and Southern Flow Paths

LEGEND

⬡ DEPRESSION IN GROUNDWATER SURFACE

▨ FENCED AND CAPPED LANDFILL

— 172.0 — SIMULATED GROUNDWATER ELEVATION
CONTOUR IN SAND AND GRAVEL UNIT

170.46 NODE OF PRINCETON TRANSPORT
CODE GRID AND SIMULATED HEAD

NOTE:
SIMULATION FROM PRINCETON TRANSPORT
CODE CALIBRATION RUN 0224R3

Figure 5
Simulated Sand and Gravel Head Contours

No groundwater inflow from the west in soils is expected to occur based on groundwater surface mapping at the site, which indicates the road approximates a groundwater divide. Larger site area mapping supports this interpretation. To estimate bedrock inflows from the west, a bedrock thickness of 20 feet was assumed to contribute groundwater from the west to the landfill flow path systems. The width of the zone along the road and the hydraulic gradient were based on the groundwater surface contour map (Fig. 1), which also indicates the proportion of inflow to the southern and northern flow paths (i.e., 70% to the south and 30% to the north). Bedrock K was based on the geometric mean of bedrock permeabilities measured sitewide (i.e., falling-head and packer permeability testing), and on the results of groundwater modeling.

Using Darcy's Law, K may be calculated knowing the volumetric flowrate, hydraulic gradient and area through which groundwater flows, as follows:

$$Q = KiA \qquad (2)$$

and, rearranging, $K = \dfrac{Q}{iA}$

where:
Q = volumetric flow rate (ft³/day)
K = hydraulic conductivity (ft/day)
A = area through which flow occurs (ft²)
i = hydraulic gradient (ft/ft)

The following values were used for each flow path:

South	North
Q = 6,300 ft³/day	Q = 3,000 ft³/day
i = 0.0017	i = 0.0015 ft/ft
A = 27,000 ft²	A = 52,000 ft²
K = 140 ft/day (4.9x10⁻² cm/sec)	K = 38 ft/day (1.4x10⁻² cm/sec)

Results of direct measurement of seepage flux (with seepage meters) into the lake at the southern discharge area were consistent with the volumetric flowrate Q calculated for the southern flow path system.

Hydraulic Conductivity Testing

The results of rising-head and pressure (packer) testing are presented in Table 3. Hydraulic conductivity values from rising-head test data were calculated using AQTESOLV Software.[1] Based on results of testing, K values for the soil units in which well screens are located were estimated to range from 0.28 to 280 ft/day (9.8x10⁻⁵ to 1x10⁻¹ cm/sec). Values estimated at well screens placed in bedrock ranged from less than 0.00037 to 57 ft/day (1.3x10⁻⁷ to 2.0x10⁻² cm/sec).

Of primary interest are K values measured at well screens within the southern and northern chemical flow paths. Based on a review of the chemical distribution in groundwater in the southern flow path, we concluded that MW-5A, MW-8B and MW-212B monitor groundwater within sandy soils. The geometric mean of K values measured at MW-8B and MW-212B is 24 ft/day (8.5x10⁻³ cm/sec). (No data are currently available for MW-5A.) Geometric mean is used to average hydraulic conductivity over a given area because horizontal values tend to be lognormally distributed.[2] A value of greater than 170 ft/day (6.1x10⁻² cm/sec) was calculated for MW-8C, which is screened in somewhat coarser sand than MW-8B. This estimate of 170 ft/day is considered more representative of K in the southern flow path, considering: (1) the coarse texture of soils present at MW-212 and MW-8, (2) the general tendency for single well K tests in soil to underestimate formation K, (3) the results of other methods of K estimates described above, and (4) the results of the aquifer pumping test.

In the northern flow path, well screens that monitor the sand and gravel include MW-10B, MW-208B,C, MW-15A, MW-210B,C and MW-306B. The geometric mean of calculated values for these well screens is 48 ft/day (1.7x10⁻² cm/sec). (No data are currently available for MW-15A.) This mean value is consistent with values calculated for other wells north of the landfill.

Table 3
Permeability and Packer
Testing Results

WELL	ELEVATIONS (ft MSL)			CALCULATED PERMEABILITY (cm/sec)			OPEN HOLE FALLING-HEAD TEST
	GROUND	TOP OF SANDPACK	BOTTOM OF SANDPACK	RISING-HEAD TEST	TEST ZONE ELEVATION (ft MSL)	PACKER TEST VALUE	
MW-2A	179.8	172.8	158.3	3.0E-04			
MW-4A	173.7	168.7	154.2	3.3E-03			
MW-8A	191.5	87.5	80.0	3.9E-04 (9.7E-04)			
MW-8B	191.5	116.5	96.5	6.8E-04 (7.2E-04)			
MW-8C	191.5	171.5	151.5	6.1E-02			
MW-9B	173.0	60.0	55.0	9.8E-05			
MW-9C	172.8	129.8	112.8	5.0E-03			
MW-10B	192.7	108.5	99.0	4.5E-02			
MW-10C	192.8	173.0	166.0	1.1E-04			
MW-10D	193.5	160.5	148.5	3.6E-03			
MW-201A	171.0	39.0	26.0	1.1E-03			
MW-201B	172.3	122.3	107.3	1.5E-02			
MW-202A	171.4	131.4	108.9	3.0E-03			
MW-203A	172.0	156.0	148.0		73-91	2.0E-06	
					84-91	1.0E-06	
MW-206A	202.0	162.6	147.0	6.0E-04	164-159	2.0E-04	
					159-154	*	
					154-149	6.0E-04	
MW-208A	175.0	57.0	45.0	4.4E-03	58-53	7.0E-06	
					54-49	1.0E-03	
					50-45	7.0E-06	
					46-41	*	
MW-208B	174.1	106.6	94.1	8.0E-03			
MW-208C	174.0	146.0	134.0	2.4E-03			
MW-209A	196.2	121.2	106.2		115.1-110.1	8.0E-05	
					107-102	1.0E-05	
					116.2-96.2		4.0E-04
MW-209B	196.0	146.0	133.5	5.0E-03			
MW-210A	171.3	61.8	36.3	2.2E-03			
MW-210B	171.2	61.7	36.2	1.1E-02			
MW-210C	171.2	140.2	126.2	5.4E-02			
MW-211A	173.5	98.5	85.5		101-105	8.0E-06	
MW-211B	173.0	153.0	139.0		148-146		
MW-212A	174.4	59.4	47.4		58.4-53.4	3.0E-05	
					54.3-41.1	*	
MW-212B	174.8	113.3	100.3	1.0E-01			
MW-212C	175.2	152.2	140.2	9.8E-03			
MW-213A	180.6	93.6	51.6	7.2E-05	39.6-84.6	3.0E-06	
					77.3-72.3	3.0E-06	
					84-73	*	
					90.6-80.6		6.0E-04
					90.6-85.6		3.0E-04
MW-213B	179.6	141.6	129.6	9.1E-04	90-110		8.0E-05
P-1	204.1			2.0E-04			
MW-301A	179.9	135.45	128.45		126.80-120.95	1.3E-07	
					130.80-124.95	5.1E-06	
					134.80-128.95	4.1E-06	
					138.80-132.95		
MW-301B	179.6	154.90	142.90	2.0E-02			
MW-302A	179.3	153.29	144.79		159.59-145.79	2.0E-02	
					157.39-151.59	*	
MW-302B	179.83	172.83	159.83	5.5E-04			
MW-303A	200.00	177.30	159.40		166.45-160.60	*	
					170.45-164.60	*	
					174.45-168.60	*	
					178.45-172.60	*	
MW-304A	176.48	132.48	114.98		126.28-120.48	*	
					130.28-124.48	*	
					134.28-128.48	*	
MW-304B	176.31	149.31	129.81				
MW-305A	171.07	136.07	123.07		114.87-107.07	*	
					120.57-114.77	*	
MW-305B	176.33	155.33	136.33	2.5E-02			
MW-306A	171.51	119.01	113.11		121.71-115.91	4.0E-03	
					121.01-115.91	3.0E-03	
MW-306B		164.25	151.55	4.6E-02			

NOTES
1. Elevations of well installations based on survey by E.C. Jordan Co., May 1988, and well construction logs
2. Data collected by E.C. Jordan Co. in 1984, 1987, and 1988.
* Tested zone would not accept measurable flow of water

Groundwater Model

A three-layer groundwater flow and transport model was configured representing the bedrock (Layer 1), sand and gravel (Layer 2) and clay silt/fine sand (Layer 3) geology present at the site. The primary interest was in calibrating the Layer 2 (sand and gravel) heads to those observed at the site. To achieve the best steady-state match of computed and observed heads (Fig. 5), K in the southern flow path was adjusted to 175 ft/day (6.2x10⁻² cm/sec) and in the northern flow path was adjusted to 50 ft/day (1.8x10⁻² cm/sec). Simulation of the aquifer pumping test with the model indicated good correlation of observed and simulated heads at the end of pumping (Fig. 6) validating this portion of the model.
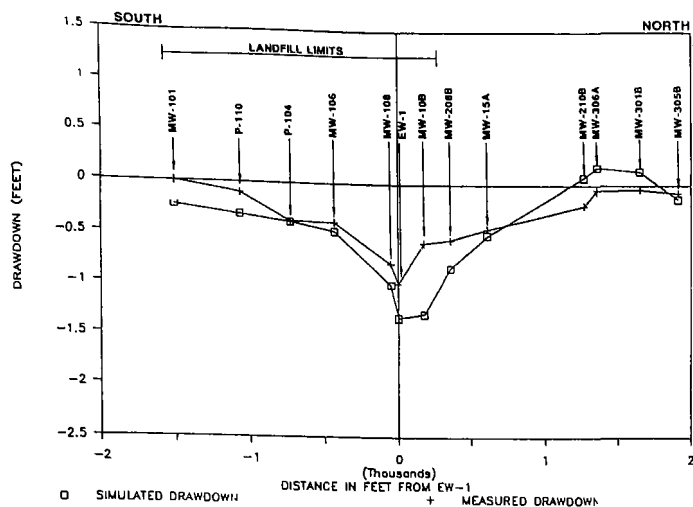
Figure 6
Measured and Simulated Drawdown Aquifer Pumping Test

Aquifer Pumping Test

Based on results of the aquifer pumping test, the geometric mean K was calculated from transmissivity (T) estimates for well screens within the southern and northern flow paths by dividing T by the aquifer thickness. These values were 140 ft/day (4.8×10^{-2} cm/sec) and 80 ft/day (2.8×10^{-2} cm/sec) for the southern and northern flow paths, respectively. Because pumping tests generally provide the most accurate measurements of bulk aquifer parameters and the pumping test values are comparable to the range of values calculated using the other methods, values derived from the pumping test are believed most representative of the actual flow path K.

Hydraulic conductivities and groundwater flowrates (assuming a porosity of 0.25 and a hydraulic gradient of 0.0017 for the south and 0.0015 for the north) estimated using the five methods described are summarized in Table 4.

Table 4
Permeability Estimates

| METHOD | SOUTHERN FLOWPATH | | | NORTHERN FLOWPATH | | |
| | PERMEABILITY | | GROUNDWATER VELOCITY | PERMEABILITY | | GROUNDWATER VELOCITY |
	cm/sec	ft/day	ft/yr	cm/sec	ft/day	ft/yr
Geometric Mean of Well Screens with Flowpath	8.5×10^{-3}	24	60	1.7×10^{-2}	48	110
Landfill Operational History	8.5×10^{-3}	24	60	1.3×10^{-2}	37	81
Water Balance	4.9×10^{-2}	140	350	1.4×10^{-2}	38	83
Groundwater Model	6.4×10^{-2}	180	450	1.8×10^{-2}	50	110
Aquifer Pumping Test	4.9×10^{-2}	140	350	2.8×10^{-2}	80	80

NOTES: cm/sec - centimeters per second
ft/day feet per day
ft/yr - feet per year

Groundwater velocities are calculated based on horizontal hydraulic gradients of 0.0017 ft/ft for the southern flowpath and 0.0015 ft/ft for the northern flowpath and a porosity of 0.25 (for both flowpaths). Gradients are the two-year arithmetic mean for the period May 1988 to May 1990.

CONCLUSIONS

Considering site histories of waste disposal and discharge, fluid mass balance of annual inflows and outflows from a site area and traditional hydraulic conductivity testing, simple Darcy-based groundwater flow calculations may be used to accurately estimate K of chemical groundwater flow path systems. Providing site hydrogeology does not indicate a highly stratified, nonuniform subsurface and the chemical distribution is well defined, estimates of K within a factor of 2 or 3 of calibrated groundwater model and pumping test derived values were obtained. Given the often high cost and effort associated with aquifer pumping tests at Superfund sites (e.g., considering water storage and treatment requirements), the alternative methods for estimating K presented herein are believed to be relatively accurate, appropriate and cost-effective.

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Use of Groundwater Modeling During Superfund Cleanup

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ABSTRACT

Numerical modeling for both groundwater flow and contaminant transport predictions has long been used during RI/FS at federal or state Superfund sites. The need for accurate predictive modeling does not end when the selection of the remedial alternatives is complete; rather, it becomes a necessary tool to design the remedial system, to assess the continuing applicability of the remedial design, to determine risks associated with remediation and to predict changes in the remedial approach that may become necessary through time.

At the Seymour site in Indiana, groundwater flow and transport modeling were used to help design the remedial action which consists of pumping-and-treating, a soil vapor extraction system, bioremediation of contaminated soils and a low permeability cap placed over the 13-acre site. The soils and groundwater are contaminated with a mixture of approximately 10 major contaminants with an additional 25 minor constituents. Because the compounds have different affinities for the aquifer materials, the vertical and horizontal distributions of chemicals in the groundwater change with distance from the source. Since the original pump-and-treat system was specified, after the FS was prepared, the hydraulic capture and treatment parameters have had to be modified because of changes in the plume configuration and the types of contaminants being extracted. A new three-dimensional model was constructed to predict the number and pumpage of extraction wells and to specify the final design of the groundwater treatment system. The model will continue to be used to refine the treatment process as the concentrations of various chemical constituents change during remediation. The model will also be used to optimize the extraction well flowrates so that the cleanup goals will be achieved within the specified time period.

Part of the groundwater treatment system consists of an air stripper to remove the changing mixture of VOCs from the groundwater. The stripper emissions are vented to the atmosphere in such a manner that the 1×10^{-6} excess cancer risk will not be exceeded at the site's nearest receptor. The groundwater model will, therefore, continue to be used over the entire period of remediation to predict concentrations emanating from the air stripper so that a risk assessment may be performed prior to the actual emission. The pumping system will be optimized based on the results of the risk assessment so that the air stripper emissions when added to the vapor extraction system emissions will not exceed the 1×10^{6} cancer risk.

INTRODUCTION

The purpose of this paper is to provide a case study example of the need for this practical approach to modeling activities. The case study is based on our experience with the remediation of the Seymour site in Indiana, one of the first sites to be placed on the NPL and also one of the first sites to reach the remediation stage. This paper will present the types of design applications of a numerical flow and transport model that were performed after the ROD was issued in response to changes in the understanding of the site geology and changes in the size of the area of concern surrounding the site.

DESCRIPTION OF THE SEYMOUR SITE

History

The Seymour site is a 13-acre facility that was formerly occupied by Seymour Recycling Corporation which recovered solvents and other organic products from industrial wastes. In 1980, the facility was shut down by the U.S. EPA due to releases of contaminants into surface water and the air and due to a series of explosions that occurred at the site.

Many different chemicals were handled at the Seymour site, including 1,2 dichloroethene, trichloroethene, tetrachloroethene, as well as tetrahydrofuran, acetone, phenol, benzoic acid, benzene, toluene, 1,4-dioxane, chloroethane and various alcohols. Considerable quantities of the liquid contaminants have migrated to the subsurface where they now form portions of a plume in the aquifer beneath and near the site.

In 1980, the U.S. EPA removed stored drums and tanks from the site and excavated approximately one foot of surface materials. These materials were replaced by a low permeability cap covering approximately 75% of the site. From 1984 to 1986, the U.S. EPA conducted a RI at the site and in 1986 the FS and the ROD were also issued. The recommended alternative in the ROD was modified during Consent Decree negotiations with the PRPs involved with the site and in 1988 construction began on the remedial facilities. The cleanup measures include a pumping-and-treatment system (initial plume stabilizing and long-term), a soil vapor extraction system, in situ bioremediation of contaminated soils and a low permeability, RCRA-type cap placed over the 13-acre site. A schematic of the site and its environs is shown in Figure 1. The plume as it was known in 1985 is shown in Figure 2.

Hydrogeology

The Seymour site is underlain by various facies of the Atherton Formation. A cross section of the geology is shown in Figure 3. Above the shale bedrock, which dips to the southeast, lies a 10 to 20 foot thick coarse sand and gravel layer known as the Deep Aquifer. This layer was probably deposited by fluvial action and it increases in thickness towards the southeast. Towards the northwest, the Deep Aquifer thins out until it is replaced by different glacio-fluvial deposits associated with the White River Flood Plain. The groundwater flows to the south-southeast in the Deep Aquifer and is heavily influenced by the pumping activities of nearby supply wells.
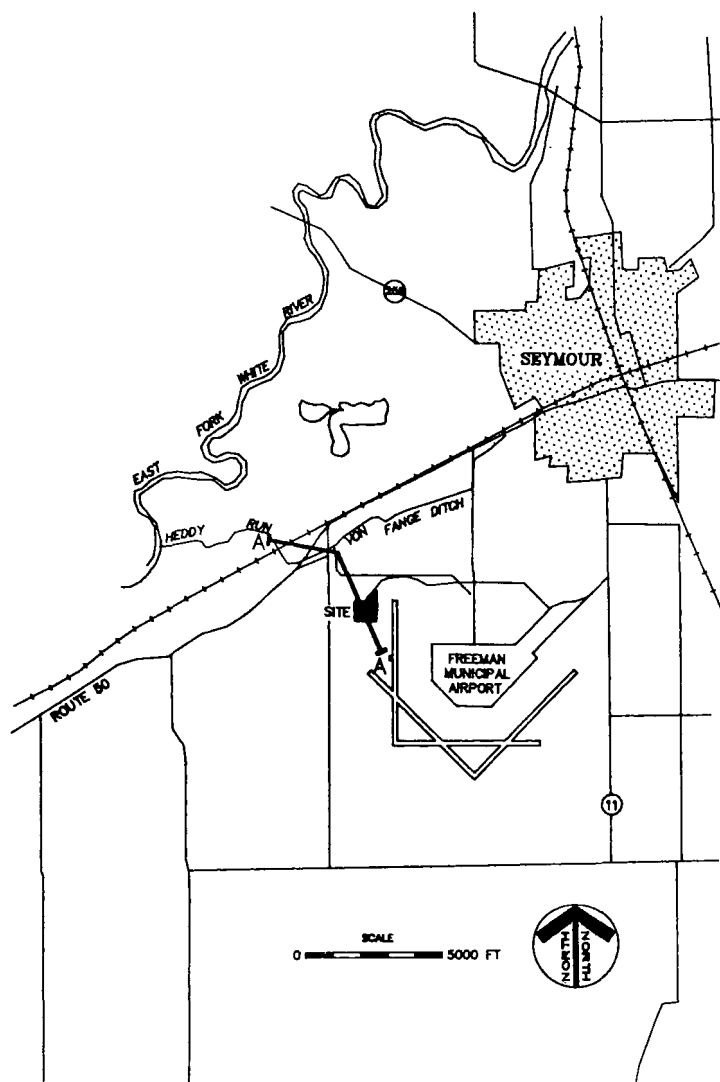
Figure 1
Site Location

Above the Deep Aquifer lies a lower permeability lacustrine deposit known as the confining layer. This layer is from 5 to 35 feet thick, acts as a confining unit to the Deep Aquifer and also thins out to the northwest where it is replaced by the White River Flood Plain Deposits.

Above the confining layer are located glacio-fluvial and eolian deposits known as the Shallow Aquifer. These are unconfined and finer grained than the Deep Aquifer and are similar to the White River Deposits into which they grade towards the northwest. In the vicinity of the site, the shallow aquifer is from 20 to 35 feet thick and it increases in thickness up to 60 feet towards the northwest. The groundwater flows north and west towards the White River in the Shallow Aquifer.

The White River Deposits were previously not known to be significantly different from the configuration of the aquifers to the south. However, recent geologic borings in this area have shown medium to coarse sands throughout the 60-foot thickness of the deposits without any indication of layering or lower permeability units. These changes have had to be incorporated into the flow model as will be described below.

Distribution of Contaminants

The major portion of the contaminants is located in a plume in the shallow aquifer as shown in Figure 4. Note that a change in gradient, which is caused by a change in the permeability of the deposits, occurs at the contact between the Shallow Aquifer and the White River Deposits. The plume shows evidence of this change by taking a sharp bend to the west at the contact.

In its movement north and west, the plume has been separated into its constituents according to the retardation factor of each chemical. This separation process has resulted in the leading portions of the plume being composed predominantly of 1,4-dioxane and several alcohols. Tetrahydrofuran occurs along with 1,4-dioxane closer to the site and contaminants such as chloroethane and the less mobile compounds like benzene and toluene, occur together at increasing concentrations closer to the site.

The plume of contaminants has also been sinking as it moves north and west. Cluster wells show that the plume occupies the upper portions of the Shallow Aquifer near the site and gradually sinks to approximately 60 feet (to the top of the bedrock) in the White River Deposits.

FLOW AND TRANSPORT MODELING

The knowledge of the geology of the site was limited during the FS and the White River Flood Plain formation was not known. At that time, a three-dimensional finite difference model was constructed and used to evaluate various alternative pumping scenarios. This process resulted in selection of the U.S. EPA's preferred alternative which was modified during the Consent Decree negotiations. The model and pumping system proved to be inadequate when later data showed that the plume was larger than had been thought and that significant changes in geology occurred along the plume's migration route.

Model Construction and Calibration

A new three-dimensional finite difference model was constructed in 1989 in response to the changed conditions at the site. This new model was made much larger than the model in the FS and included the changes in geology that had been recently observed.

Groundwater flow at the Seymour site was modeled with the USGS Modular Three-Dimensional Finite-Difference Groundwater Flow Code, also known as MODFLOW. MODFLOW is well-documented, publicly available and generally accepted within the scientific community.

Model Discretization

As shown in Figure 5, the model covers the Seymour site and a large amount of the surrounding area. The model grid covers 29 mi^2 around the Seymour site with an east-west dimension of 29,000 ft and a north-south dimension of 28,000 ft. The model is much larger than the area of interest in order to incorporate regional groundwater flow effects. The model boundaries extend to the topographic highs located south and west and to the East Fork of the White River to the north of the site. The eastern boundary of the model was planned to extend past the cone of depression caused by the City of Seymour's pumping wells located approximately 2,500 feet west of the site.

The maximum cell dimension in the model is 1,600 ft. These large cells were placed away from the areas of interest near the site, such as in the extreme eastern and western areas. Finer grid spacings were used near the location of the Seymour site. The smallest cells measure 200 ft on a side.

The model contains three layers corresponding to the Shallow Aquifer (Layer 1), the Confining Unit (Layer 2) and the Deep Aquifer (Layer 3). The Shallow Aquifer is assumed to be unconfined and the lower two layers are confined. The flow of groundwater between model layers is represented in the model using a leakance term. The leakance term incorporates the vertical permeability characteristic of each layer.

In the original model, Layer 3 pinched out north of Von Fange Ditch. During the later investigation northwest of the site, this was determined to be inaccurate. Layer 3 sediments continue as far as the furthest northwest drilled well point. With this new information, Layer 3 sediments are predicted to extend up to the East Fork of the White River. In the model, Layer 3 sediments continue north up to the East Fork of the White River as part of hydraulic conductivity Zone 4.

Hydraulic conductivity Zone 4 includes all three layers north of the site in the area where the confining unit disappears. Another leakance zone was set up in the northern portion of the grid to include the leakance due to the incorporation of Zone 4.
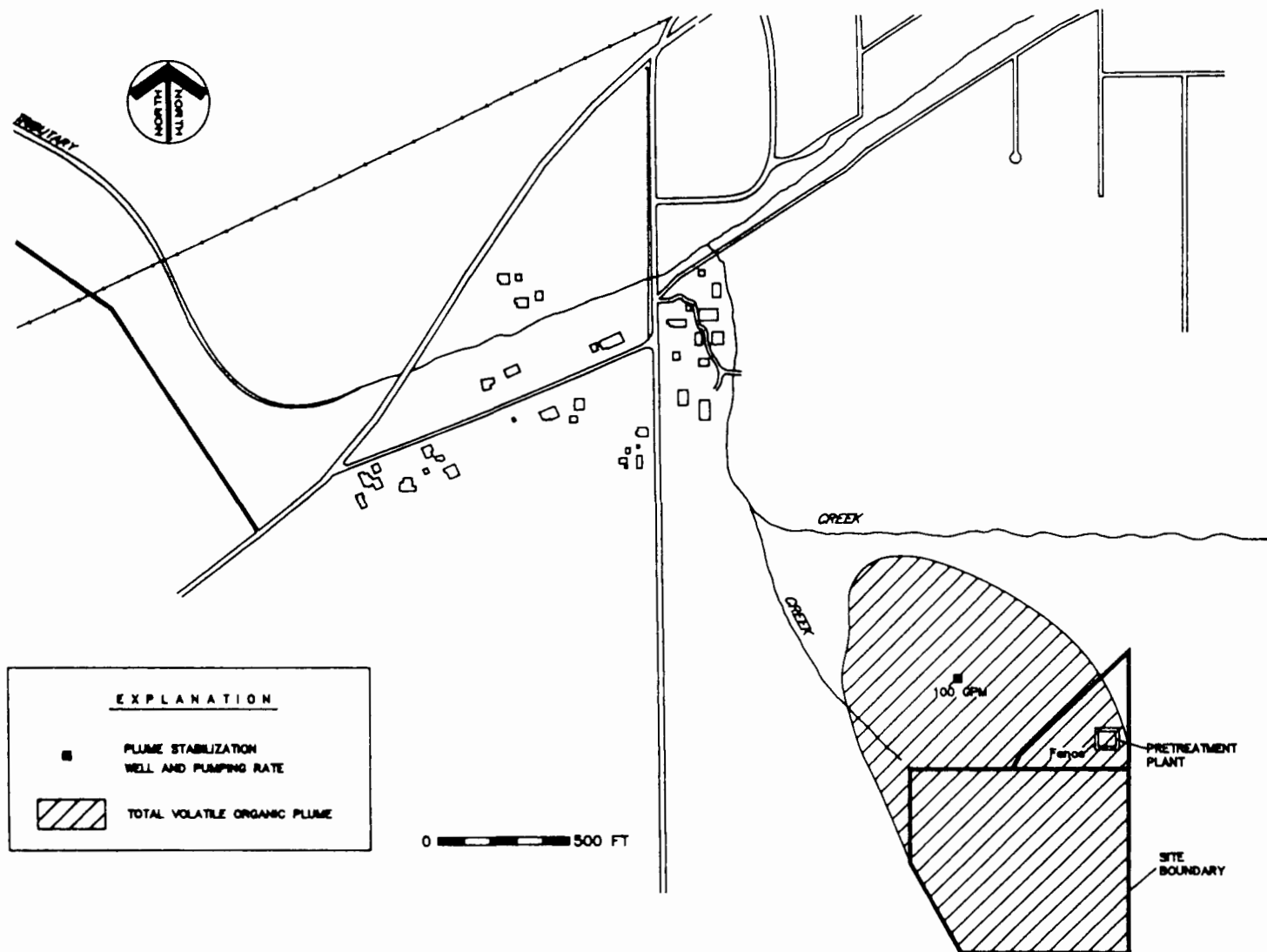
Figure 2
Extent of Total Volatile Organic Plume
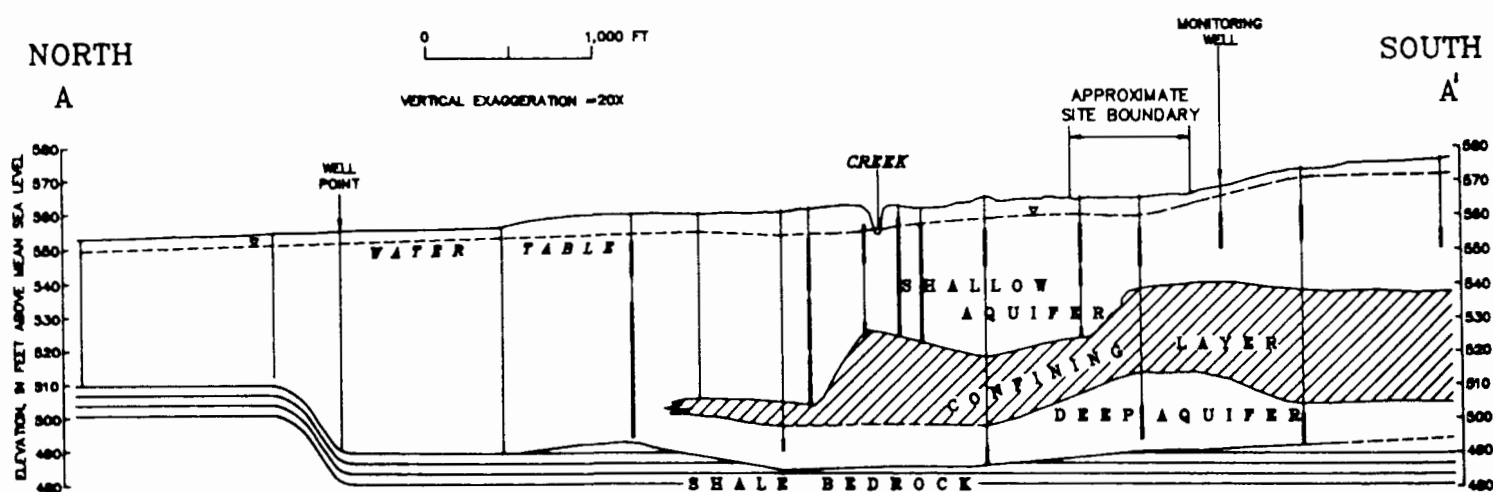as Defined During the Remedial Investigation

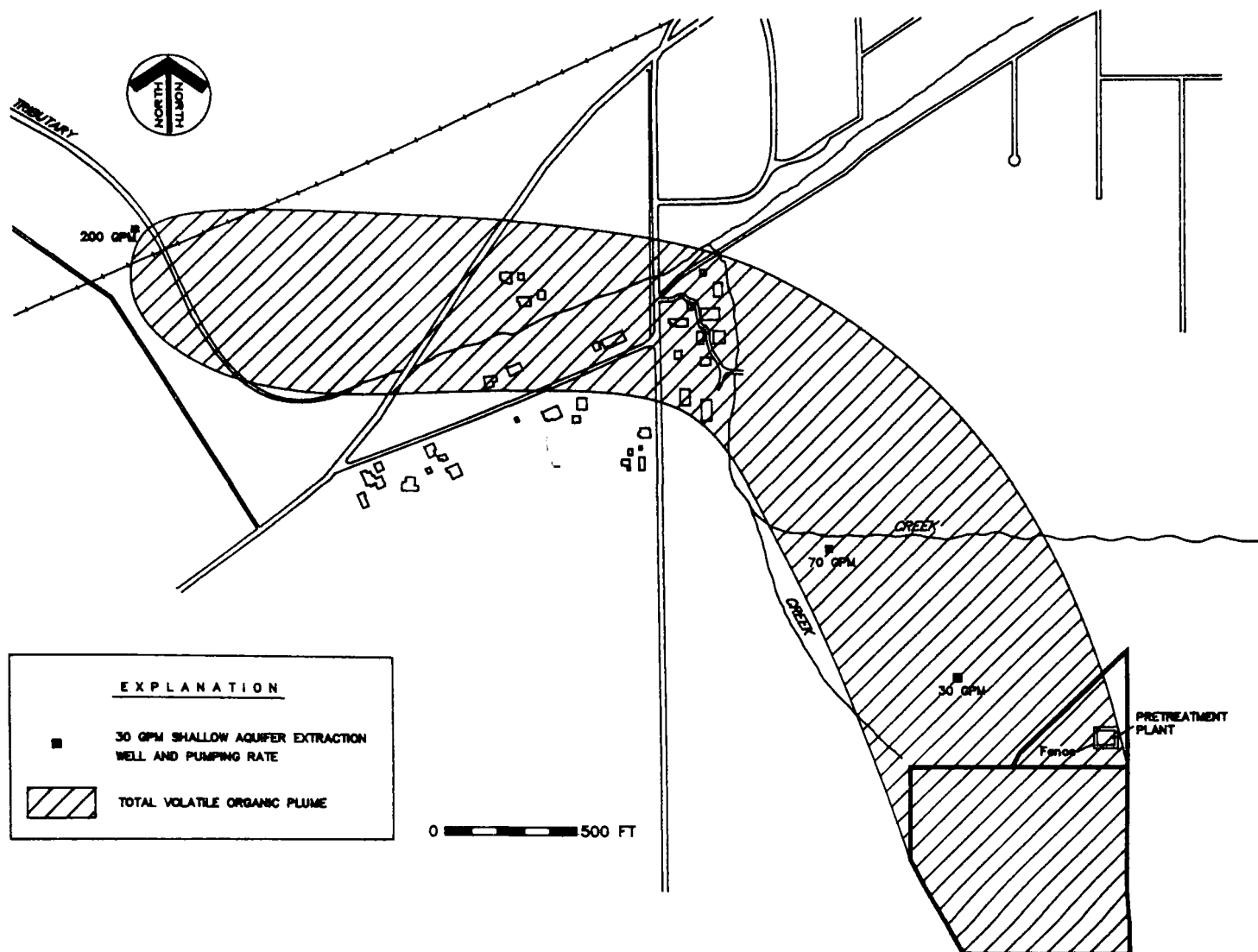Figure 3
Hydrogeologic Cross Section

Figure 4
Extent of Total Volatile Organic Plume as Defined
in June 1990

Boundary Conditions

Three primary types of numerical conditions were used in the model to represent these physical boundaries to the system. The model boundary conditions are termed constant head, constant flux and head-dependent flux boundaries.

Constant head boundaries in Layer 1 and the White River Deposits are used to represent all surface water features, including the East Fork of the White River and other small streams. Elevations for the surface water bodies were estimated from the USGS topographic maps of the area.

East-West Creek is represented by a head-dependent flux condition. The creek occasionally goes dry and so it could not be classified as a constant head boundary. It is termed a head-dependent flux boundary or, more specifically, a drain.

Von Fange Ditch and Heddy Run are represented by river boundaries. This configuration allows the groundwater to pass under the river nodes in Layer 1 and is more representative of field conditions.

Automatic Calibration Technique

The model was calibrated using a nonlinear least-squares technique known as the Marquardt Algorithm. This technique is often referred to as automatic calibration or inverse modeling. Inverse techniques determine optimum aquifer parameter values for a given model configuration (grid spacing and boundary conditions) that provide the best statistical calibration. The calibration for the model was arrived at through an iterating procedure involving inverse model runs and subsequent redefinition of aquifer parameter zones and boundary conditions.

The steady-state calibration was performed by comparing model-calculated water levels to those measured in the field on Sunday, April 18, 1990 between 1:30 p.m. and 7:30 p.m. The values of the residuals of all calibration targets used are shown in Table 1 and the modeled water-level contours along with the residual values are shown in Figure 6.

Contaminant Transport Modeling

The groundwater flow model was calibrated to steady-state conditions over an area much larger than the Seymour site. A regional flow model was developed in order to use realistic hydrologic boundaries. This large scale was not appropriate for analysis of contaminant transport near the site, however, where a smaller scale and much finer grid were required. Thus, a new model was developed that was applicable to an area north and west of the Seymour site in the area of groundwater contamination. Boundary conditions and aquifer properties were defined by the previous groundwater flow modeling effort.

This form of transport analysis has been called the Grid Refinement Approach or the Telescopic Mesh Refinement technique. This technique was developed to account for regional groundwater flow conditions at a local scale (Fig. 7).
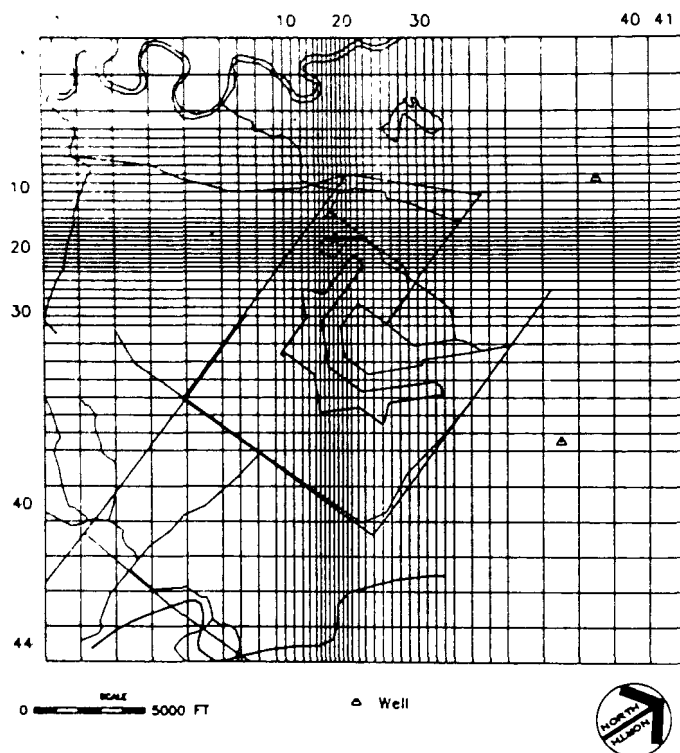
Figure 5
Model Grid

Table 1
Comparison of Observed and Calculated Heads

Well	I (Row)	J (Col)	K (Layer)	Observed Head (ft above mean sea level)	Calculated Head (ft above mean sea level)	Residual (ft)
212B	12	16	1	556.800	555.853	0.947
131B	12	18	1	556.600	555.976	0.664
133	13	19	1	557.600	557.075	0.295
305B	14	18	1	557.700	557.471	0.259
136	15	19	1	558.000	558.210	-0.170
130	15	17	1	558.000	557.868	0.122
134	16	22	1	558.300	559.303	-0.753
209B	17	22	1	559.100	559.777	-0.677
137	16	21	1	559.000	559.344	-0.334
141	17	18	1	558.800	559.043	-0.253
207B	17	17	1	558.500	558.904	-0.434
204A	18	17	1	559.200	559.306	-0.146
204B	19	18	1	559.800	559.704	0.116
203B	19	16	1	559.800	559.485	0.565
202B	20	16	1	560.800	560.149	0.651
146	20	20	1	560.300	560.722	-0.422
147	22	19	1	561.200	561.467	-0.317
201	24	19	1	561.800	563.334	-1.59
144	24	17	1	563.700	562.592	1.08
200	25	15	1	570.100	566.402	3.66
308D	11	16	5	555.600	554.771	0.659
333	12	21	5	556.600	555.554	1.07
PI-A	12	15	1	557.900	555.338	2.56
308A	14	17	1	555.600	555.135	0.275
PI-B	11	20	1	556.100	555.721	0.359
PI-E	9	16	1	554.100	554.326	-0.246
PI-D	10	10	1	555.800	553.394	2.48
PI-L	6	11	1	552.500	552.328	0.222
PI-E	6	13	1	553.600	552.853	0.567

No additional calibration was performed on the Seymour transport model. This includes both groundwater flow and contaminant transport analyses. In the transport model, contaminant concentrations were initialized in the model at observed concentrations and simulated into the future. The purpose of the analysis was not to determine how the plume developed, but to estimate the loading of contaminants to the recovery system and to determine the influence of the pumping on the plume's configuration as compared to monitoring well analytical results.

In all cases, the source of contamination was assumed to be controlled and its continued contribution to the groundwater was assumed to be negligible.
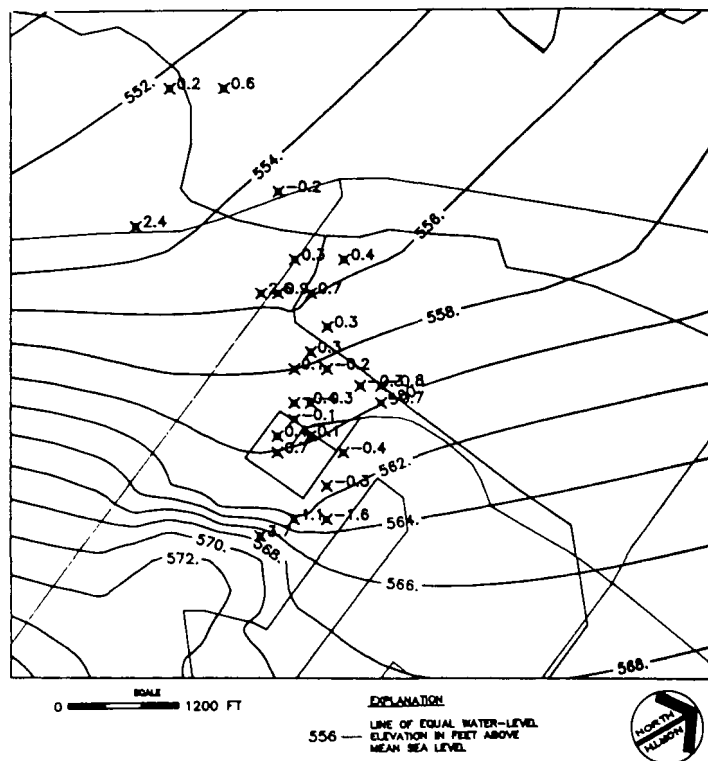
Figure 6
Calibrated Residuals in Layer 1

The transport analysis as described here proceeds in two phases after construction of the local scale refined model. In the first phase, an analysis of convective transport (particle-tracking) is used to determine the capture zones of several recovery well scenarios. After determining that the pumping rates for each scenario capture the area of the contaminant plume, a solute transport model is run to estimate contaminant concentrations in each recovery well.

Additional parameters required for the transport model included porosity, dispersivity and retardation coefficients. The porosity was estimated at 0.3 (30%). This value was chosen as a representative value for sand and gravel formations. No site-specific measurements were available. Longitudinal dispersivity was estimated to be 200 ft, with a transverse dispersivity of 20 ft. Dispersivity is a scale-dependent variable and is normally estimated to be 10% of the length of the contaminant plume. The Seymour plumes for mobile contaminants, such as tetrahydrofuran, are approximately 2,000 ft long. Retardation factors were obtained from the RI data for each contaminant simulated in the model.

Three example compounds that were simulated are as follows:

- Chloroethane $R = 2.1$
- Tetrahydrofuran $R = 1.02$
- 1,4-Dioxane $R = 1.0$

The spatial distribution of each compound was used as the initial conditions for the contaminant transport model. Two different sets of initial conditions were used for each compound representing average concentrations and maximum observed contaminations. The data used to determine the initial spatial distribution were the analytical results from the fall 1989 and spring 1990 sampling events. The raw data were contoured by hand by Geraghty & Miller personnel and the contours were digitized for input into the model.
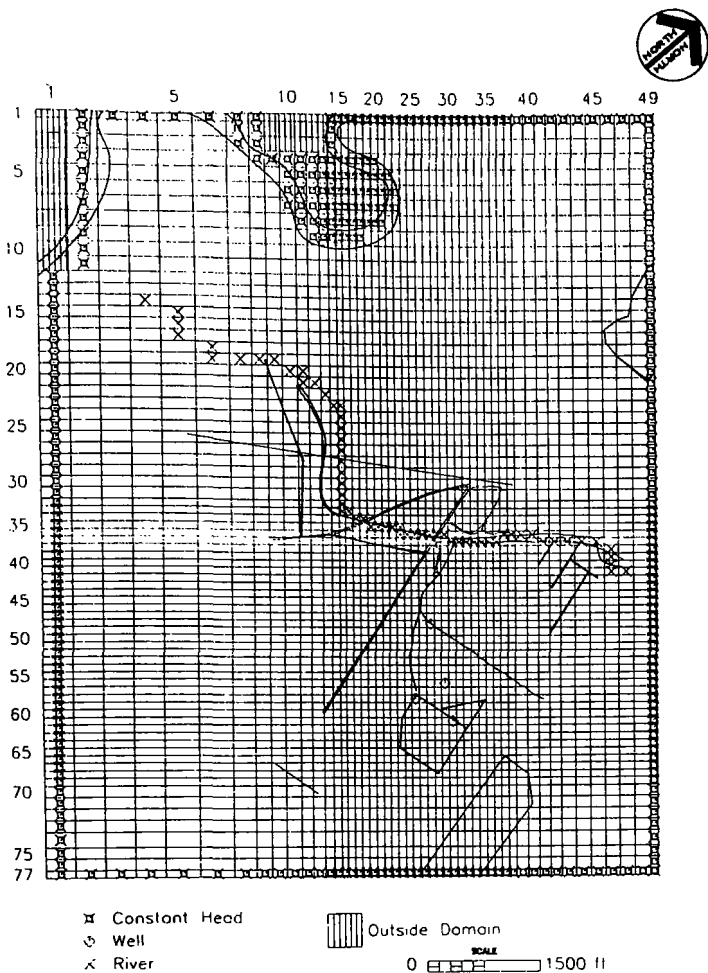
Figure 7
Refined Finite-Layer Grid for Layer 1

Constant Head
Well
River
Outside Domain
0 [scale] 1500 ft

APPLICATIONS OF THE MODEL
TO REMEDIAL DESIGN AND OPERATION

The new flow and transport model is being used to design the final pumpage and treatment system at the Seymour site. As shown in Figure 8, hydraulic capture analysis using particle tracking is helping to locate extraction wells and to specify their pumping rate. Concentration profiles such as shown in Figure 9 for chloroethane are helping to predict the concentration through time of each contaminant at each pumping well. The concentration vs time graphs are allowing the system designers to specify the appropriate mix of treatment technologies (air stripping, carbon adsorption and biological treatment) at the appropriate time. One alternative, for example, is that the extraction well (E5) that will intercept the 1,4-dioxane portion of the plume may be discharged directly to the city's sewers for treatment in the city's POTW provided that the concentration profile shows that no significant concentration of other contaminants will be intercepted by this well over the anticipated life of the remedial action. This information is critical to the continued discharge to the POTW from this portion of the plume. The presence of other contaminants could cause this portion of the remediation to be changed in the future, perhaps by adding a pretreatment system.

Similarly, the concentration profiles for the two other plume stabilizing extraction wells seen in Figure 8 closer to the site (E3 and E4) have been generated. These are shown for chloroethane and tetrahydrofuran in Figures 9 and 10. The operation of these wells is constrained by associated air and water emissions from the pretreatment facility. The object of the extraction system is to minimize these emissions while maximizing the rate at which contaminants are extracted from the

aquifer. The model is being used to generate the concentration profiles from which air risks and the level of carbon treatment may be evaluated depending on the pumping rates and locations of the extraction wells. The pumping rates will be adjusted to provide treatment of the groundwater in the most cost-effective manner while maintaining air emissions below the 1×10^{-6} excess cancer risk rate and while maintaining compliance with effluent discharge limitations. An alternative pumping scenario is shown in Figure 11. The predicted air risk from this pumping strategy is too great and therefore will not be feasible without treatment of the emissions. The cost of this treatment must be evaluated against the incremental decrease in cleanup time to determine the best course of action.
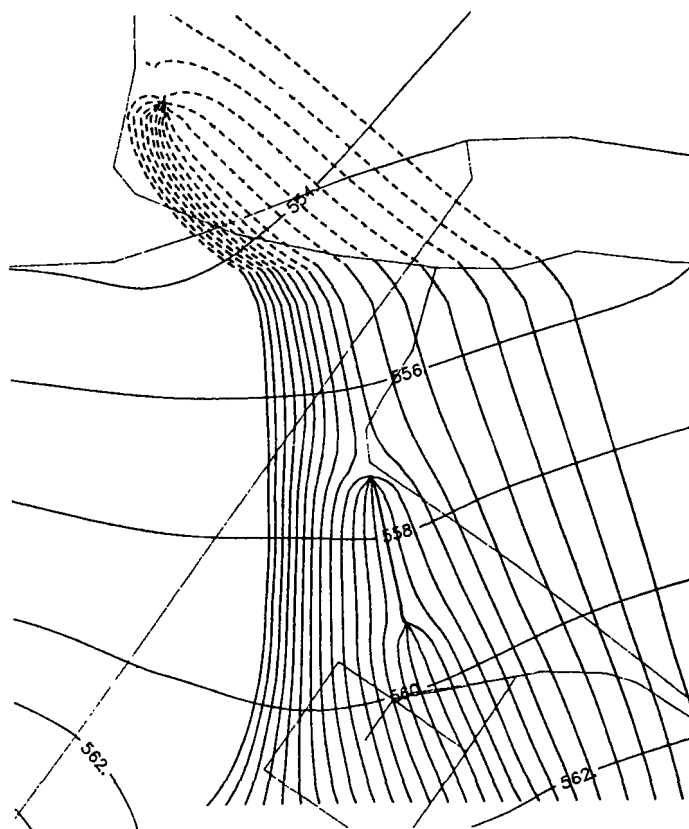
Figure 8
Particle Traces in Layer 1
Total Plumage - 180 gpm
E5=100 gpm; E3=30 gpm; E4=50 gpm

As sampling is performed to verify that site cleanup is proceeding, the new monitoring data will be used to update the solute transport initial conditions annually. In this manner, the predictions of concentrations in the extracted groundwater will become increasingly more accurate.

CONCLUSION

It has become evident through our experiences at the Seymour site that numerical modeling at hazardous material cleanup sites will be used for other tasks in addition to selection of a remedial alternative. Modeling will be an indispensable tool for determining risks, for optimizing the operation of an extraction system and for designing various components of a groundwater treatment system. For these applications a model must be as accurate as possible, i.e., capable of being updated in terms of its construction for groundwater flow and in terms of its initialization for solute transport simulation. With these attributes, a model will incorporate the best possible information prior to its use as a basis for design.
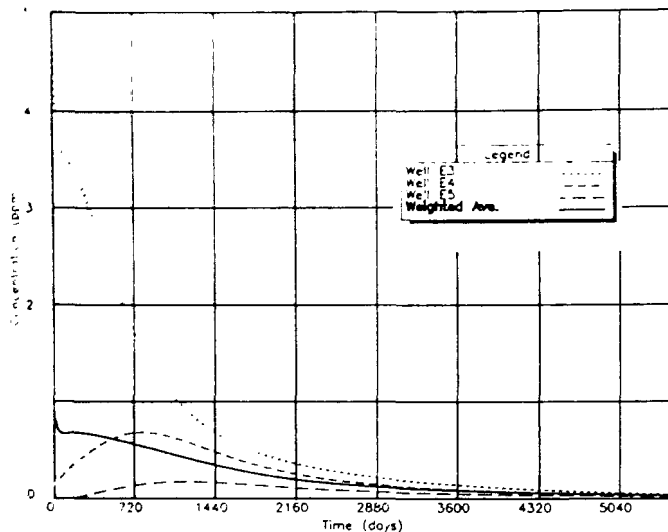
Figure 9
Concentration of Chloroethane (ppm) Over Time (days)
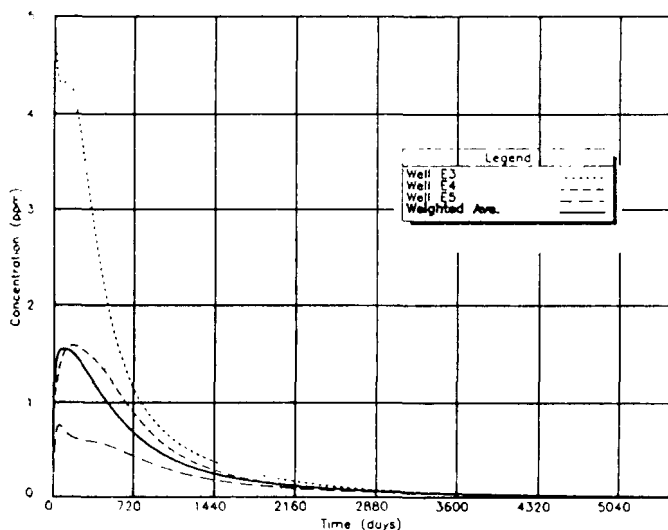Based Upon Maximum Concentrations

Figure 10
Concentration of Tetrahydrofuran (ppm) Over Time (days)
Based Upon Maximum Concentrations

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Particle Traces in Layer 1
Total Pumpage — 310 gpm
E5=120 gpm; E1=50 gpm; E2=60 gpm; E3=30 gpm; E4=50 gpm
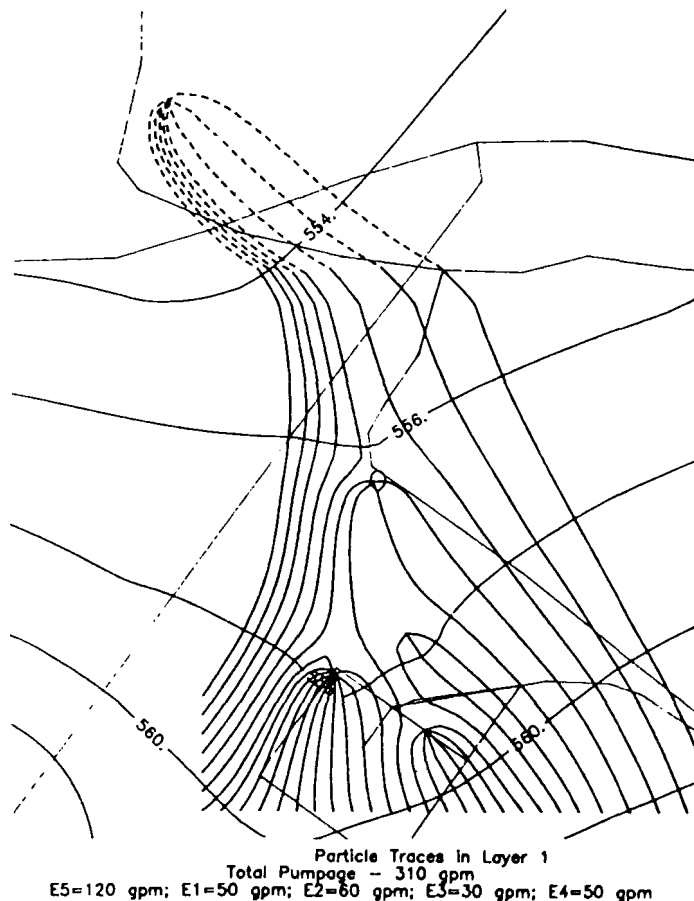
Figure 11
Alternative Pumping Scenario

Modeling of On-Site Air Concentrations At Superfund Sites

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ABSTRACT

This paper proposes a semianalytical model to estimate on-site air concentrations, based on the principle of mass conservation, continuous plume behavior and local meteorological conditions. The predictive scheme is based on the conventional "box" model, but is refined to incorporate considerations such as wind shear near the surface, development of plume thickness and atmospheric stability. The model has been tested against measurements of air concentrations utilizing the measured air emission rates for several Superfund sites. Preliminary findings indicate that the model predictions are in good agreement with direct measurements of on-site air concentrations at these sites. The proposed model is supported by a computer program that incorporates parameters utilized by the U.S. EPA in the UNAMAP6 Gaussian plume models.

INTRODUCTION

The ability to estimate on-site air concentrations with reasonable accuracy has assumed an increasingly prominent role in evaluating potential public health risks associated with activities at contaminated sites. The need for air concentration estimates may arise during: (1) assessment of base line risks associated with Superfund sites; (2) comparison of the risks associated with different remedial alternatives for contaminated site cleanups; (3) evaluation of on-site workers' health risks resulting from the development of contaminated industrial properties; and (4) determination of site cleanup criteria based on a prescribed acceptable public health risk. Errors introduced into the estimates of on-site air concentrations will extend into subsequent estimates of health risks and thus undermine the usefulness of the modeling effort and subsequent risk analyses. Accurate estimation of on-site air concentrations for a contaminated site is therefore essential to provide meaningful predictions of health risks for decision-makers.

Air emissions at contaminated sites normally are classified as continuous ground-level area-source emissions with negligible buoyancy effect and low source strength. Exposures to such emissions for on-site workers and nearby residents are of particular concern to the public and regulatory agencies. Estimation of the on-site air concentration by applying a conventional diffusion model, Gaussian or non-Gaussian, is inappropriate because the atmospheric dispersion mechanism for short-range dispersion is different from that for long-range dispersion. Taylor's theory of diffusion by continuous movements provides a typical illustration of this fact.[1] Furthermore, most dispersion models are derived with the given assumption that an infinite concentration, or some prescribed initial concentration, exists at the source location; these models fail to address the spatial variation of on-site air concentrations.

To address the limitations of applying conventional dispersion modeling techniques to the estimation of on-site air concentrations, a variety of approaches have been considered. The simplest approach to modeling the on-site air concentration is to modify the Gaussian point source solution and apply it to an area source by treating the area emissions as a concentrated point emission located either at the center of the actual source or upwind by a virtual distance. Turner[2] defined the virtual upwind distance by backcalculating the lateral dispersion coefficient from the Pasquill-Gifford curves using a reduced source width. Another similar virtual upwind point source dispersion equation was recommended by the U.S. EPA.[3] Both approaches, however, create an unrealistic estimate of the spatial variation of concentrations within the source area, depending on the size of the source.

A second approach is the "box" model which has been widely used in urban air pollution.[4,5,6] Gifford and Hanna[6] have proposed a formula with an empirical coefficient to correlate predicted concentrations to field observations. The empirical coefficient was derived from extensive air pollution data (average annual emissions and concentrations of particles for 44 United States cities and SO_2 data for 20 United States cities). This box model approach was greatly simplified in a document published by the U.S. EPA addressing the development of an advisory level for PCB cleanup,[7] by assuming a uniform mixing within a 2-meter high virtual box. The box model provides a useful tool in estimating the on-site air concentration. Its predictions, however, can be overly conservative if the model is not calibrated and validated by field measurements.

A third approach models short-range air dispersion from area sources based on K-theory.[8] K-theory involves application of the atmospheric diffusion equation using empirical eddy diffusivities for the time-averaged turbulent flux. The approach employs the solution of a two-dimensional atmospheric diffusion equation.[9,10] This model is more complicated than a Gaussian model and the expected improvement in accuracy has yet to be evaluated.

This paper proposes a simple but effective model[11] based on the principle of mass conservation, continuous plume behavior and local meteorological conditions. The model, referred to as the modified box model, has been developed to estimate the on-site air concentration that most Gaussian air dispersion models are unable to predict. The modified box model is refined from the conventional box model to incorporate considerations of wind shear near the surface, development of plume thickness, vertical concentration distribution and atmospheric stability while at the same time maintaining that model's simplicity. It calculates the on-site or near-field air concentrations from an area source utilizing emission estimates and on-site meteorological observations. The model's predictions have been compared with field observations of air emissions and on-site air concentrations. Preliminary findings indicate that the model predictions are in good agreement with direct measurements of on-site air concentrations at waste sites.

ESTIMATING ON-SITE AIR CONCENTRATIONS

If one represents the contaminated site of interest as a finite area source of strength E, the pollutants emitted can be considered to be contained within an imaginary plume boundary from the upwind edge to the down-wind edge of the area as shown in Figure 1. The height of the imaginary boundary, Zi, is a function of the downwind distance, oncoming wind velocity and atmospheric stability. Based on Gaussian distribution, more than 95% of the pollutants will be entrapped within a depth of 2.15 δ_z, where δ_z is the standard deviation of the vertical concentration distribution.
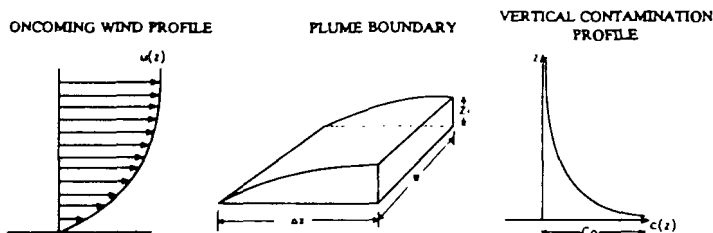
Figure 1
The Modified "Box" Model

If c(z) is the concentration at the downwind edge of the area source and c'a is the ambient concentration beyond the imaginary boundary layer, the conservation of mass states that

$$\int_s (c(z) \quad c_a) \; \vec{u}(z) \cdot \vec{n} \; dS \quad 0,$$ (1)

where:

$c(z)$ is the air concentration at the downwind edge, g/m^3
$u(z)$ is the atmospheric wind velocity at height z, m/sec
n is the unit vector normal to the imaginary boundary
S is the surface of the imaginary plume boundary, m

If the background air concentration, c_a, and the lateral dispersion are neglected, Equation 1 can be rewritten as:

$$\int_A E \; dA = \int_o^{z_i} \int_o^W c(z) \; u(z) \; dy \; dz,$$ (2)

where:

A is the size of the area source, m^2
W is the width of the area source, m
E is the area source strength, g/m^2-sec
y,z are the rectangular coordinates, with y the cross-wind direction and z the azimuth direction

The wind profile, u(z), in the above equation can be described by a power-law velocity profile:[12]

$$u(z) = u_{10} \; (\frac{z}{10})^P$$ (3)

where:

u_{10} is the surface wind speed at 10 m height, m/sec
z is the height above ground, m
p is the wind profile exponent

It is generally accepted that the vertical concentration distribution in a continuous plume follows the Gaussian distribution such that c(z) can be expressed in terms of the ground-level concentration:

$$c(z) = c_o \; exp(- z^2/2\sigma_z^2)$$ (4)

where:

co is the ground-level concentration downwind of the source, g/m^3

By substituting u(z) and c(z) with the relationships illustrated in Equations 3 and 4, respectively, Equation 2 can now be presented as follows:

$$E \cdot \Delta X \cdot W \quad \int_u^{2.15\sigma_z} \int_o^W c_o \cdot exp(-z^2/2\sigma_z^2) \cdot u_{10} \cdot (z/10)^P \; dy \; dz$$ (5)

where:

ΔX is the downwind distance from the upwind edge of the source, m. The integration can be manipulated and simplified to:

$$c_o = [\quad u_{10} \; \sigma_z^{p+1} \; I(p)]^{-1} \; E \cdot \Delta X$$ (6)

where:

$$I(p) = \frac{1}{10^P} \int_{\theta=0}^{\theta=2.15} \theta^P \; exp(-\theta^2/2) \; d\theta$$

The integration for I(p) can be performed with a simple numerical integration scheme. Figure 2 displays I(p) for various wind profiles. Default values for the wind-profile exponent as recommended by the U.S. EPA[13] can be readily incorporated into this refined box model. The standard deviation of the vertical concentration distribution can be defined under site-specific conditions or can be defined in accordance with many standard procedures.[13,14,15] A power-law expression for δ_z, which reflects the various atmospheric stabilities, is preferred in the current modeling for mathematical simplicity and consistency with U.S. EPA air dispersion models.
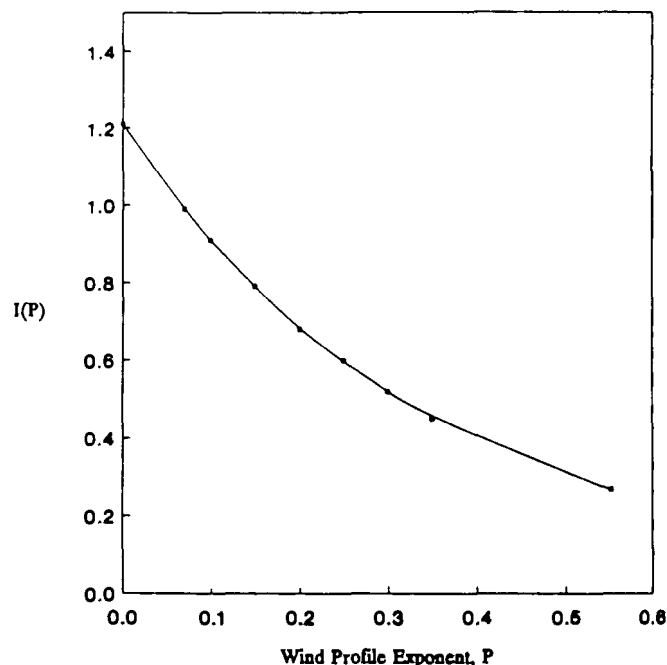

Figure 2
The Integration Function Utilized in Figure 6

Since Equation 6 takes into consideration the ambient wind speed and atmospheric stability, the real-time meteorological data and the joint frequency of occurrence of wind-speed and wind-direction classified by the Pasquill-Gifford stability categories [or STAR[17]] can be incorporated to yield an annual average concentration, c:

$$\bar{c} = \sum_{i=1}^{6} \sum_{j=1}^{6} \sum_{k=1}^{16} f_{ijk} \frac{\Delta X \; E}{(u_{10})_j \; (\sigma_z)_i^{P_i+1} \; I(p_i)}$$ (7)

where:

i is the wind speed category
j is the atmospheric stability category
k is the wind direction category
f_{ijk} is the frequency of time in a year for specified i, j and k

A computer program has been developed to perform the above averaging process.

MODEL COMPARISONS

On-Site Air Concentrations

Field observations of air emission rates were employed in Equation 6 to yield on-site air concentrations at two waste sites under undisturbed conditions. Predictions from the modified box model were then compared to the results of direct on-site air measurements in order to verify the accuracy of the model.

At the first site (Landfill 1), sulfur dioxide (SO_2) and total hydrocarbon (THC) concentrations were reported in a Superfund remedial investigation.[17,18] Air samples were collected 6 inches above the surface at 100 different locations at the site. Data consisting of 32 field observations and 10 background measurements (remaining after quality control on the sampling procedures) were examined in the current assessment.

For SO_2, 8 out of 32 surface samples and 7 out of 10 background samples were below the detection limit of the instrument. The observed background concentrations were all within 1.5 times the detection limit, which indicated that the true background concentration fluctuated around the detection limit. To yield a reasonable arithmetic mean, samples below the detection limit were assigned a value of 0.5 times the detection limit. For THC, all observations were above the detection limit. However, the average background concentration exceeded the average concentration of all surface samples. Table 1 shows the sample statistics for SO_2 and THC. To determine the statistical significance of the observed data, the Wilcoxon Rank Sum Test was conducted in addition to the analysis of variance for both chemical compounds. The average SO_2 concentration was concluded to be statistically significantly different from the background concentration based on the Wilcoxon Rank Sum Test with a p-value of 0.0101. The THC concentrations, however, were concluded to vary insignificantly from the background concentration, since they failed both the analysis of variance and the Wilcoxon Rank Sum Test (p-value > 0.5) and therefore were not considered further in this comparison.

Table 1
Statistics for Air Concentration Sampled from Landfill 1[17]

Chemical Constituent	Sulfur dioxide		Total hydrocarbons	
Sample	Background	Surface	Background	Surface
No. of Samples	10	32	10	32
Data Range, ppmv	<0.01 - 0.015	<0.01 - 0.047	2.2 - 4.2	2.0 - 4.0
Mean	0.0077	0.01703	2.9	2.628
Standard Deviation	0.00437	0.0114	0.611	0.549
Skewness	1.0799	1.0367		
Coefficient of Variance	56.79	67.17	21.07	20.89
P - Value	0.0101		> 0.5	
Summary				
Mean	0.00933 ppmv or 24.88 ug/m^3		undistinguishable ...	

Direct emission measurements at the same site were performed using the surface flux chamber technique. The mean SO_2 emission rate computed from 18 measurements was 3.33 $\mu g/m^2$-sec, with a standard deviation of 9.05 $\mu g/m^2$-sec. Considering the inhomogeneity of soil contamination at a large waste landfill, such variation in the emission rate is not unexpected. Both the emission and ambient air measurements were conducted during the day. The annual average wind speed

of 3 m/sec, as reported from a nearby weather monitoring station, was employed as the ambient wind speed. Three average atmospheric stabilities were assessed to provide a comparison. Based on an annual mean wind speed of 3.0 m/sec and an atmospheric stability of D class that was considered to characterize the site, Table 2 shows that data for the measured mean SO_2 concentration differs from the modified box model prediction by only 2%.

Table 2
Comparison of the Predicted and Measured SO_2 Emission Rates at Landfill 1[17]

Atmospheric Stability	Ambient Wind Speed, m/s	Emission rate, ug/m^2·s		Air concentration, ug/m^3			
		Measured		Measured		Predicted	
		Mean	High*	Mean	High*	Mean	High*
B	2	3.33	12.38	24.88	55.28	12.99	48.28
B	3	3.33	12.38	24.88	55.28	8.66	32.19
B	4	3.33	12.38	24.88	55.28	6.49	24.14
C	2	3.33	12.38	24.88	55.28	20.08	74.65
C	3	3.33	12.38	24.88	55.28	13.39	49.77
C	4	3.33	12.38	24.88	55.28	10.06	37.39
D	2	3.33	12.38	24.88	55.28	36.63	136.18
D	3	3.33	12.38	24.88	55.28	24.41	90.75
D	4	3.33	12.38	24.88	55.28	18.32	68.09

* : High value is defined as Mean + 1 S.D.

In another recent Superfund site (Landfill 2) remedial investigation,[19] limited on-site air samples were taken at an undisturbed waste site with specified upwind/downwind sampling locations. Downwind samples collected during the day were statistically undistinguishable from the upwind sample. The nighttime samples, however, were distinguishable from the upwind sample and were adopted for the current analysis. Chemical vapor emission rates were also measured using the surface flux chamber technique. The chemical vapor emission rates are summarized from the report[19] and tabulated as follows:

Chemical Constituent	Number of Samples	Emission rate, μg/m^2-sec	
		Mean	S.D.
Benzene	7	9.98×10^{-3}	2.67×10^{-3}
Toluene	7	1.37×10^{-2}	4.35×10^{-3}
1,1,1-Trichloroethylene	4	1.00×10^{-2}	4.13×10^{-3}

Surface meteorological observations made concurrently with the emission rate measurements indicated that air samples were collected under a near calm condition with an average wind speed of approximately 0.8 m/sec.

The modified box model was used with F stability and a wind speed of 0.8 m/sec to yield on-site air concentrations. The results are presented in Table 3. The modified box model underpredicts the on-site air concentration by a factor ranging from 5 to 8. Given the experimental uncertainty involved in field measurements of emission rates and air concentration, the concentrations estimates are considered to be consistent with the field measurements.

Near-Field Air Concentrations

In addition to estimating on-site air concentrations, the modified box model can be used to estimate the near-field air concentrations provided that the receptor is located within a short distance from the area source (e.g., < 2.5 source-widths downwind of a source has been considered an appropriate distance) such that the cross-wind dispersion is insignificant. An examination of the model accuracy was conducted by com-

paring concentrations predicted by the modified box model with those predicted by a series of other air dispersion models. Ambient air concentrations for a California landfill (Landfill 3) reported in a study by Baker[20] were used as criteria for the comparison.

Ambient vinyl chloride concentrations were measured for 5 days at two receptor locations, Sites A and B, located within one source-width distance downwind of the landfill. Baker[20] compared the field observations to the predictions of four air dispersion schemes as follows:

• The maximum ground-level concentration resulting from a ground-level point source located at the center of the landfill

• The maximum ground-level concentration modified from Taylor[1] by utilizing a virtual upwind point source to represent a square area source

• A virtual point source approximation similar to Turner[2] but with modifications of the virtual downwind distance and empirical coefficients

• A simple box model developed for estimation of urban air pollution with adjusted downwind distance.

Hourly surface meteorological observations recorded at a nearby airport were employed to characterize the on-site meteorological conditions. Unfortunately, on-site air emission measurements were not conducted during the Landfill 3 air sampling program and 30 of the 120 hours measured at the nearby airport during the experiment were under conditions of no wind. In his model evaluation, Baker assumed that the receptors were directly downwind of the landfill and assigned an ambient wind speed of 1 m/sec for all no-wind conditions. Excluding the hours when winds were not upwind of the landfill, nearly 70% of the time that the receptors were assumed to be downwind of the landfill were under no-wind conditions. Although it is a generally accepted approach in air dispersion modeling to assign a wind speed for no-wind conditions, the uncertainty introduced in the concentration estimate by such meteorological adjustments should not be ignored.

Table 3
Statistics for Air Samples from Landfill 2 and Comparison of the Predicted and Measured Air Concentrations[19]

| Chemical Constituent | Emission rate (ug/m^2·sec) | | Stability | Wind speed (m/sec) | Air Concentration | | |
	Mean	High*			(ppbv)	Measured (ug/m^3)	Predicted Mean	High*
Benzene	9.98E-03	0.01265	D	0.5	1.55	5.04	0.22	0.28
			D	0.8			0.18	0.22
			D	1			0.11	0.14
			E	0.5			0.71	0.90
			E	0.8			0.45	0.56
			E	1			0.36	0.45
			F	0.5			1.48	1.87
			F	0.8			0.92	1.17
			F	1			0.74	0.94
Toluene	1.37E-02	0.0181	D	0.5	2.6	9.98	0.30	0.40
			D	0.8			0.24	0.32
			D	1			0.15	0.20
			E	0.5			0.98	1.29
			E	0.8			0.61	0.81
			E	1			0.49	0.65
			F	0.5			2.03	2.68
			F	0.8			1.27	1.68
			F	1			1.02	1.34
1,1,1-trichloroethane	1.00E-02	0.01413	D	0.5	2.4	11.34	0.22	0.31
			D	0.8			0.18	0.25
			D	1			0.11	0.16
			E	0.5			0.71	1.01
			E	0.8			0.45	0.63
			E	1			0.36	0.50
			F	0.5			1.48	2.09
			F	0.8			0.93	1.31
			F	1			0.74	1.05

Due to the lack of on-site emission measurements, emission estimates were developed from an analytical model.[21] The emission estimates were later supported by backcalculated annual average landfill emission rates using the ambient monitoring data, local meteorological data and the ISCST Gaussian air dispersion model.[22] Table 4 presents the measured and predicted vinyl chloride concentrations at receptor sites

A and B during the Landfill 3 air study as reported by Baker. Of the four models considered by Baker (Models 1 through 4), Models 1 and 4 were consistently found to perform less effectively than the other models and are not addressed further in this analysis. Estimates from three other models, a K-theory model (Model 5), a simple box model (Model 6) and the modified box model, are also included in Table 4 for comparison.

Table 4
Model Estimates and Measured Vinyl Chloride Concentrations (ppb) at Landfill 3

Site	Method	March 7-8	March 8-9	August 5-6	August 6-7	August 7-8	Average
A	Measured	12	5	7	12	9	9
	Model 1	25.1	19.4	40.0	45.7	45.5	35.1
	Model 2	9.1	7.3	14.8	16.7	16.9	13.0
	Model 3	4.9	4.0	8.0	9.0	9.1	7.0
	Model 4	45.9	42.8	76.7	81.1	87.3	66.8
	Model 5	6.6	5.1	11.7	11.9	11.9	9.4
	Model 6	116.0	108.2	193.9	205.0	220.6	168.7
	Modified	6.5	4.8	10.7	11.2	10.5	8.8
B	Measured	5	7	2	4	2	4
	Model 1	24.3	13.1	30.4	32.4	32.2	26.5
	Model 2	11.5	6.1	14.2	15.3	15.2	12.5
	Model 3	6.5	3.7	8.4	8.7	8.9	7.2
	Model 4	35.5	28.6	62.8	62.0	66.7	51.1
	Model 5	3.3	2.3	5.7	5.6	5.7	4.5
	Model 6	40.4	32.6	71.5	70.6	76.0	58.2
	Modified	9.3	6.7	15.9	16.7	15.5	12.8
····· with adjusted meteorological conditions ·····							
B	Measured	5	7	2	4	2	4
	Model 2	7.1	4.5	1.2	0.1	2.2	3.0
	Model 3	3.0	2.5	1.1	0.2	1.4	1.6
	Modified	4.9	4.6	0.9	1.7	2.7	3.0

Measured ·	Landfill 3 (20)
Model 1	Ground-level point source (2)
Model 2	Virtual point source, Turner (2)
Model 3	Virtual point source, USEPA (3)
Model 4	Simple box, Urban Air Pollution (6)
Model 5	K-theory (8)
Model 6	Simple box, USEPA (7)
Modified	Modified box model

For Site A, concentrations predicted from the modified box model differ from the measured concentrations by 3 to 45%, as shown in Table 4. (Table 5 summarizes the predicted hourly vinyl chloride concentrations for all 5 days using the proposed model.) The modified box model and the K-theory model appear to provide similar concentration estimates to those estimated by the two virtual-point Gaussian approaches (Models 2 and 3) but with improved accuracy. In contrast, the simple fixed-height box model (Model 6) utilized in the development of U.S. EPA's PCB cleanup advisory overpredicts by approximately 20-fold.

For Site B, all models except the K-theory approach performed poorly in predicting the ambient vinyl chloride concentrations. A further examination of the site topography, however, indicated that a ridge north of Site B directs most nighttime draining air and emissions away from this site.[20] If one assumes that the air current was obstructed by the ridge during the calm condition and was able to pass over the ridge under other wind conditions, then the dispersion model should predict negligible concentration under the calm conditions. Table 4 presents the model predictions from the three Gaussian models incorporating these screened meteorological conditions. Using this more realistic representation of meteorological conditions, it is apparent that the modified box model performs well in predicting the near-field air concentrations.

DISCUSSION

While the concentrations predicted by the modified box model compare well with measured concentrations at the sites studied, the accuracy

of the model may vary depending on the specific site conditions. While the modified box model resembles the mathematical expression of the boundary-layer technology used in air emission estimation,[23] it differs in the vertical representation of the plume dispersion and dependence on the atmospheric conditions.

Table 5
Model Estimates at Landfill 3 Using the Modified Box Model

Hour	Station A					Station B				
	March 7-8	March 8-9	August 5-6	August 6-7	August 7-8	March 7-8	March 8-9	August 5-6	August 6-7	August 7-8
10:00 AM	0	0	0	7.29	0	0	0	0	14.33	0
11:00 AM	5.15	0	0	0	0	9.99	0	0	0	0
12:00 PM	0	0	0	0	0	0	0	0	0	0
1:00 PM	0	1.06	0	0	0	0	0	0	0	0
2:00 PM	0	1.55	0	0	0	0	0	0	0	0
3:00 PM	0	0	0	0	0	0	0	0	0	0
4:00 PM	0	0	0	0	0	0	0	0	0	0
5:00 PM	0	0	0	0	0	0	0	0	0	0
6:00 PM	0	2.99	0	0	0	0	0	0	0	0
7:00 PM	0	0	0	0	0	0	0	0	0	0
8:00 PM	8.64	0	0	0	0	0	0	0	0	0
9:00 PM	0	0	0	0	0	5.05	0	0	0	0
10:00 PM	24.69	0	0	0	0	35.91	0	0	0	0
11:00 PM	24.69	12.35	0	0	34.97	35.91	17.95	0	0	51.52
12:00 AM	9.88	24.69	0	34.97	34.97	14.36	35.91	0	51.52	51.52
1:00 AM	9.88	0	34.97	34.97	34.97	14.36	14.36	51.52	51.52	51.52
2:00 AM	24.69	12.35	34.97	34.97	34.97	35.91	17.95	51.52	51.52	51.52
3:00 AM	9.88	0	34.97	34.97	34.97	14.36	14.36	51.52	51.52	51.52
4:00 AM	9.88	9.88	34.97	34.97	34.97	14.36	14.36	51.52	51.52	51.52
5:00 AM	9.88	9.88	34.97	34.97	13.99	14.36	14.36	51.52	51.52	20.61
6:00 AM	0	12.35	34.97	34.97	13.99	14.36	17.95	51.52	51.52	20.61
7:00 AM	3.51	8.78	34.97	4.97	6.21	5.34	13.34	51.52	7.66	9.57
8:00 AM	0	0	0	0	8.29	0	0	2.29	0	12.76
9:00 AM	5.15	0	12.43	12.43	0	9.99	0	19.15	19.15	0
Average	6.08	4.00	10.72	11.23	10.51	9.34	6.69	15.92	16.74	15.53

Figure 3 displays the variation of on-site concentrations in terms of emission source sizes. In general, the model is relatively insensitive to changes in atmospheric stability with the exception of stability classes A and F. Figure 3 shows that the on-site air concentration utilizing the wind-profile exponent for urban environments is almost independent of the source characteristic length (or the downwind distance from the upwind edge of the source) for all atmospheric stabilities except Stability A.

The effect of source sizes on the air concentrations becomes more apparent if one normalizes the on-site air concentrations by the concentration calculated for a 50-m long area source (Figure 4). The gradual variation of air concentrations with respect to source characteristic length is a result of the balance between the total emissions (source characteristic length), atmospheric stability (plume thickness) and wind shear.

In the modified box model, the plume thickness is represented by a power-law relationship, and the wind shear is implicitly conveyed by a power-law velocity profile. In an extremely unstable atmosphere (Stability class A), the power-law formula for δ_z may overestimate the plume thickness as much as 5-fold (based upon the ratio of plume thickness derived from the power-law formula and Briggs equations[14] at a distance of 3000 m). Thus, the modified box model may underpredict the air concentration for an area source under Stability A. In an extremely stable atmosphere (Stability Class F), the wind-profile exponent recommended by the U.S. EPA, which can be as high as 0.55, may not reflect the actual aerodynamic roughness characterized by the local topography. As a result, more rapid spatial variation of on-site air concentration with downwind distance is observed from the model estimates. More precise determination/selection of the dispersion coefficient,[24,25] mixing layer and wind shear would certainly improve the model's dependence on the source characteristic length.

The on-site or near-field air concentration is determined by on-site emission estimates and prevailing meteorological conditions. While emissions from a contaminated site are insensitive to the atmospheric conditions, the on-site or near-field air concentrations are inevitably affected by the atmospheric mixing. Table 3 shows how an arbitrarily

assigned atmospheric stability (e.g., Stability D), which did not represent the observed atmospheric conditions (Stability F) for Landfill 2, underestimated the air concentration by 40- to 60-fold. The extent of this underestimation was substantially reduced when the atmospheric stability was adjusted to reflect the nighttime no-wind conditions (Stability F). Accurate determination of the prevailing meteorological conditions is thus essential to yield a meaningful prediction of the on-site air concentration.
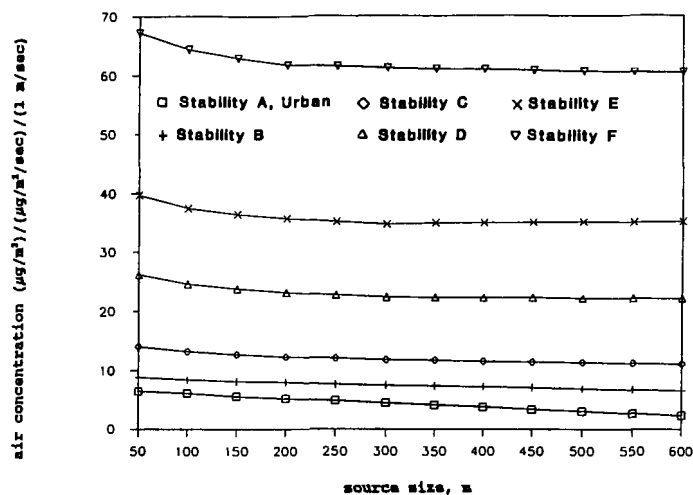

Figure 3
Variation of On-site Air Concentration with
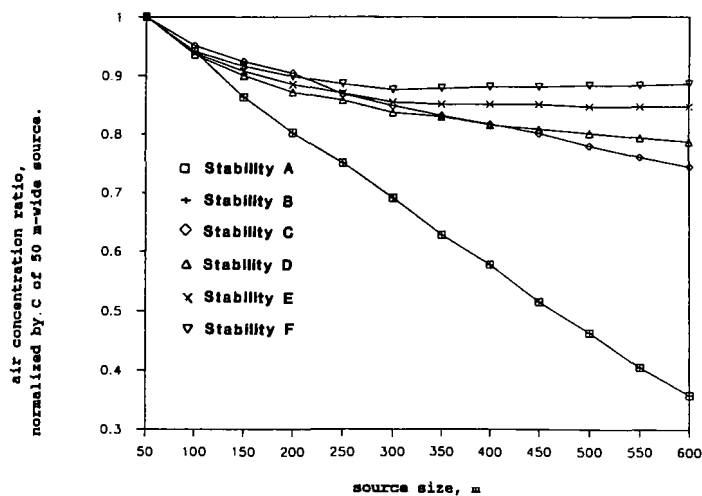Respect to Emission Source Size

Figure 4
Relative Variation of On-site Air Concentration
with Respect to Emission Source Size

CONCLUSION

A modified box model has been developed to correlate the emission rates and the on-site or near-field air concentrations based on the principle of mass conservation, continuous plume theory and local meteorological conditions. It has been tested against measurements of air concentrations and emission rates for two Superfund sites and a waste landfill (with estimated emission rate). Preliminary findings indicate that the model results agree well with direct air measurements and that the model may provide enhanced accuracy over other predictive schemes.

The modified box model also can be used in conjunction with the STAR Summaries and other default values (wind profile exponents and

vertical dispersion coefficients) utilized by the U.S. EPA to yield an annual average concentration in the assessment of public health risks.

ACKNOWLEDGMENT

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Arsenic Behavior in Soil and Groundwater at a Superfund Site: San Joaquin Valley

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ABSTRACT

Studies at a California Superfund site will determine whether arsenic in groundwater and soil is naturally occurring or the result of anthropogenic activity. As part of a contamination assessment ongoing since 1982, more than 3,700 groundwater samples from 240 monitor wells have been analyzed for arsenic, selenium, bromacil and 32 VOCs at the 2-mile by 0.5-mile site. Each well is screened in one of four aquifers: 0 to 50 ft, 51 to 100 ft, 101 to 150 ft and 151 to 200 ft. Arsenic concentrations in groundwater exceeding the U.S. EPA maximum contaminant level (MCL) (50 μg/L) have been measured at 50 of the 240 wells. Thirty-one of those 50 wells are screened in the surficial aquifer (0 to 50 ft). A key issue in this study is the fact that the arsenic is concentrated in the upper 50 ft of groundwater.

Variations of arsenic concentrations as a function of lateral distance and time and the suspended/dissolved nature of the arsenic have been measured. Arsenic concentrations of samples from the 50 wells vary from 20 to 1,100 μg/L. Variations of arsenic concentrations range from 50 to 500 μg/L at the same well within 3 months. The lateral variability of arsenic in groundwater is well demonstrated at a cluster of three wells separated by fewer than 100 ft, all screened in the surficial aquifer. These wells have arsenic concentrations ranging from 61 to 178 μg/L. Arsenic concentrations in dissolved and suspended fractions are being compared to total arsenic concentrations, time and the concentrations of other chemical species. The results will have important implications on the transport mechanism for arsenic at this site.

Adjacent to monitor wells with either high or low concentrations of arsenic, soil samples have been composited on 5-ft. intervals and analyzed for arsenic. Also, soil arsenic values have been compared to the groundwater concentrations. Off-site background samples have been collected, analyzed and compared to the on-site soil samples. There is no evidence that the arsenic on-site is related to anthropogenic activity. Naturally occurring minerals in the soil may be the sole source of arsenic in groundwater at this site.

INTRODUCTION

The potential for groundwater and soil contamination by VOCs, selenium, bromacil and arsenic at Sharpe Site (commonly referred to as SHAD), a Superfund Site in the San Joaquin Valley, was first recognized in 1980 by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) during a preliminary record search.

The contamination assessment, which has been ongoing since 1982, now includes the results of 1,800 soil gas analyses for VOCs, 436 soil analyses for VOCs and arsenic and 3,760 groundwater samples from 240 monitor wells. The groundwater samples have been analyzed for arsenic, selenium, bromacil and 32 VOCs. This portion of the study was funded by USATHAMA to investigate the source of elevated arsenic in groundwater at SHAD.

Through a combination of record searches and field investigations, it has been determined that the VOCs were released to the ground as waste materials at several identified but unrelated locations at the study site. The soils at those locations are sources for VOCs that are being rinsed into the groundwater by infiltrating surface water. The addition of VOCs into the groundwater has resulted in plumes of contamination. The plumes of VOCs are significant to the study of arsenic contamination because the plumes are tracers which permit detailed mapping of groundwater flow regimes.

In addition to VOCs, arsenic is also present in the groundwater and soil beneath the study site. Arsenic concentrations in groundwater have been measured in excess of the U.S. EPA maximum contaminant level (U.S. EPA MCL) of 50 μg/L at 50 monitor wells. Arsenic concentrations in groundwater beneath this site vary within a range of 5 μg/L and 1,100 μg/L. Some of the wells have exceeded 50 μg/L arsenic only once in the 8-year sampling history. Others are consistently above the 50-μg/L concentration. Selected soils have been analyzed by the U.S. EPA's extraction procedure toxicity and California Department of Health Services Waste Extraction Test. Those soil samples did not meet the criteria for classification as hazardous waste.

The possible reasons for elevated arsenic concentrations in groundwater at this site are as follows:

- The elevated concentrations of arsenic in groundwater may be caused by the off-site or on-site use of arsenicals (i.e., rodenticides or herbicides).
- Arsenic, a component of naturally occurring minerals in the subsurface at this site, may be more soluble in the presence of the organic compounds known to exist here.
- The arsenic concentrations in the groundwater may be the result of naturally occurring mineral assemblages in contact with groundwater which reflect conditions unique to the San Joaquin Valley.

The data presented in this report are significant because the behavior of arsenic in groundwater has been well documented from more than 3,700 groundwater samples collected from 240 monitor wells and correlated with arsenic in 439 soil samples. The behavior of arsenic in soil and groundwater at this site may provide information relevant to arsenic behavior at other locations.

The San Joaquin Valley is underlain by several thousand feet of unconsolidated sediments which represent the distal fan deposits of clastics shed from the Coastal Range located west of the study site and the Sierra Range to the east. The Quaternary sediments have been reworked by rivers that have drained the San Joaquin Valley since the sediments were deposited.

Episodic deposition and contemporaneous reworking of the sediments by braided streams have resulted in an extremely complex cross section of discontinuous, intercalated lenses of sands, silts, clays and a minor amount of organic material beneath the study site (Fig. 1). In most cases, aquifers are laterally discontinuous within 1,000 ft. Pump tests have demonstrated that aquifers are connected vertically. The pattern of VOC contamination shows that the aquifers are connected horizontally.

Monitor wells have been installed in clusters of three or four wells, each screened in a successively deeper aquifer. The shallowest zone (A-zone aquifer) exists from approximately 10 ft to 50 ft below ground surface (bgs). The second zone (B-zone aquifer) extends from 50 ft to 100 ft bgs. The third zone (C-zone) extends from 101 ft to 150 ft bgs. The fourth zone (D-zone aquifer) extends from 151 ft to approximately 300 ft bgs. Water levels are recorded each time a groundwater sample is collected for chemical analysis. Additionally, most wells now have pressure transducers and automated telemetry systems that produce daily waterlevel measurements.

The seasonal changes in the groundwater gradient are well documented. The natural regional direction of groundwater flow is to the northwest. Intensive groundwater pumping for agricultural irrigation immediately west of the site during the summer months causes groundwater flow to become more westerly.

LAND USE

The study site is a military depot 2 miles by 0.5 mile used for the interim storage and repair of heavy equipment and aircraft. The land around the site is used primarily for growing row crops, most notably alfalfa. Irrigation of fields that are used for alfalfa production require intensive pumping of groundwater wells for irrigation during the summer months. The irrigation pattern is to pump water for 10 days each month during the summer to provide water for the alfalfa.

BEHAVIOR OF ARSENIC IN GROUNDWATER

Areal Distribution of Arsenic-Contaminated Groundwater

Fifty wells at this site have ever had arsenic concentrations in groundwater in excess of the U.S. EPA MCL. An average of 15 samples has been analyzed for arsenic from each well involved in this investigation. From those 50 wells, 13 wells have had arsenic concentrations in excess of 50 μg/L only one time. If the 13 wells are eliminated from consideration, the remaining 37 (of the total 240) with arsenic-contaminated groundwater represent only 15% of the wells (Fig. 2).

The mobility of arsenic relative to trichloroethene (TCE) can be inferred by comparing the locations of arsenic-contaminated wells with TCE-contaminated wells. TCE plume locations and concentration gradients have been established. Of the 240 total monitor wells, 118 (49%) have had concentrations of TCE in excess of 5 μg/L. If the dissolved arsenic is being transported by the advective flow of groundwater, the monitor wells downgradient from wells high in arsenic, as defined by the TCE plumes, should also have anomalous arsenic concentrations. Comparing the locations of arsenic-contaminated groundwater with the TCE plumes, there appears to be no correlation between the TCE plumes and arsenic-contaminated groundwater (Fig. 2).

The concentration gradient of arsenic in groundwater can be calculated at a cluster of monitor wells designated as the 439 series, all screened in the shallowest aquifer; these wells are located within 30 ft of each other (Fig. 3). At this location, the concentration gradient of arsenic is 390 μg/L per 100 ft. If this gradient is representative of this site and the background level of arsenic in groundwater is less than 50 μg/L, the maximum extent of the most concentrated arsenic-contaminated water (1,100 μg/L) would be on the order of 300 ft. Although arsenic is very soluble in the groundwater near certain wells at this site, it is not mobile.

Vertical Distribution of Arsenic in Groundwater

Groundwater samples have been analyzed from 240 wells and other sampling points on and off the site. The wells include 56 residential wells of unknown depth. The remaining monitor wells are distributed among the aquifer zones: A-zone 72, B-zone 52, C-zone 44, CD-zone 9 and D-zone 7. Arsenic-contaminated groundwater in excess of the U.S. EPA MCL has been measured at 50 of the 240 wells. Of those 50 wells, arsenic-contaminated groundwater exists primarily in the
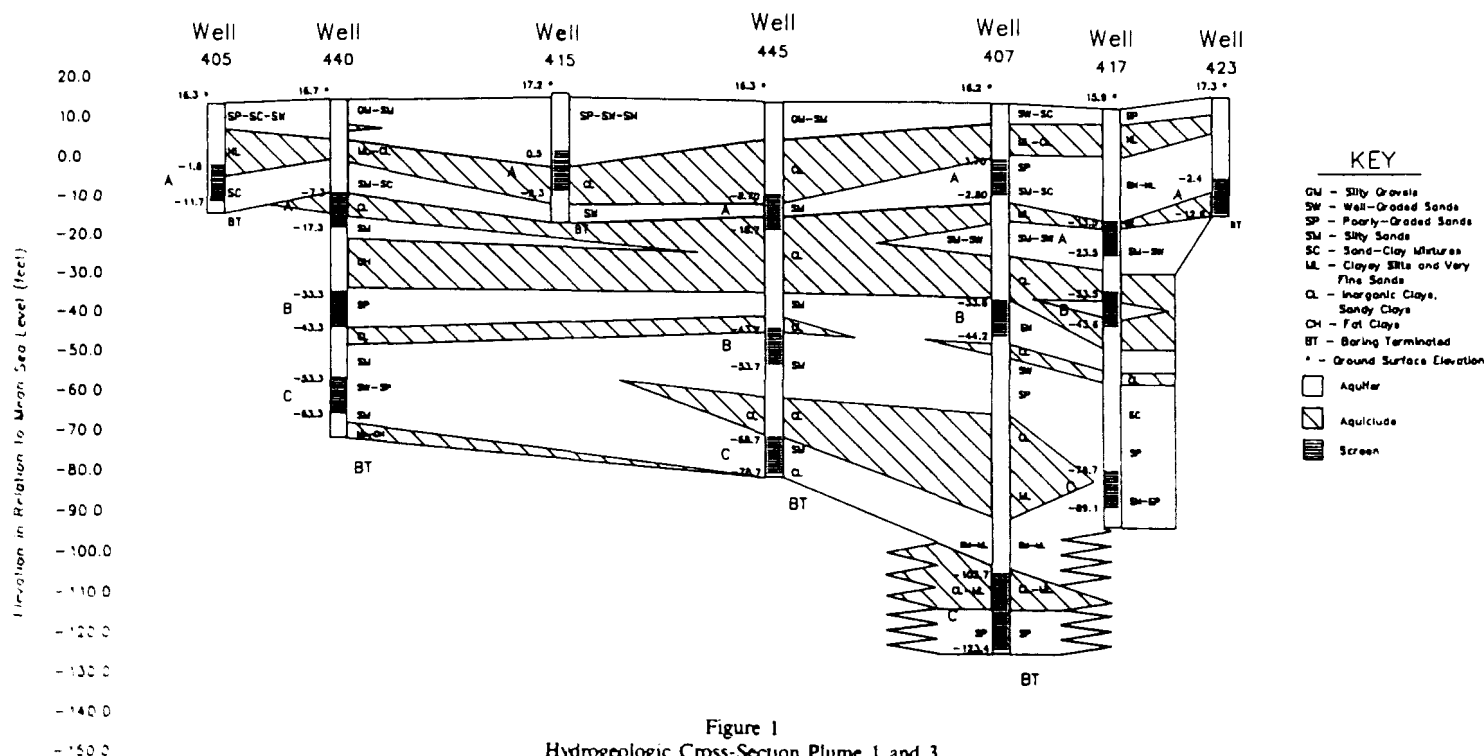
Figure 1
Hydrogeologic Cross-Section Plume 1 and 3
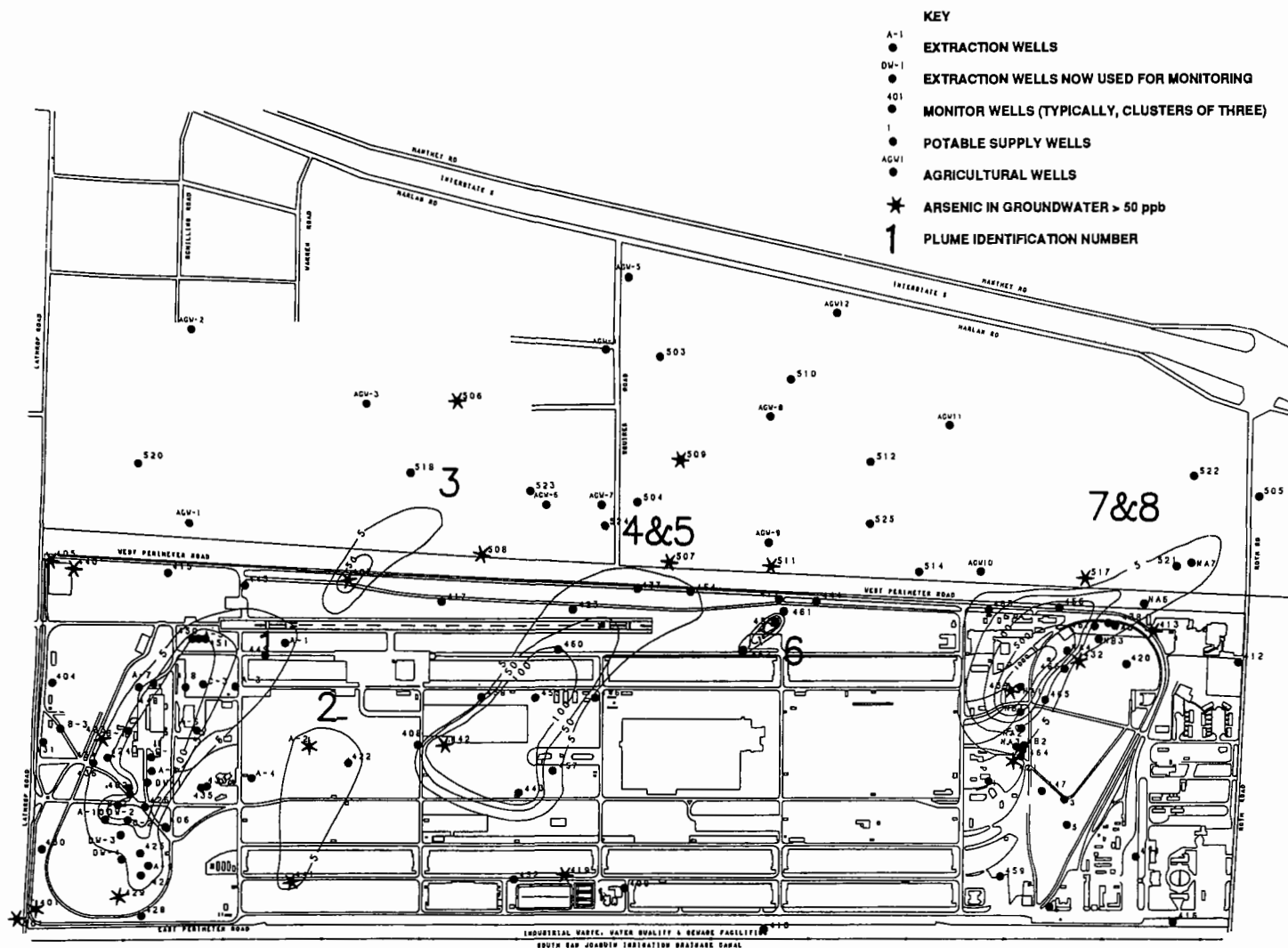
Figure 2
Well and TCE Plume Locations
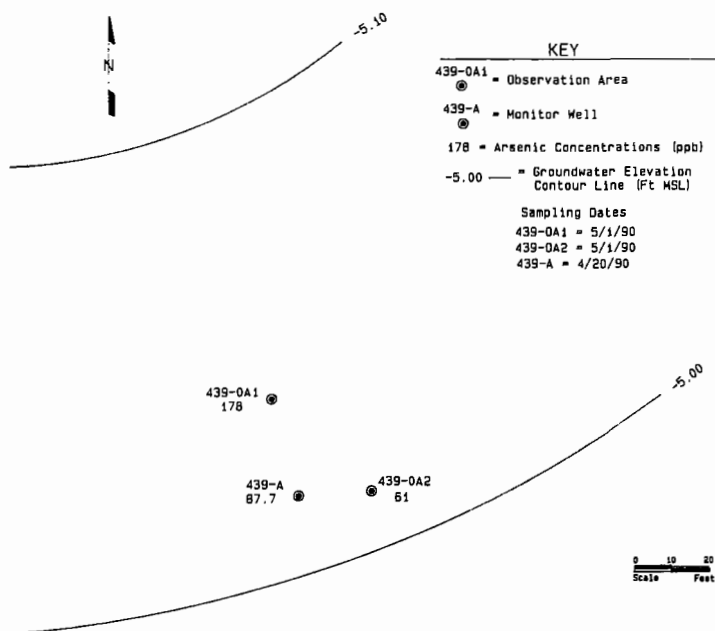
Figure 3
Arsenic Concentrations (ppb) in Groundwater at Well Cluster 439

shallowest zone. Arsenic concentrations greater than 50 μg/L were found in 31 wells in the A-zone, 7 wells in the B-zone, 3 wells in the C-zone and 2 wells in the D-zone (Fig. 4).

Prior to April 1990, groundwater samples from this site were analyzed only for VOCs, arsenic, selenium and bromacil. In April/May 1990, 66 wells were sampled and analyzed for 31 inorganic components that may be related to the behavior of arsenic, in addition to arsenic, VOCs, bromacil and selenium. The wells were selected on the basis of their historical arsenic concentrations. The wells with consistently high or low arsenic concentrations were selected.

The distribution of orthophosphate and vanadium are similar to arsenic. There are positive correlations between arsenic and orthophosphate and vanadium (Fig. 5 and 6). As with arsenic, the highest concentrations of dissolved orthophosphate and vanadium in these samples are restricted to aquifers within 50 ft of the surface (Fig. 7 and 8). Since phosphates, arsenates and vanadates have similar geochemical characteristics in general and similar distribution patterns at this site, the three components may have a similar source.

ARSENIC VARIATION WITH TIME

A total of 3,700 analyses of arsenic in groundwater has been recorded since 1984. Some wells have been sampled as frequently as twice a week, others once monthly, quarterly or annually. The wells with the highest sampling frequency have been sampled 66 times.

The wells with the highest average arsenic concentrations show the
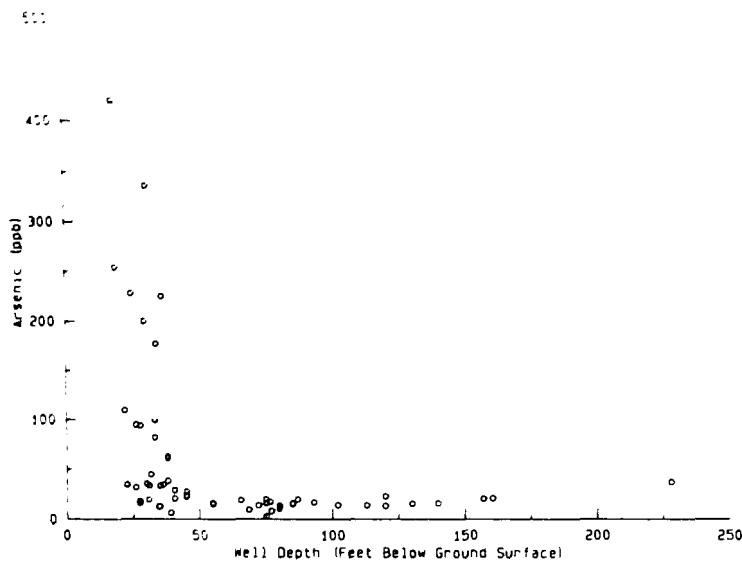
Figure 4
Arsenic Concentrations vs. Well Depth

U.S. EPA Method 3050 and analyzed according to U.S. EPA Method 7060. It should be noted that U.S. EPA Method 7060 is intended to analyze contaminants rather than whole samples, which is necessary for geochemical modeling.

As a working hypothesis, it was assumed that the arsenic source in the groundwater is naturally occurring arsenic minerals within or adjacent to the aquifers. The relatively dense arsenic-bearing minerals should be heterogeneously distributed, reflecting the various energy environments of fluviatile deposition.

Soils were sampled adjacent to 10 monitor wells, half with high arsenic and half with low arsenic. The soil data were analyzed for correlation with the groundwater from those wells and for the variations of arsenic in soil with increasing depth.

The arsenic concentrations were grouped by depth interval (0 to 5 ft, 5 to 10 ft, 10 to 15 ft, etc. and 30 to 35 ft). The groups were assumed to be paired sets and tested for sameness using the sign test. At the 95% confidence level, it can be said that arsenic concentration increases with depth to 15 ft. The 30- to 35-ft interval has a higher median arsenic value than all of the intervals above it. The concentration of arsenic
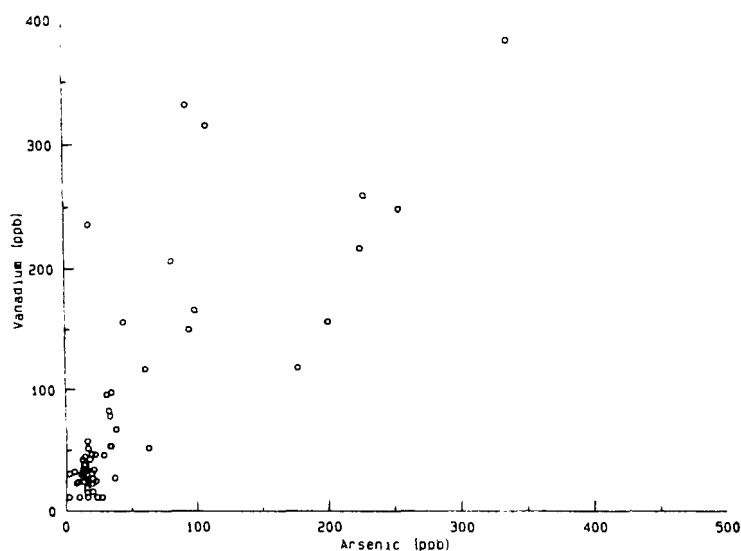
Figure 6
Arsenic Concentrations vs. Orthophosphate Concentrations

Figure 5
Arsenic Concentrations vs. Orthophosphate Concentrations

greatest variability of arsenic concentrations. As an example, Monitor Well (MW) 407A has been sampled 21 times since 1982. The lowest concentration measured was 11 μg/L; the highest was 952 μg/L. The average arsenic concentration in groundwater in MW 407A has been 358 μg/L (Fig. 9). Wells with low mean arsenic concentrations tend to show less variation (Fig. 10).

Arsenic concentrations were measured in both filtered and unfiltered fractions in the 66 samples collected in the April/May 1990 sampling event. The arsenic dissolved varied between 50 and 99%. X-ray diffraction analyses have been performed on the filtered solids collected with these samples. Quartz, calcite, dolomite, feldspars, mica and minor quantities of expanding clay have been identified in the filtered solids. No naturally occurring arsenic phases were recognized.

ARSENIC IN SOILS

To evaluate the soil as a source for arsenic in groundwater, 439 soil samples have been collected and analyzed for arsenic. The samples were collected with 18-in long split-spoon sampling tubes and composited over 5-ft intervals. The 439 soil samples were prepared according to

Figure 7
Orthophosphate Concentrations vs. Well Depth
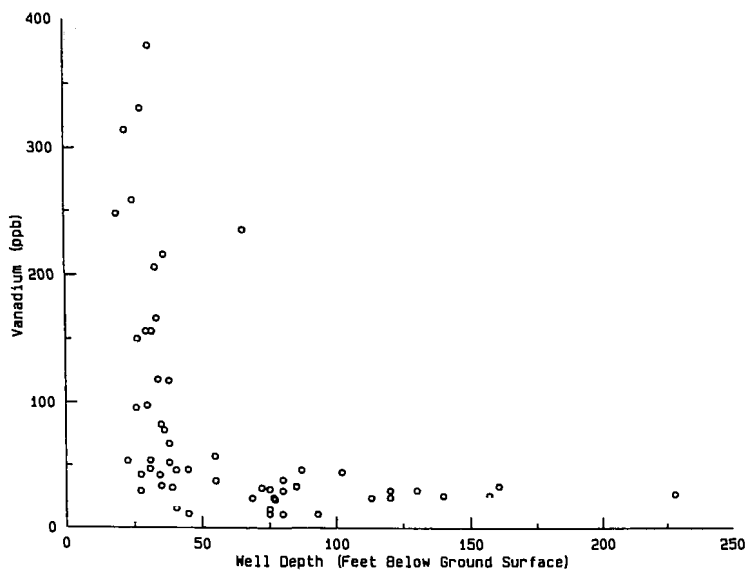
Figure 8
Vanadium Concentrations vs. Well Depth
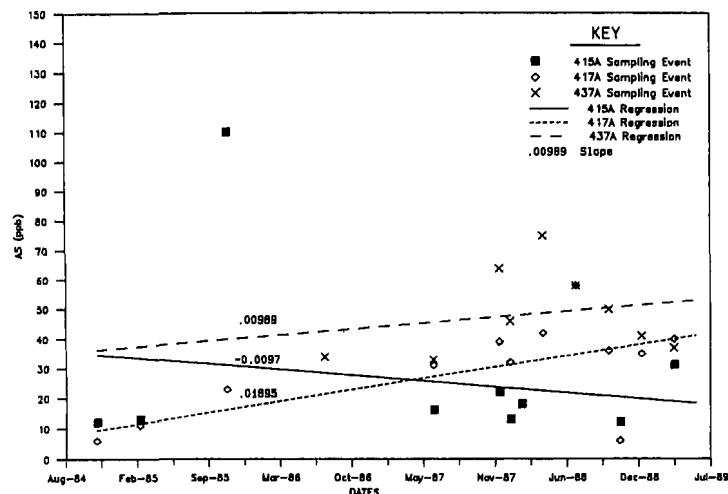
Figure 10
Historic Arsenic Concentrations in Groundwater at Monitor Wells
415A, 417A and 437A

Figure 9
Historic Arsenic Concentration Trends in Groundwater at MW-407A

more concentrated in the soil at this site than it is in the source rocks from which it was derived.

Recently, additional sampling was done in the immediate vicinity of the highest reading, 109 ppm, to test whether or not it is anomalous. A boring was completed within 0.5 ft of the first sample location. Additional samples were collected in a grid pattern around the sample location. Samples were collected with a split-spoon sampler and composited at 5-ft intervals. The results suggest that either the sample with 109 ppm is an extreme value in the natural distribution of arsenic in the subsurface at this site or error was introduced.

CONCLUSIONS

As a result of this investigation, the behavior of arsenic in soil and groundwater at this site can be summarized as follows:

- Arsenic concentrations in excess of the U.S. EPA MCL of 5 $\mu g/L$ have been measured in only 15% of the monitor wells at this site. The distribution of arsenic in the groundwater is not controlled by groundwater flow. Arsenic concentration gradients are approximately 400 $\mu g/L$ per 100 ft. Apparently, arsenic is not mobile in the groundwater at this site.
- Arsenic-contaminated groundwater is most soluble in the monitor wells that are screened within 50 ft of the ground surface, i.e., arsenic is more soluble in wells that are nearer the surface and probably in equilibrium with the atmosphere.
- The coefficient of variation of dissolved arsenic is related to the mean arsenic concentration at a given monitor well, i.e. a high percentage of variation in dissolved arsenic exists at most of the wells with high dissolved arsenic concentrations.
- The concentration of arsenic in soil increases with depth to 35 ft bgs. Either the depositional environment did not result in geochemical homogeneity, or infiltrating surface water is progressively leaching the arsenic-bearing minerals near the surface, or the source of the arsenic in the groundwater is not naturally occurring minerals.
- The arsenic concentration in shallow soil to a depth of 2 ft bgs beneath the study site is in the same statistical population as surface soil offpost.

The source of the excessive arsenic in the groundwater at this site is still being studied. The data will aid in evaluating potential sources.
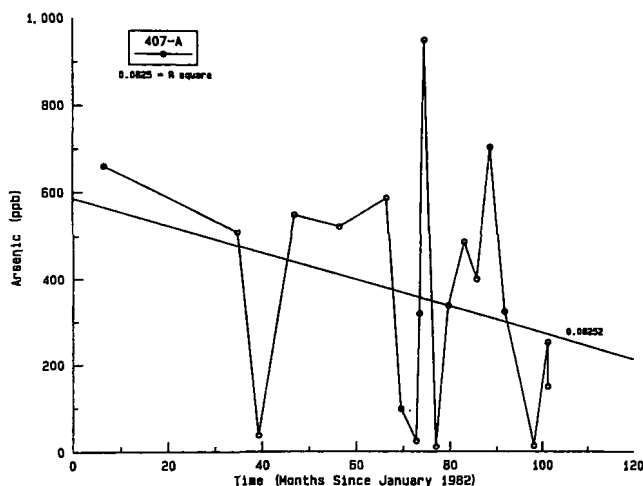
in soil increases with depth.

A second hypothesis, that pesticides were the source materials for arsenic in the groundwater, was investigated by measuring arsenic in soils collected from surface depressions upgradient from monitor wells with consistently high arsenic concentrations. Samples from soil borings were also collected within the only known pesticide storage area at the facility. Off-site samples were collected to establish natural background values of arsenic in soil in the vicinity of the facility.

The frequency distribution and the mean of the arsenic concentrations of 20 off-site soil samples were compared to 39 soil samples collected from 0 to 5 ft on-site using the Wilcoxon rank sum test. At a 95% confidence level, the two samples are from the same population. No evidence exists that differences occur in arsenic concentrations between off-site and on-site soil.

The average concentration of all 439 soil samples was 5.7 ppm. The average arsenic concentration of granite = 1.5 ppm, basalt = 2.0 ppm and shale = 6.6 ppm. No evidence indicates that arsenic is significantly

Role of Environmental Fate and Transport Data in Health Assessments: Four Case Studies

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ABSTRACT

In health assessments developed by the Agency for Toxic Substances and Disease Registry, data and information on the release of hazardous substances into the environment are evaluated to assess any current or future impact on public health, develop health advisories or other health recommendations and identify studies or actions needed to evaluate and mitigate or prevent human health effects. Analyses of fate and transport data and information are primarily used in the health assessment process as a guide to highlight the significance or sensitivity of an environmental pathway that may lead to a human exposure. We describe four case studies to illustrate the use of fate and transport data in the health assessment process.

INTRODUCTION

The Agency for Toxic Substances and Disease Registry (ATSDR) is charged under CERCLA, as amended, to perform health assessments for each site listed, or proposed to be listed, on the NPL. In addition, ATSDR may perform a health assessment on a RCRA facility in response to a petition from a citizen. In an ATSDR health assessment, data and information on the release of hazardous substances into the environment are evaluated to assess any current or future impact on public health, develop health advisories or other health recommendations and identify studies or actions needed to evaluate and mitigate or prevent human health effects.

An ATSDR health assessment differs from a U.S. EPA risk assessment in several important details. Health assessments are qualitative, site specific and concentrate on medical and public health perspectives. U.S. EPA risk assessments are quantitative, compound-oriented and use statistical and biological models to calculate numerical estimates of risk.

Environmental engineers and health scientists who perform health assessments evaluate all available data and information on a hazardous waste site. These data and information come from three sources: environmental data bases, health outcome data bases and community concerns. The assessor first identifies the contaminated media and contaminant transport mechanisms (that is, environmental pathways). Then the chemical- and site-specific factors are evaluated to determine how they are influencing the environmental fate or transport of the contaminants in the environmental media.[1]

Analysis of the chemical- and site-specific factors that influence fate and transport of contaminants can lead to three different approaches within a health assessment. These analyses can be used to: (1) determine why or how contaminants have reached a certain monitoring location or exposure point; (2) rule out environmental pathways (for example, movement of contaminant "X" within the surficial groundwater will not occur because the organic carbon partition coefficient indicates it will strongly sorb to soil); or (3) highlight the sensitivity of an environmental pathway (for example, rapid and significant movement of contaminant "X" is highly likely because of the sandy nature of the subsurface geology). Analyses of fate and transport data and information, however, are primarily used in the health assessment process as a guide to highlight the significance or sensitivity of an environmental pathway that may lead to a human exposure. Furthermore, fate and transport analyses are not a substitute for quality monitoring data.

Using case studies, we illustrate how fate and transport analyses are not a substitute for quality monitoring data.

Using case studies, we illustrate how fate and transport analyses are used in the health assessment process to evaluate the environmental and human exposure pathways and to lead to recommendations to further evaluate public health implications and to protect public health. All case studies are based on actual site data and information.

CASE 1

The LMN site is the location of a former mixing and batching operation. The extensive contamination at the now closed site is the result of the disposal and release of many substances, including creosote. Two major constituents of creosote are naphthalene and 2-methyl-naphthalene. This discussion highlights the importance of the mitigation of groundwater as an environmental pathway for these two compounds at this site.

The groundwater became contaminated from the percolation of wastewater and the leaching action of rainwater on contaminants in the soil column. Free product consisting of creosote has been found floating on top of the water table. The groundwater contamination is comprised of many substances, including 2-methylnaphthalene and naphthalene. In the surficial groundwater, the maximum levels detected of both compounds combined exceed 20,000 ug/L.

Some of the chemical-specific factors that would influence the transport and fate of naphthalene and 2-methylnaphthalene are listed in Table 1.[2,3] Both compounds are bicyclic aromatic hydrocarbons and are relatively water soluble and volatile in comparison to the related polycyclic aromatic hydrocarbons (PAHs). Although less lipophilic than the PAHs, both compounds would tend to adsorb onto organic rich sediments and soils and to moderately bioconcentrate based on the log octanol-water partition

coefficients and bioaccumulation factor.

Site-specific factors favor the transport of both compounds in the groundwater. The former facility was situated on the eastern flank of a hill, which slopes eastward to a small river. The surficial groundwater flows to the east and downward until near the river and bordering wetlands where the hydrogeological gradient is upward. The competency of the bedrock in this area varies, but fracturing is apparent especially in the bedrock valleys and depressions. The available monitoring data for the shallow bedrock aquifer indicate a hydraulic connection between the overburden and bedrock aquifers, although the transfer of water from one aquifer to the other is impeded by a layer of till overlying the bedrock.

Table 1
Fate and Transport Data for Naphthalene and 2-Methylnaphthalene

FACTOR	NAPHTHALENE [2]	2-METHYLNAPHTHALENE [3]
CAS#	91-20-3	91-57-6
Molecular Formula	$C_{10}H_8$	$C_{11}H_{10}$
Molecular Weight	128.16	142.2
Log Octanol-Water Partition Coefficient	3.30	3.86
Water Solubility (mg/L at 25° C)	31.7	24.6
Vapor Pressure (mm Hg at 25° C)	0.082	0.068
Henry's Law Constant (atm-cu m/mol)	4.83×10^{-4} 5.53×10^{-4}	2.6×10^{-4} 5.18×10^{-4}
Bioconcentration Factor	39.8-1,000 aquatic animals	40-300 rainbow trout 470-2,800 starry flounder 28-190 coho salmon

Most of the contaminated surficial groundwater, and probably most of the shallow bedrock groundwater, discharges to the river. A component of the contaminant plume extends east of the river because: (1) the hydrogeological gradient from the east is more gentle than that from the west and (2) a thick layer of sediment in the river retards some of the discharge. The groundwater contamination is excessive but is mostly contained within the site boundaries because of: (1) the incoming groundwater flow from the other side of the river; (2) the slow rate of the northerly flowing surface water; and (3) the presence of a northward trending bedrock incline beneath the river.

Contaminated groundwater discharges into the river. Attenuation by the organic-rich sediments is likely a predominant fate of 2-methyl-naphthalene and naphthalene, rather than discharge to the river surface water. Based on the difference between the concentration of select contaminants detected in groundwater at a depth of 5 ft and that detected in a seepage meter, an estimated 90 to 100% of the organic contamination is trapped in the sediments. The results of monitoring of the sediments highlight the importance of the bioaccumulation pathway. Naphthalene and 2-methylnaphthalene were detected in sediments from all depths monitored (to 36 in.) at levels to 36,000 and 21,000 ug/kg, respectively.

Decreases in contaminant concentrations in the sediments at this location may occur by one of three mechanisms. First, biodegradation of these two compounds occurs, especially in sediments with acclimated microorganisms, and is expected to be a major route of loss from sediment.[2,3] Second, following resuspension, sediment-bound naphthalene and 2-methylnaphthalene can be transported downstream (and off-site) with surface water flow. Resuspended sediments will tend to resettle where surface water flow is reduced. In support of this interpretation, naphtha-

lene and 2-methylnaphthalene have been detected in the downstream surface sediments at levels to 1,200 and 920 ug/kg, respectively, and as far as 0.5 mi downstream in a pond.

Third, these compounds may be released in solution from the sediments to the surface water. Contamination of surface water is likely of less importance than contamination of sediments or groundwater. Any contaminant released or not trapped by the sediments will be rapidly diluted. Groundwater from the site is estimated to discharge to the river at a maximum rate of 0.03 ft³/sec and to represent less than 1% of the river's discharge upstream or downstream of the site. In addition, any naphthalene and 2-methylnaphthalene present in solution would tend to volatilize based on the calculations using Henry's Law constants. Decomposition via biodegradation and photolysis and adsorption to particulates are other mechanisms of loss from surface water for these chemicals.[2,3] Monitoring of the river's surface water has resulted in the sporadic, low-level detection of naphthalene (<21 ug/L) and 2-methylnaphthalene (<21 ug/L) and demonstrates that surface water is not a predominant pathway.

Although fish bioconcentrate naphthalene and 2-methylnaphthalene to moderate extents, fish also tend to metabolize these compounds.[2,3] Limited monitoring data are available for the fish in the river. Fish from on-site locations and the pond downstream were found to contain detectable levels of naphthalene and 2-methylnaphthalene. Not enough information is available to determine: (1) the effect of trophic level on contaminant concentration, (2) the distribution of these compounds to the edible fillet, (3) the relative contribution of sediment and surface water to the contamination and (4) the influence of distance from the site. A chain pickerel (*Esox niger*), however, from the site contained the highest level of contamination detected (1.2 mg/kg 2-naphthalene and 2.3 mg/kg naphthalene). Once fish are removed from naphthalene and 2-methylnaphthalene, depuration is rapid.[2,3] These compounds continue to be discharged from the groundwater to the river, however, and additional characterization of the fish contamination in the vicinity of the contamination should be considered.

The environmental pathways that can be highlighted as important are related to groundwater, sediment and, perhaps, fish. Human exposure to naphthalene and 2-methylnaphthalene might occur via ingestion of fish and incidental ingestion of sediment and dermal contact with sediments. Because no water supply wells intercept the overburden or shallow bedrock groundwater, exposure to these chemicals via ingestion of groundwater is unlikely. Details regarding groundwater and contaminant transport in deep bedrock are not available, but exposure appears unlikely because no deep bedrock wells are near the site and other wells are less likely to be installed in fractures bearing contamination from this source. Because surface water and probably ambient air are not contaminated to a great extent, humans are not likely to be exposed via these pathways at this time.

CASE 2

The QRS site is the location of a series of former dye manufacturers. During the production of some dyes, mercury was used as a catalyst. For 40 yr, 3,000 to 5,000 lb of unrecovered mercury were released annually. Most of the mercury was released in the effluent discharging into the nearby wetlands and in sludges discarded on top of a nearby hill.

Chemical-specific factors that would influence the transport and fate of mercury depend on the species of mercury present; however, the relative proportion of each species present is apt to change as local conditions change. Transport and fate data for some mercury species are given in Table 2.[3,4] This case example highlights methylated mercury in soil and sediments, although other environmental media also are impacted.

Surface run-off containing mercury-contaminated sludges and soils migrated down the hill and into the wetlands. From the wet-

land areas, soluble and particulate bound mercury were transported off-site from the wetlands via a brook to a nearby river. In the river, sediments, fish and, to a lesser extent, surface water are contaminated by mercury.

The potential exists for the methylation of mercury in the environment, particularly in wetland areas and river sediments.[3-5] Dimethylmercury and methylmercury are formed from inorganic mercury by both biotic enzymatic and nonenzymatic processes and abiotic mechanisms. Biological methylation of mercury can occur in aerobic and anaerobic environments and depends on: (1) the quantity of divalent mercuric ion present, which depends on the pH, redox potential and the presence of organic ligands; and (2) the abundance of microorganisms, which depends in part on the presence of wet, organic soils and specifics regarding microbial metabolism. A competing microbial process, demethylation, also can occur. Because of the various factors involved in methylation and demethylation, the amount of methylated mercury produced would be difficult to predict. The detection of dimethylmercury in the wetland soils/sediments and methylmercury in the surface water supports this interpretation; however, the available monitoring data are limited.

Table 2
Fate and Transport Data for Select Mercury Compounds[3,4]

FACTOR	MERCURY	MERCURIC CHLORIDE	METHYLMERCURY	DIMETHYL-MERCURY
CAS#	7439-97-6	7487-94-7	22967-92-6	593-74-8
Molecular Formula	Hg	$HgCl_2$	CH_3Hg	C_2H_6Hg
Molecular Weight	200.59	271.5	215.62	230.66
Water Solubility (mg/L)	56	7.4×10^{-4} at 25 C	NA	NA
Vapor Pressure (mm Hg)	2×10^{-3}	NA	NA	NA
BCF*	$10,000^1$ $63,000^3$	$10,000^1$	$40,000^2$	NA

NA– Not available.
* BCF, bioconcentration factor.
[1] Bioaccumulation factor for oyster and saltwater fish.
[2] Bioaccumulation factor for oyster.
[3] Bioaccumulation factor for freshwater fish.

Dimethylmercury and methylmercury have different chemical and physical properties. Methylmercury is both water and lipid soluble. Therefore, methylmercury tends to be found in surface waters and to bioconcentrate in fish and other organisms. Most of the mercury found in fish is in the form of methylmercury; however, methylmercury also may be formed from inorganic mercury in the intestine and liver of fish.[4,5] The recent monitoring of off-site fish for mercury and methylmercury indicates that more than 95% of the mercury found in the fish is in the form of methylmercury. The fish fillet contained more total mercury and methylmercury than did the remainder of the fish (that is, the offal).

Dimethylmercury is lipophilic, nearly insoluble in water and very volatile. Dimethylmercury would tend to remain bound to organic-rich soils or sediments until volatilized when exposed to air. Factors that might increase the chance of volatility are: (1) a lack of moisture in the vadose zone, (2) warm temperatures, (3) sunlight, (4) a decrease in the barometric pressure and (5) soil movement activities. Because the monitoring data are limited and site-specific factors would influence volatilization, the sensitivity of this pathway at this site would be difficult to predict; however, baseline monitoring of ambient air resulted in the sporadic

detection of dimethylmercury at levels near the method's detection limit.

Human exposure to methylated mercury may occur via ingestion of fish (methylmercury) and incidental ingestion of surface water, sediments and soils (methylmercury and dimethylmercury); via dermal adsorption from soils, sediments and surface water (methylmercury and dimethylmercury); and via inhalation (dimethylmercury). Special concern exists in the wetland areas if soils are disturbed because of the uncertainties mentioned previously.

In lieu of additional soil and sediment characterization, a near real-time monitoring method for dimethylmercury in ambient air was recommended and developed. This method is being used at the QRS site during remediation activities entailing soil and sediment excavation. Because of the elevated levels of mercury in fish, a health advisory was issued jointly by several state agencies warning against the consumption of fish obtained from the river.

CASE 3

The HIJ site is an inactive landfill that operated from 1963 to 1981. Various wastes were disposed of at the site, including municipal wastes, septage, industrial wastes and hospital wastes. Although many contaminants have been detected in sampling of the on-site media, toluene is considered a contaminant of concern—primarily because it was detected in shallow groundwater samples at concentrations up to 100,000 ug/L.

Some of the chemical-specific factors that could influence the fate and transport of toluene are listed in Table 3. Although toluene is a liquid at room temperature, it is sufficiently volatile (based on vapor pressure) that the majority of toluene in the environment exists in air. Furthermore, the Henry's Law constant for toluene indicates that it is moderately volatile when dissolved in water. Toluene that is released to surface water and soils tends to evaporate quickly. On the basis of the log values of the octanol-water partition coefficient and the organic carbon partition coefficient, toluene will be moderately retarded by adsorption to soils rich in organic matter, but will be readily leached from soils with low organic content. In addition, because of toluene's lipophilic properties, it also has a moderate tendency to bioaccumulate in the fatty tissues of aquatic species.[6]

Table 3
Fate and Transport Data for Toluene[6]

FACTOR	TOLUENE [6]
CAS#	108-88-3
Molecular Formula	$C_5H_5CH_3$
Molecular Weight	92.15
Log Octanol-Water Partition Coefficient	2.79
Log Organic Carbon Partition Coefficient	2.47
Water Solubility (mg/L at 20° C)	515
Vapor Pressure (mm Hg at 20° C)	22
Henry's Law Constant (atm-cu m/mol)	6.66×10^{-3}
Bioconcentration Factor	10.7 fish 4.2 mussels

The major site-specific factor that influences the environmental pathways is the hydrogeology of the site. Most of the unconfined shallow groundwater flows to the east of the landfill and is

discharged to a swamp and creek or forms leachate ponds. The confined deep aquifer underlying the site, which is the source of potable water in the vicinity of the site, was not contaminated. The hydrogeology of the site indicates that there is an upward hydrogeological gradient between the deep and shallow aquifers that causes groundwater to leak into the shallow aquifer and finally be discharged to the creek.

Because of the sandy nature of the soil at the site, toluene is not expected to be significantly attenuated by the sediment at the surface water discharge areas. Furthermore, since toluene tends to volatilize relatively rapidly from surface waters, the sensitivity of the air environmental pathway is highlighted. Sampling and analysis of on-site sediment and surface water were not performed. A photoionization detector was used to analyze ambient air around the surface water areas; results indicated elevated levels of organic vapors.

On the basis of the analysis of the chemical- and site-specific factors, the major potential exposure route to toluene at the site was determined to be through incidental inhalation by trespassers or through inhalation by residents living near the site. For that reason, on-site ambient air monitoring for toluene, under varying meteorological conditions, was recommended. Furthermore, if appreciable concentrations of toluene were detected in the air on the site, additional sampling at potential exposure points (residential areas), under varying meteorological conditions, was recommended. Although toluene is known to moderately bioaccumulate in aquatic species, this is not an environmental pathway of concern because it was determined that the creek and other potentially affected surface waters did not support edible aquatic organisms. Sampling of the surface water and sediment, to verify that these do not pose human exposure pathways of concern for incidental ingestion or dermal contact, was recommended.

CASE 4

At the KK site, filling operations reportedly occurred in 1978 after peat deposits were excavated. The landfill material consists of lead-acid battery casings that are buried in both the saturated and unsaturated zones. The layer of casings is estimated to be 6 to 12 ft thick. A thin layer of sand covers the battery cases.

The site lies just west of a freshwater marsh. Numerous aquatic organisms, including freshwater clams, live in the marsh. A canal cutting through the site connects this marsh with another march located west of the site. A large lake is located at the north end of the property. The groundwater flow direction in the surficial aquifer is toward the marsh east of the site. The surficial aquifer discharges to this marsh and has contributed to the contamination of the marsh. The marsh flows into a small stream to the southeast of the landfill, which eventually empties into a bay.

Some of the chemical-specific factors that would influence the fate and transport of lead are listed in Table 4. The chemistry of lead in aqueous solution is highly complex because it can be found in many different forms. Lead has a tendency to form low-solubility compounds with the major anions of natural water. In the environment, the divalent form is the stable ionic species of lead. Hydroxide, carbonate, sulfide and, sometimes, sulfate may act as solubility controls in precipitating lead from water. The amount of lead that remains in solution depends on the pH of the water and the dissolved salt content. A significant fraction of lead in water is expected to be in an undissolved form, which can consist of colloidal particles or larger undissolved particles of lead carbonate, lead oxide, lead hydroxide or other lead compounds incorporated in other components of surface particulate matter from run-off.[7]

Except for some shellfish, lead does not appear to bioaccumulate significantly in fish. The predominant fate of lead in surface water is sorption to sediments. The adsorption of lead is pH dependent, increasing with increasing pH.[7]

Table 4
Fate and Transport Data for Lead[7]

FACTOR	LEAD [7]
CAS#	7439-92-1
Molecular Weight	207
Water Solubility (mg/L at 25° C)	insoluble
Vapor Pressure (mm Hg at 980° C)	1

Surface water appears to be the primary environmental medium for migration of contaminants off-site. Lead was detected in water samples from the marsh. Only total lead was reported; the lead compounds were not differentiated. Unfiltered samples contained lead at a maximum of 46 mg/L; filtered samples, at a maximum of 1 mg/L. The water in the marsh has a pH near 7. The chemical-specific properties of lead suggest some possibly sensitive environmental pathways. Lead has a tendency to be adsorbed to sediments. Since lead was found in the surface water, an expected environmental pathway would be the adsorption of lead from the surface water to the sediments. Monitoring data confirm that lead is concentrating in the sediments at 17,741 mg/kg. Since the marsh discharges to a nearby stream, the contaminated water and sediments may be transported by this surface water flow. This lead transport process should be somewhat limited by the low flow of the marsh. Since lead has been shown to bioaccumulate in some shellfish, bioaccumulation of lead from the water and sediments by the claims is a potentially sensitive environmental pathway.

The vapor pressure of lead indicates that it is not volatile. Accordingly, volatilization of lead from the surface water to the air is not considered a sensitive environmental pathway. Site-specific characteristics rather than chemical-specific characteristics indicate that transfer of lead from surface water to groundwater is not a sensitive environmental pathway. Because the surficial aquifer discharges to the marsh, discharge from the surface water to groundwater is unlikely.

The possible human exposure pathways are ingestion of contaminated surface water and contaminated shellfish and dermal exposure to surface water. Because the site area is relatively uninhabited, exposure to surface water is expected to be infrequent and incidental. The clams are not consumed at all. Therefore, under current site use scenarios, the human exposure pathways are incomplete.

CONCLUSIONS

Analysis of the chemical- and site-specific factors that influence fate and transport of contaminants can lead to three different approaches within a health assessment. These analyses can be used to: (1) determine why or how contaminants have reached a certain monitoring location or exposure point; (2) rule out environmental pathways; or (3) highlight the sensitivity of an environmental pathway. Analysis of these factors, however, is primarily used in the health assessment process as a guide to highlight the significance or sensitivity of an environmental pathway that may lead to a human exposure. Fate and transport analysis, however, is not a substitute for quality monitoring data.

The four case studies illustrate how the analysis of fate and transport data is used in the health assessment process to highlight the sensitive environmental pathways. This analysis helps the assessor to determine the likely human exposure pathways. This guides further evaluation into the land use and behavior patterns around a site and helps to determine if the human exposure

pathway is complete, as shown in Cases 3 and 4. In Cases 1 and 2, where human exposure pathways are complete, potential public health implications can then be determined and appropriate actions to protect public health can be recommended.

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Sensitivity Analysis of Surface Water Modeling Assumptions and the Impact On Risk Assessment

Case II: Seasonal Variation in Temperature and River Flow in Tidal and Nontidal Models

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ABSTRACT

This paper presents the second in a series of case studies on sensitivity analysis of parameters used in the Exposure Analysis Modeling System (EXAMS Version 2.92). The first case study presented the variability in the concentrations of three chemicals, vinyl chloride (VC), hexachlorobutadiene (HCB) and benzo(a)pyrene (BaP), in tidal and nontidal models with various values for dispersion and reaeration. This second case study presents the results of tidal and nontidal models using actual data on seasonal variation in flow and temperature in the Delaware River. High and low values for river flow and temperature were run in the tidal and nontidal models resulting in eight versions of the model.

The most significant effect of all variables tested was the more than 300-fold decrease observed in the upstream concentrations in the water column as a result of a 7-fold increase in flow in the tidal models. For all other scenarios (tidal versus nontidal, warm versus cold temperature and chemical properties), the changes in water column concentrations between model runs were either proportional to the changes in the value or minimal (less than 50%).

Risk assessors frequently use standard worst case assumptions to predict exposure concentration such as 7-day, 10-year flow values frequently used. For drinking water intakes in tidal systems upgradient from the source, the impact of flow on the exposure concentration is significant. Use of worst case data to represent lifetime risk can result in an overestimation of the average lifetime risk.

There were significant differences in the concentrations in the benthic and suspended sediment and the relative distribution of the mass of the chemicals between the water column and the benthic sediment due to differences in chemical properties.

INTRODUCTION

Risk assessors are aware that a single number cannot accurately represent risk because of the uncertainty inherent in predicting human health and environmental effects. Risk estimates are numerical values based on the concentration at the point of exposure and the potential of the chemical to have an adverse health effect on man or his environment. The focus of this paper is to examine the uncertainty present in estimates of exposure concentrations obtained from surface water models and the impact on estimates of risk.

Surface water models are frequently used to estimate exposure concentrations for drinking water intakes, recreational use of rivers and lakes and impacts to aquatic life. Data for site-specific model parameters such as flowrates and mixing characteristics require long-term base line data and/or are expensive to obtain. Therefore, risk assessors and modelers rely on data available in the literature for similar aquatic systems or estimation of several parameters from a limited data base. Frequently, there is a range of values to select from and a degree of

uncertainty is added to the model. Even when site-specific data are available, the variability in aquatic systems adds uncertainty.

These sources of uncertainty need to be understood by the modeler so that the risk assessor can develop a range of potential risk estimates around the variability in exposure concentrations. The uncertainly can be quantified by a sensitivity analysis which describes the effect of using several values for different model parameters in all possible combinations.

This paper presents the second in a series of case studies on sensitivity analysis of parameters used in the Exposure Analysis Modeling System (EXAMS Version 2.92).[1] The first case study presented the variability in the concentrations of three chemicals in tidal and nontidal models with various values for dispersion and reaeration. The model simulated the Delaware River using long-term low flow conditions reported in the literature. Low flow, worst case conditions are typically assumed for risk assessment purposes.

This second case study presents the results of tidal and nontidal models using actual data on seasonal variation in flow and temperature in the Delaware River. High and low values for river flow and temperature were run in the tidal and nontidal models resulting in eight versions of the model.

Flow rate is highly variable in all rivers and streams within and between years. Although the U.S. Geological Survey (USGS) maintains gauging stations throughout the United States, there still are many rivers and streams without sufficient information. Typically, modelers rely on estimating annual average flows for different periods based on the area of the watershed and flow/area relationships for nearby watersheds with a gauging station.

There are several ways that flow can affect the final concentration. Flow determines the flushing rate, velocity, depth, width, cross sectional area and, as a result, the reaeration rate. Temperature is also a critical parameter and controls the rates of many processes affecting the fate of pollutants in surface water such as volatilization and biodegradation. This study investigated the effect of temperature on volatilization. Other chemical-specific processes, biodegradation, photolysis and hydrolysis, were assumed to not occur.

METHODS

Model Construction

The EXAMS model parameters and values used for this study are presented in Table 1.

The EXAMS surface water model is built by dividing the river into a series of connected segments. Each segment consists of compartments that represent different media, e.g., benthic sediment or water column.

Table 1
Physical, Hydrogeological and Chemical Parameters Typically Needed for Surface Water Models

Physical	Hydrological
Bed geometry	- velocity of flow
- width	- rate of flow (advection)
- depth	- tidal and non-tidal mixing
- length	(dispersion)
	- reaeration rates
Sediment characteristics	
- total organic carbon	Chemical
- bulk density	
- percent water	- biodegradation
	- hydrolysis
Climate	- photolysis
- temperature	- sorption to sediments
- wind speed	

The segments and compartments are connected by advective and/or dispersive flow. In our model, the water columns of adjacent segments in a downriver direction were connected by advective flow, low or high rates of discharge. Advective flow entered the first segment only and no additions from tributaries were included.

Dispersion was used to connect the sediment and water in all forms of the model and to describe the effect of tides in the tidal models. The sediment and water columns were connected by a moderate dispersion factor, 0.00001 m²/hr in all models. This same factor was used to connect adjacent water column compartments in the nontidal model. In the tidal model, the upriver mixing induced by tides was described with a factor of 5 x 10⁴ m²/hr for dispersion between one water column and the adjacent upriver water column. This tidal dispersion factor is the highest of the two values used in the first case study.

The model consisted of 11 segments each with four media, sediment, pore water, water column and suspended sediments. EXAMS also allows for incorporation of biota, but this medium was not included. The segments were 2000 feet in length for a total of 22,000 feet or 3.6 river miles. A steady-state format of EXAMS was used assuming an infinite, continuous source of the three chemicals. For the tidal model, the chemical load was added as a diffuse source into the middle segment and to the first segment into the advective flow for the nontidal model.

Second order process models are used to describe the kinetics of the chemical reactions. The program is based on a series of mass balances for each compartment that give rise to a single differential equation for the contaminant in the water column and the benthic zone in each segment.

Changes Between Case I and Case II Models

The values used in Case I for model parameters for the dispersion coefficient and fraction organic carbon in the sediment of 0.1 m²/hr and 0.0001, respectively, were changed for Case II to 0.00001 m²/hr and 0.01, respectively. The changes were made to more accurately represent river conditions. The most important impact of the changes is likely to be an increase in the mass of chemical located in the sediments with lesser impacts to the concentration in the water.

Also, the load added via seep flow in the Case I model was changed to a drift load addition in Case II. The change was made to avoid exceeding the solubility limit for the chemicals at the cold temperature in the seep flow and to achieve strict comparability among cases. EXAMS will not allow the solubility to be exceeded.

Model Variables

High and low values for flow rate and temperature were used in the eight versions of the model prepared for this analysis (Table 2). Site-specific data were obtained from rating tables and discharge rates and temperature for 1986-1987 provided by the USGS for the Delaware River at Trenton, New Jersey. The river is not tidal at this point so that the tidal construct of the model does not strictly apply to this section. The

highest and lowest mean monthly rates of discharge and temperature, 4.1 x 10⁵ and 3 x 10⁶ m³/hr and 2 and 27 °C, respectively, were selected. The values for bed geometry, depth, width and cross-sectional area, were calculated from the rating tables provided by USGS.

Table 2
Model Variables

		LOW	HIGH
Flow / Geometry			
Water			
	volume (m3)	2.7 E+5	6.2 E+5
	area (m2)	2.1 E+5	2.7 E+5
	depth (m)	1.3	2.3
River Flow			
	flow rate (m3 / hr)	4.1 E+5	3.0 E+6
Temperature (deg. C)		2	27
Tidal Dispersion (m2 / hr)		0.1	5.4 E+5

Since the width, depth and cross sectional area of the bed geometry change with flow rates, the variability in these parameters is automatically included in any study of the variation in flow. The reaeration coefficient, K_{o2}, was calculated from a value of 0.8/day and the depth. As a result, the coefficients for high and low flow were different because the depths at high and low flow are 2.3 and 1.3 m, respectively.

Study Chemicals

Each model was run with three chemicals, vinyl chloride (VC), hexachlorobutadiene (HCB) and benzo(a)pyrene (BaP). These three chemicals were also used in the first case study because they represent a range of chemical properties. The minimum information needed on chemical properties for EXAMS is molecular weight, Henry's Law constant, vapor pressure, solubility and octanol-water partition coefficient (Kow) (Table 3). Note that the first case study incorrectly suggests that molecular weight is not required.

Table 3
Chemical Properties of Study Chemicals

Chemical	Henry's Law Constant (atm * m * 3/ mol)	Water Solubility (mg / L)	Kow (mg / L: mg / L)	Molecular Weight
Vinyl Chloride (VC)	8 2 E-2	2.7 E+3	24	63
Hexachlorobutadiene (HCB)	4 75	1 5 E-1	6.0 E+4	2 61 E+2
Benzo (a) pyrene	1 6 E-6	1.2 E-3	1 2 E+6	2.52 E+2

Source EPA, 1986

VC is volatile and has little tendency to sorb to sediments as shown by the high Henry's Law constant and low Kow. HCB is both volatile and sorbs to sediments, while BaP has a low volatility and strong tendency to sorb to sediments.

These values for chemical properties were obtained from a variety of sources in the literature; however, they do not necessarily represent the average of the reported values. In particular, the value for vapor pressure for HCB used for this study is the highest reported for this chemical. The selection was biased to achieve a particular representa-

tion of different chemical properties.

Parameters to simulate biodegradation, hydrolysis and photolysis were set at zero to avoid multiple process effects. In a "real" world model, these processes, in particular photolysis for BaP, play an important role in fate and transport.

RESULTS

The most significant effect of all variables tested was more than 300-fold decrease in the upstream concentrations in the water column

Table 4
Concentration of Chemicals in Water Column

| | | Concentration of Chemicals in Water Column (mg / l) | | |
		VC	HCB	BaP
Low Flow Tidal				
Cold				
	Upriver	1.2E-10	1.3E-10	9.8E-11
	Source	1.2E-08	1.2E-08	8.7E-09
	Downriver	6.3E-09	6.6E-09	5E-09
Warm				
	Upriver	1.1E-10	1.2E-10	9.8E-11
	Source	1.1E-08	1.2E-08	8.7E-09
	Downriver	5.8E-09	6.4E-09	5E-09
High Flow Tidal				
Cold				
	Upriver	3.4E-13	3.5E-13	2.5E-13
	Source	1.7E-09	1.7E-09	1.2E-09
	Downriver	1.3E-09	1.3E-09	9.8E-10
Warm				
	Upriver	3.4E-13	3.4E-13	2.5E-13
	Source	1.7E-09	1.7E-09	1.2E-09
	Downriver	1.3E-09	1.3E-09	9.8E-10
Low Flow Nontidal				
Cold				
	Source	1.2E-08	1.2E-08	8.8E-09
	Downriver	1.0E-08	1.1E-08	8.8E-09
Warm				
	Source	1.2E-08	1.2E-08	8.8E-09
	Downriver	8.5E-09	1.0E-08	8.8E-09
High Flow Nontidal				
Cold				
	Source	1.7E-09	1.7E-09	1.2E-09
	Downriver	1.6E-09	1.6E-09	1.2E-09
Warm				
	Source	1.7E-09	1.7E-09	1.2E-09
	Downriver	1.6E-09	1.6E-09	1.2E-09

VC - Vinyl Chloride
HCB - Hexachlorobutadiene
BaP - Benzo (a) pyrene

with a 7-fold increase in flow in the tidal models (Table 4). For all other scenarios (tidal versus nontidal, warm versus cold temperature and chemical properties), the changes in water column concentrations between model runs were either proportional to the changes in the value or minimal (less than 50%).

There were significant differences in the concentrations in the benthic and suspended sediment and the relative distribution of the mass of the chemicals between the water column and the benthic sediment due to differences in chemical properties (Table 5).

The following section discusses the variation in concentration of the chemicals in the water column and benthic sediment in the eight different forms of the model. All references to concentration in this paper apply to the water column unless otherwise specified. Also, the chemical load in the models was equal for all chemicals so that the total mass of chemical in each system is the same. Therefore, differences in the concentration of a chemical in any compartment can be directly related to chemical-specific processes.

Table 5
Distribution of Chemicals Between Benthic Sediments and Water Column

| | Percent of Total Mass | | |
	VC	HCB	BaP
Low flow (tidal and nontidal)			
Water	95	6	<1
Sediment	5	94	99.9
High flow (tidal and nontidal)			
Water	97	10	<1
Sediment	3	90	99.88

VC - Vinyl Chloride
HCB - Hexachlorobutadiene
BaP - Benzo (a) pyrene

Flow Rate

In the tidal model, the upstream concentration decreased 300-fold when the flowrate was increased by 7-fold, regardless of the temperature or chemical.

In both models, there was a 7-fold decrease in the concentration in the source and downstream segments when the flow rate was increased 7-fold from 410,000 m^3/hr to 3,000,000 m^3/hr. The decrease can be partially accounted for by the approximately 2-fold larger volume. The actual concentrations were approximately 3.3 x 10^{-10} mg/L for high flow and 2.3 x 10^{-9} mg/L, for low flow. In the tidal model, the downstream concentration was 2- to 3-fold lower than the source segment for all chemicals. In the nontidal model, the downstream concentration was reduced by 10 to 50% of the source concentration for all chemicals.

Temperature

The only impacts of temperature were slight decreases in the downstream concentrations for VC and HCB, approximately 10 and 5%, respectively, in the warm low flow models versus the cold low flow models. The impact of temperature in the high flow models was even lower for the volatile versus nonvolatile chemicals. This was true for both tidal and nontidal models.

The concentration of all chemicals in the source segment within the tidal or nontidal models, varied by less than 20%, regardless of temperature.

Chemical Properties

The main impact of chemical properties is on the relative distribution of the total mass between the water column and the sediment with small differences between the low and high flow models. For all three chemicals, the relative distribution did not change between tidal and nontidal. For VC, the water:sediment ratio was 95 to 5 at low flow and 97 to 3 in the high flow models. HCB was 6 to 94 at low flow and 10 to 90 at high flow. BaP was less than 1% in the water and greater than 99% in the sediment in both models.

In the water column, the concentration differences due to chemical properties were small. BaP concentrations were slightly, approximately 30%, lower than VC and HCB, which were generally similar. The slightly lower values for BaP water column are due to the higher concentration of this chemical in the suspended sediments.

Discussion and Comparison of Case I and II Results

Interpretation of the results of the model in terms of impact on the risk assessment process is simplified by the fact that risk for both carcinogenic and noncarcinogenic effects is proportional to the concentration for a single exposure pathway such as drinking water.[2] For carcinogens, the proportionality is direct so that a decrease in the concentration of 50% would cut a 2×10^{-6} probability of cancer risk (two cases of cancer in a million people) to 1×10^{-6}. For the index to describe noncarcinogenic health effects, the Hazard Index, the relationship is inversely proportional. Therefore, a HI value of 1 becomes 0.5 when the concentration is cut in half.

For multiple pathways where the risk is added across exposure routes such as ingestion of water while absorbing chemicals through the skin during swimming, the proportionality between risk and concentration breaks down.

Estimation of risk is inherently variable. Many of the exposure assumptions have a range of values associated with them. For purposes of this report, changes in the concentration of less than 50% or one half the risk level, are considered negligible.

The impact of dispersion and reaeration on the concentration and hence the risk were fairly low, 2- or 3-fold impacts within the range of literature values. Case I reported the results of the EXAMS model with variations in reaeration and dispersion. The models indicated that changes in the dispersion coefficient had a greater impact than changes in the reaeration coefficient for the tidal models. A 5-fold change in the dispersion coefficient results in a 3-fold change in concentration of the three chemicals. Two- and 4-fold changes in the reaeration coefficient resulted in minimal (less than 10%) changes in the concentration,

The results of Case II indicate that flowrate can have a significant impact on the concentration and hence risk estimate. A 7-fold increase in flow rate results in a 300-fold decrease in the upriver concentration in the tidal model.

Risk assessors should be aware of this impact when selecting the typical low flow rates used in a surface water model. They should be sensitive to use of standard worst case conditions for flow based on 7-day, 10-year flow values. For drinking water intakes in tidal systems upgradient from the source, the impact of flow is significant. Use of low flow data to represent lifetime risk can result in an overestimation of the average lifetime risk.

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Potential Risks to the Marine Environment from Sunken Ships at Bikini Atoll

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ABSTRACT

This investigation examines the potential for release of fuel and oil from ships sunk at Bikini Atoll during the nuclear testing era. Historic data and site investigations provided a basis for determining the magnitude of the threat. A simple model was employed to estimate the dimensions, trajectory and duration of chronic oil spills at various release rates.

Historic accounts suggest that a significant portion of the available fuel load was released during the BAKER event, an underwater nuclear detonation. Current low rates of chronic release of product suggest that some fuel may still remain in the vessels. The highly deteriorated condition of the ships suggests the possibility of increased rates of release in the future. Potential impacts to the marine environment were assessed by estimating the dimensions and trajectories of minor, medium and major spills. A major spill (>4,000 gal/hr) occurring during normal trade wind conditions would result in an oil slick 3.5 mi wide by 67 mi long, extending beyond the boundary of the atoll in a northwesterly direction away from the sunken ships. Key ecological receptors to an event of this magnitude would be shallow reef flat environments and their associated fisheries, sea turtles and seabirds.

Attempts to recover the fuel could result in unacceptable short-term and long-term impacts to the marine environment. No remedial action is the recommended alternative for this site.

INTRODUCTION

Although health risks from radionuclide contamination of the islands remain the major concern of the Bikini people, they have expressed concern over the potential for a catastrophic release of fuel oil from the sunken ships in the lagoon and subsequent destruction of fisheries and coral reefs from which they derive subsistence. In addition, the draft Environmental Impact Statement for the Rehabilitation and Resettlement of Bikini Atoll[2] identified the need to conduct further investigations of this largely unknown threat. This investigation was initiated to gather historical information, conduct preliminary site investigations and provide qualitative estimates of the magnitude of this threat to the natural resources at Bikini Atoll.

HISTORICAL INFORMATION

Operation Crossroads consisted of two nuclear weapons tests, ABLE and BAKER, to assess the effects of nuclear weapons against naval war vessels.[1] The ABLE event, conducted on June 30, 1946, was an air drop nuclear device with a yield of 23 KT. The BAKER event, conducted on July 24, 1946, was an underwater detonation with a similar yield. As a result of these tests, 12 vessels lie within a one square mile area of the lagoon floor at a depth of 165 feet (Figure 1). The ships sank in battle-ready condition, loaded with fuel and ordnance. The

general location of the ships can be identified by an oily sheen on the surface of the water.

The target vessels used in Operation Crossroads included: attack transports, submarines, cruisers, aircraft carriers, destroyers and battleships. Major hull damage occurred to all types of vessels.[3] The vessels suffering the greatest damage during the ABLE Event were the *Carlisle* and *Gilliam*, which sank as a result of the test. The remaining vessels currently reported on the lagoon floor were sunk during the BAKER event. In a 1947 resurvey of several ships,[4] the *Saratoga* and *Pilotfish* were reported to have incurred much more extensive damage as a result of BAKER than previously estimated. Overall, ships sunk during BAKER received the most structural damage consisting of buckling of plates, breaching of hull and impairment of the boiler operation resulting in a reduced military efficiency.

A significant amount of fuel oil probably was released from the vessels that sank during Operation Crossroads. The amount of product released from the four most damaged vessels, *Carlisle*, *Gilliam*, *Pilotfish* and *Saratoga*, could account for a 50% reduction in the remaining estimated fuel load. Historical records, however, provide no information about the release of oil from specific ships.

Refined petroleum products are the major contaminants of concern in relation to potential risks to the marine environment from the sunken ships.[3] The vessels sunk in Bikini Atoll lagoon contained three types of refined petroleum products; gasoline, diesel oil (Fuel Oil No. 2) and Bunker C (Fuel Oil No. 6) (Table 1). Other potential contaminants include lead and sulfuric acid from batteries used on the submarines and radionuclides, principally cesium-137, strontium-90 and transuranics (plutonium and americium), remaining in the sediments surrounding the vessels. Overall, radionuclides in the marine environment have largely diminished by exchange of lagoonal water with the open sea. These other contaminants will not be discussed further in this investigation.

Bunker C, the predominant product, is an oil of high viscosity that must be heated to produce a more fluid consistency. It may be a residual oil from the distillation of crude petroleum, or it may be a mixture of two or more of the distillate cuts.[5] Based on the differences in physical and chemical properties of diesel oil and Bunker C, diesel fuel probably would be released to the environment more readily than the more viscous Bunker C.

Historical accounts of the fuel capacity and percent of capacity were used to calculate fuel load prior to Operation Crossroads.[3] The combined total volume of gasoline, diesel oil and Bunker C was estimated at slightly under 2 million gallons (Table 1).

The amount of product lost during Operation Crossroads is unknown. The only historical account reported observations of a "great oil slick" resulting from BAKER.[6] The oil slick was discovered during a recon-
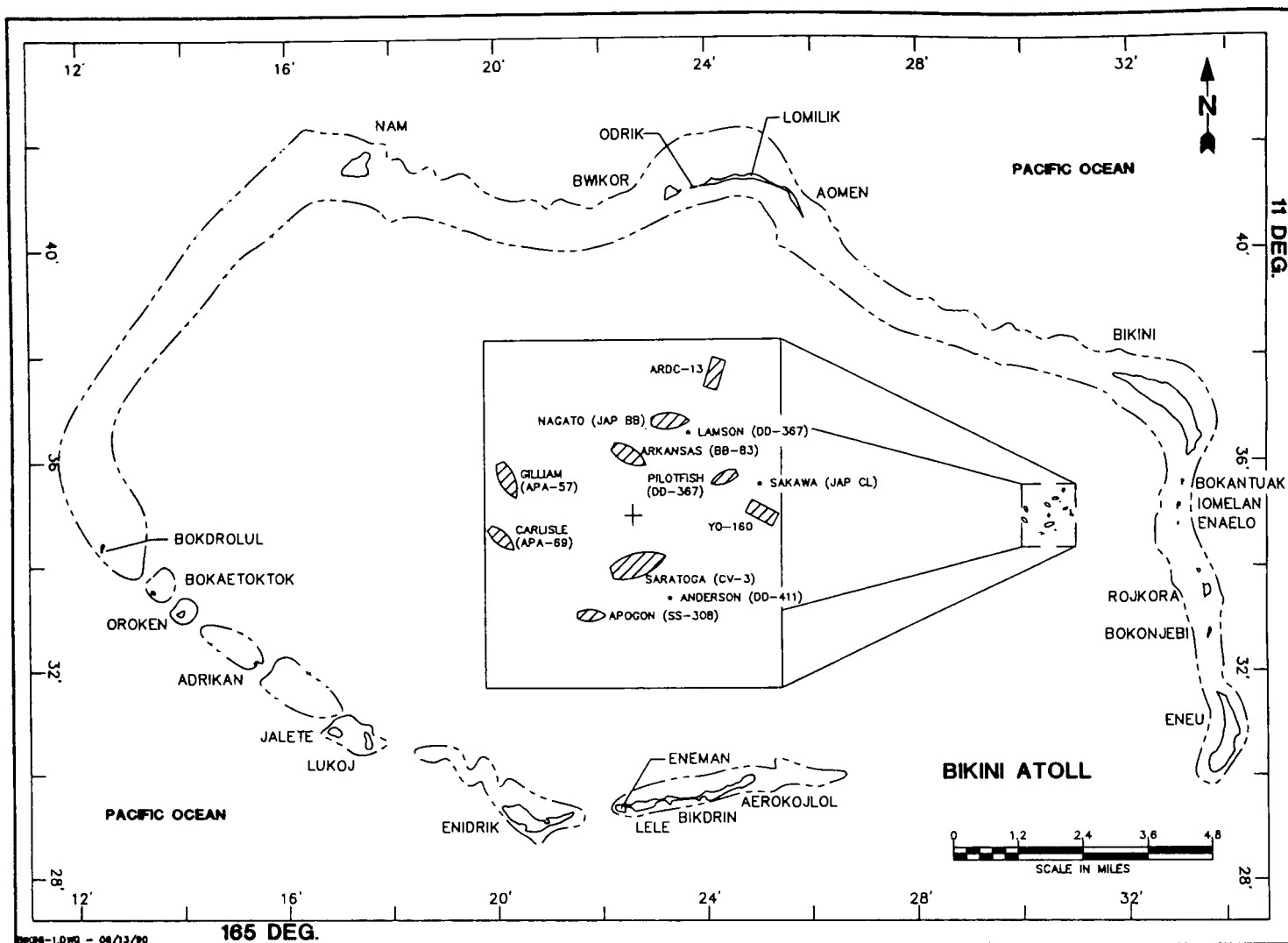
Figure 1
Location of Vessels Sunk During Operation Crossroads.
Stars Indicate Unverified Positions

naissance flight the day after the BAKER event when an area of high radioactivity was encountered on the surface ocean, miles north of Bikini Atoll. Historical accounts report that the oil slick, heavily impregnated with fission products, moved to the north from the target fleet, passed over the reef between Aomen and Bikini Islands and went out to sea. A "gummy emulsification" was noted smeared over the reefs and sandspits along the northern to northeastern flanks of the Atoll. The dimensions of the great oil slick were estimated to be greater than 1 mile in width and length, however, there was no mention of the thickness or color of the oil slick or estimate of the amount of product lost during the event.[6] If all the product, approximately 2 million gallons contained in the ships, was lost during the Baker event, an oil slick of the observed dimensions (estimated at 1.5 x 1.5 miles) would be approximately 1.3 mm thick. A surface slick with this layer thickness would be indicative of a significant surface concentration (Figure 2) and would not be unusual for oil slicks resulting from tanker or other types of petroleum product accidents.[5]

Recent observations of oil slicks emanating from the sunken ships suggest that not all product was released during the Baker event. Therefore, the estimated thickness of the slick, 1.3 mm, would have to represent an upper boundary. In addition, the observation that the oil slick had discrete dimensions suggests that the product was released fairly quickly after the BAKER event upon which little further release of product occurred.

In conclusion, these historical accounts suggest that a fairly significant amount of product could have been lost during the BAKER event; however, a quantitative estimate is unavailable. Furthermore, the remaining fuel load must be much less than the estimated 2 million gallons.

SITE INSPECTION

Location of Vessels

Prior to this investigation, the exact locations of the ships were unknown. A shallow water side-scan sonar and a shore-based navigational system were used to locate physical features, contacts, on the lagoon floor. These contacts were verified with visual observations made by diving. Nine of the 12 vessels known to have sunk at Bikini Atoll were located and marked (Figure 1). Included in the nine vessels found, the ARDC-13 is a concrete dry dock and the YO-60 is a concrete barge. The locations of two destroyers, *Lamson* and *Anderson*, and the Japanese cruiser, *Sakawa*, have not been found.

Long-term Deterioration of Vessels

The present condition of the vessels is the result of: (1) initial structural damage from Operation Crossroads, and (2) long term deterioration. Because no future catastrophic impact to the ships of the magnitude of Operation Crossroads is expected, long term deterioration is probably the most important factor influencing the rate of chronic release of product to the environment.

Table 1
Fuel Load of Ships at Bikini Atoll Prior to Operation Crossroads

SHIP	FUEL TYPE	CAPACITY	PERCENT CAPACITY	FUEL LOAD (gallons)
Anderson	Bunker C	2929 bbl	95	116867
	Diesel fuel	168 bbl	95	6703
Apogon	Bunker C	54000 gal	50	27000
Arkansas	Bunker C	37729 bbl	50	792309
	Diesel fuel	119 bbl	50	2499
	Gasoline	4000 gal	50	2000
Carlisle	Bunker C	9695 bbl	95	386831
	Diesel fuel	375 bbl	95	149063
Gilliam	Bunker C	9695 bbl	50	203595
	Diesel fuel	375 bbl	50	7875
Lamson	Bunker C	3600 bbl	50	75600
	Diesel fuel	110 bbl	50	2310
Pilotfish	Bunker C	540000 gal	95	51300
Saratoga	Bunker C	63200 gal	10	265440
	Diesel fuel	249 gal	10	1046
	Gasoline	132264 gal	10	13226
			TOTAL	1980094

bbl   barrel
gal   gallon
42 gal/barrel
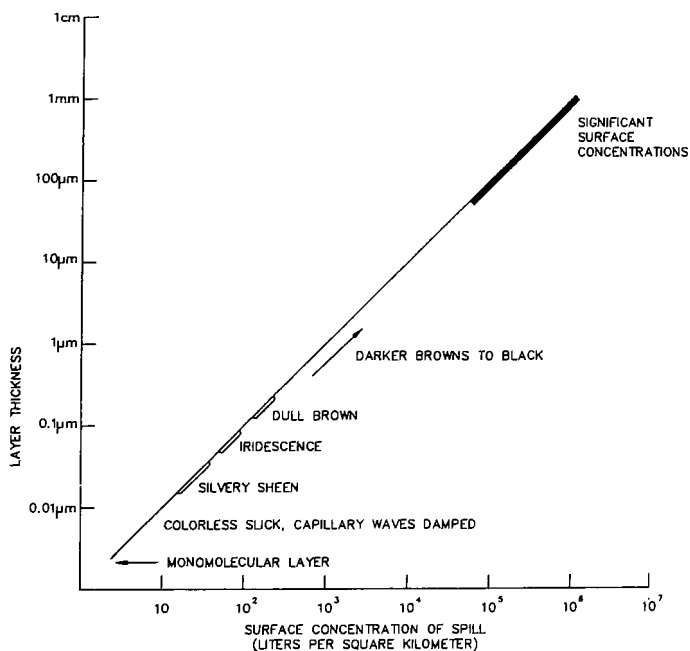
Figure 2
Approximate Classification of Slicks Based on Surface Concentration of Spill after Barger et al. (1974)

The ships have undergone significant deterioration over the past 44 years. Visual observations of the present condition of each ship were made by diving. An accelerated rate of decay of the vessels is suggested when compared with observations made of ships of the same vintage

sunk in similar oceanic conditions (e.g., the Ghost Fleet of Truk Lagoon).[7] Within a single year, significant structural changes have been observed on the flight deck and hangar deck of the *Saratoga*. In August 1989, four hellcat fighters were accessible along the starboard portion of the hangar deck. The most recent observations of this area (May 1990) revealed that the flight deck above had collapsed into the hangar deck crushing the third and fourth planes. Portions of the ship recorded as attached to the flight deck the previous year are now resting on the lagoon floor. Deteriorating metal particles rain from the ceiling of the hangar deck at the slightest disturbance to the surrounding water.

The factors influencing the rapid deterioration are unknown, but could be related to a number of variables, such as, initial blast effects to the metal and/or lack of significant marine fouling that serves to protect the surface of the ship from deterioration. Benthic invertebrate and algal growth on the ships is sparse in comparison with the heavy growth observed on the sunken ships at Truk Lagoon.[7] Significant coral growth was observed[7] on and about the sunken ships in Truk Lagoon, and no evidence of environment degradation was reported although fuel oils were slowly seeping from the ships. The deeper depths of the ships at Bikini Atoll (>130 feet) result in lower light levels when compared with the shallower sunken ships (<100 feet) found at Truk Lagoon. Although benthic invertebrate and algal growth covering the ships structure is sparse, adult and juvenile reef fishes are abundant on each ship. The composition of fish genera was similar to patch reefs at similar depths, suggesting that the ships are serving as artificial reefs.

Although the rate of deterioration of the ships cannot be measured, these observations suggest that an increased rate of chronic release of product from the ships could result from accelerated deterioration of the ships' internal compartments.

Chronic Oil Slicks

Small surface slicks have been observed frequently in the vicinity of the sunken ships. In particular, slicks have been routinely observed over the *Nagato*, *Saratoga* and *Carlisle*. Observed slick dimensions vary, indicating a variable release rate of product and/or variable surface dispersion rates which are dependent on wind conditions. These slicks appear as discrete iridescent to dull brown patches usually 5 to 10 feet in diameter, indicating a pulsed rather than continuous release of product.

Samples of surface water collected in the vicinity of the *Carlisle* were analyzed for soluble petrochemicals such as phenanthrene. Six samples were deliberately taken inside and outside the visible boundaries of the surface slick. Only one sample resulted in a concentration (0.15 mg/L) above detection limits (<0.008 mg/L), indicating a low concentration of soluble petrochemicals associated with the surface slick.

This type of chronic release has been observed over at least the last 10 years and probably has been occurring since 1946 when the maximum damage to the ships occurred as a result of nuclear testing.

Table 2
Time to Release Maximum Estimated Product (2 million gallons) from Sunken Ships at Four Spill Rates

RELEASE RATE	DURATION OF RELEASE	
CHRONIC SPILL (5 gal/hr)	16060 days	< 44 years
MINOR SPILL (40 gal/hr)	2083 days	< 5 years
MEDIUM SPILL (400 gal/hr)	208 days	< 1 year
MAJOR SPILL (4,000 gal/hr)	20 days	< 1 month

ESTIMATE OF THE IMPACT OF POTENTIAL CHRONIC RELEASES

The likelihood of a future catastrophic release of product from the ships is remote since these vessels already have incurred major physical impacts from nuclear testing. The potential for an increased rate of chronic release of product could occur, however, from ongoing structural deterioration. Impact to the marine environment is related to both spatial and temporal components of a release. Using different estimated rates of release of product, a simple model of dispersion was employed to provide an estimate of the potential lateral extent of a release to the marine environment.

Model for Estimating Oil Slick Dimensions and Trajectory

A rough estimate of the loss of product from a long-term chronic release was estimated using several approaches to provide a range of possible release rates. If the maximum volume of product, 2,000,000 gallons, were released continuously and totally over a period of 44 years (to present) and no other product remained in the ships after this time, the resulting release rate would be estimated at 5 gallons per hour (Table 2). Because small amounts of product continue to be released from the sunken ships, this estimate probably represents a high rate of current release from the ships.

The time to release the maximum product volume was also calculated for higher release rates (Table 2), assuming that a significant amount of product still remains in the sunken vessels. Release rates of 40, 400 and 4,000 gallons per hour were based on the total volume of oil discharged over a 24-hour period for three classes of spills: a minor spill of less than 1,000 gallons, a medium spill of between 1,000 and 10,000 gallons, or a major spill of greater than 10,000 gallons. The time to release the maximum estimated product at a rate for a major spill (4,000 gal/hr) would be 20 days. Order of magnitude estimates of slick dimensions for various release rates were calculated using the equations developed by Murray[8] and applied by Lukas.[9] The following equations for oil slick width (W) and length (L) were developed for a steady state oil slick emanating from a continuous source:

$$W = 2Q/(2\pi e)^{1/2} UC_b, \tag{1}$$

where

Q is the source strength (g/sec)
U is the current speed (cm/sec)
C_b is the concentration of the oil at the visible boundary (gr/cm^2)

Murray[8] found that the value of C_b was approximately 0.15×10^{-3} gr/cm^2. Using the relation Q= p oil x Volume discharge rate, and a value of 0.922 g/cm^3 for the density of oil, the width of the oil slick is found to be:

$$W \text{ (feet)} \quad 92.8 \times V(\text{gal/hr})/U(\text{cm/sec}) \tag{2}$$

For the length of the steady-state oil slick, Murray gives the expression:

$$L = Q^2/(4\pi KUC_b^2) \tag{3}$$

where

K is the turbulent diffusion coefficient (cm^2/sec)

As before, with the proper substitutions:

$$L(\text{feet}) = 8.89 \times 10^4 \times V^2(\text{gal/hr})/K(\text{cm}^2/\text{sec})U(\text{knots}) \tag{4}$$

Although the value of K should be determined experimentally for the conditions that prevail at the time of an oil spill, the value of K= 2 x 10^5 cm^2/sec that Murray found in his study can be used as an order of magnitude estimate to get:

$$L(\text{feet}) = 0.445 \times V^2 \text{ (gal/hr)}/U \text{ (cm/sec)} \tag{5}$$

Using these equations, slick dimensions were calculated for different release rates and surface current speeds (Table 3). The range of current speeds was calculated as 3% of a range of wind speeds representative of the Bikini area, in which average wind speed is 20 to 25 knots.

Table 3
Estimate of Steady State Dimensions
(after Lukas, 1978)

		Surface Current Speed (cm/sec)		
		40	20	10
Slick Dimensions	(feet)			
Chronic Spill	width	11.0	23.0	46.0
(5 gal/hr)	length	0.3	0.6	1.0
Minor Spill	width	93.0	185.0	371.0
(40 gal/hr)	length	18.0	35.0	71.0
Medium Spill	width	929.0	1855.0	3710.0
(400 gal/hr)	length	1780.0	3560.0	7120.0
Slick Dimensions	(miles)			
Major Spill	width	2.0	3.5	7.0
(4,000 gal/hr)	length	34.0	67.0	135.0
Wind Speed	(knots	30.0	13.0	6.0

This estimate is based on the largely substantiated wind stress/wind drift relationship described by Ekman.[10] A steady-state wind blowing over an infinite, homogeneous ocean, would result in a wind-induced surface current that is 3% of the wind speed at 10 m height in a direction 45° to the right of the wind direction (in the northern hemisphere).

The trajectory of a chronic release is dependent on surface currents. East to northeast trades are the dominant wind conditions at Bikini Atoll (Figure 3). Using the simple relationship above, surface drift of an oil slick would result in a net transport toward the north to northwest (326°).

SSMO   AREA 9

Figure 3
Wind Rose Summarizing Wind Direction
in Vicinity of Bikini Atoll
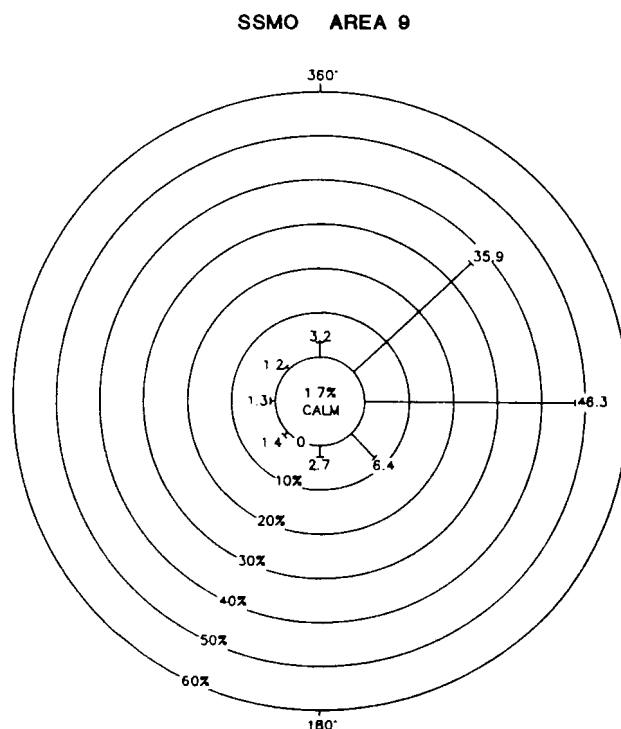
Estimated Dimensions and Trajectory of Chronic Oil Release

Estimated dimensions and trajectories of steady-state minor, medium and major oil slicks are shown in Figures 4 and 5 emanating from the general vicinity of the sunken ships. Only a major spill would result in a slick of significant surface dimensions that could possible impact natural resources. For this to occur, the chronic release rate would have to increase almost three orders of magnitude.

The dimensions for a major spill would extend beyond the physical boundaries of the atoll passing between Aomen and Bikini Islands. This trajectory is the same as that reported from historical accounts of the "great oil slick."

KEY ECOLOGICAL RECEPTORS AND DISTRIBUTION

Based on the estimated dimensions and trajectory of a major spill, the key ecological receptors impacted by a release of product to the marine environment would be shallow reef environments and their associated fisheries, seabirds and sea turtles. Direct contact by these receptors would be the principal exposure route of concern. A general summary of distribution of these receptors (Figure 6) was excerpted from an extensive environmental assessment of Bikini Atoll conducted in support of the draft Environmental Impact Statement.[2]

Shallow reef flat environments would be greatly impacted by the release of product to the marine environment. Reef flats connect islands and sand spits and are most developed in lateral extent on the windward (northeastern) side of the atoll. Significant subsistence fisheries inhabiting reef flat environments include numerous species of reef fish and giant clams.

Maintenance of the current diversity of Bikini Atoll seabirds would require the preservation of some or all of the islets on the northern and southwestern portions of the atoll.[2] The small southwestern islands which have well-developed forests constitute the only important breeding sites of Black Noddies and Red-footed Boobies on the atoll. The most important islands are Oroken, Lukoj, Bokdrolul and Bokaetoktok. Islands dominated by lower shrubs which have large breeding colonies of noddies, White Terns and Brown Boobies are Nam, Odrik/Lomilik/Aomoen and Jalete. Other islands harboring significant seabird populations are the Bokantuak/Iomelan chain between Bikini and Eneu Islands, Aerokoj/Aerokojlol Islands and Enidrik Island.

The distribution of the existing green sea turtle population at Bikini Atoll was estimated by visiting each islet and making visual observations of turtles, turtle tracks and nests. Turtle tracks and nesting sites were most abundant on islands in the southwestern part of the atoll, although turtles frequently were observed coming ashore on Bikini Island and some nests and turtles were sighted on Nam and Lomilik Islands.

Overall, the highest abundance of turtles and seabirds occurs in the
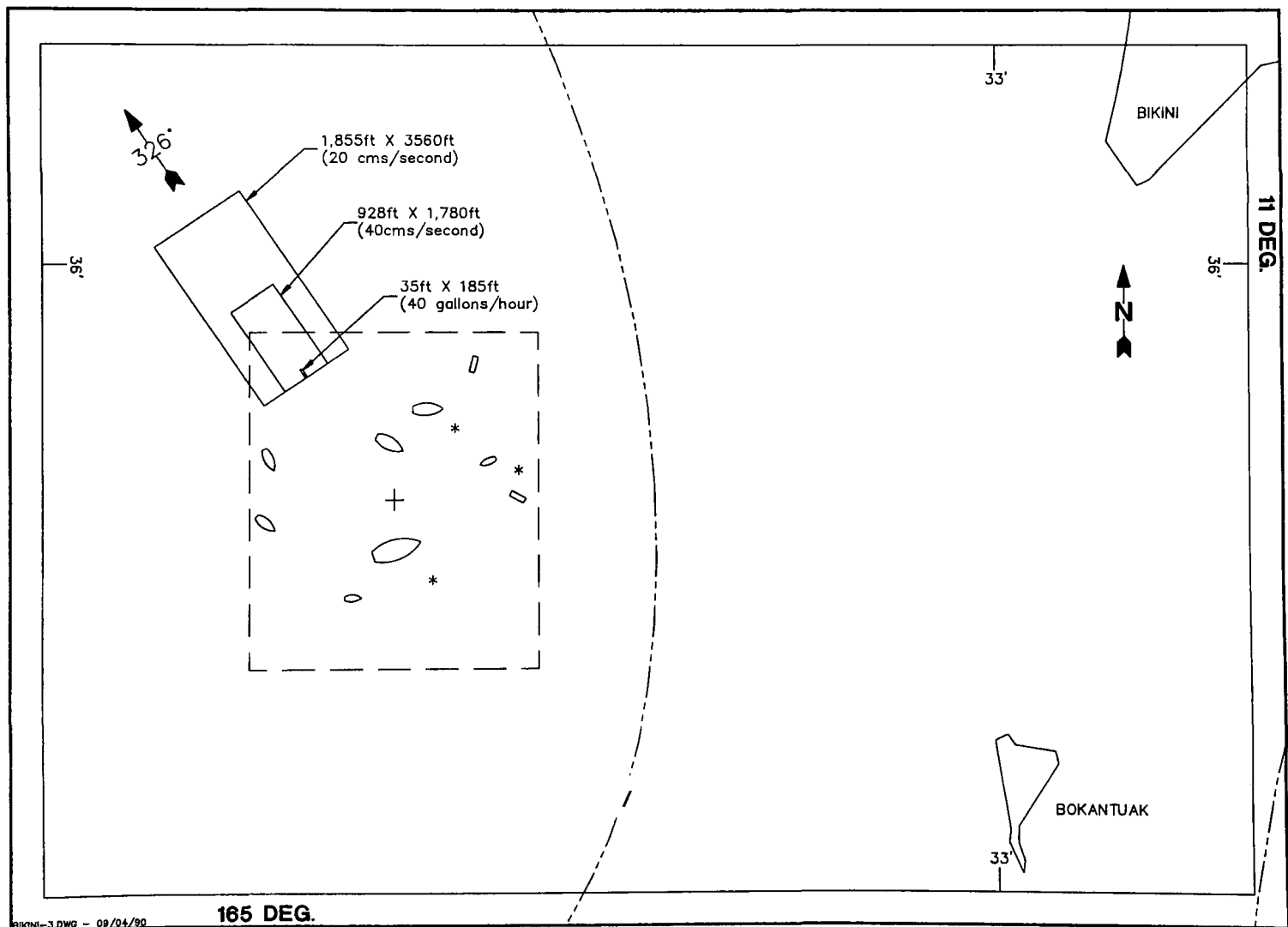
Figure 4
Calculated Dimensions of Oil Slicks for Minor (40 gal/hr)
and Medium (400 gal/hr) spills. Dimensions for Medium Spills
Shown at Two Surface Current Speeds (20 and 40 cm/sec)
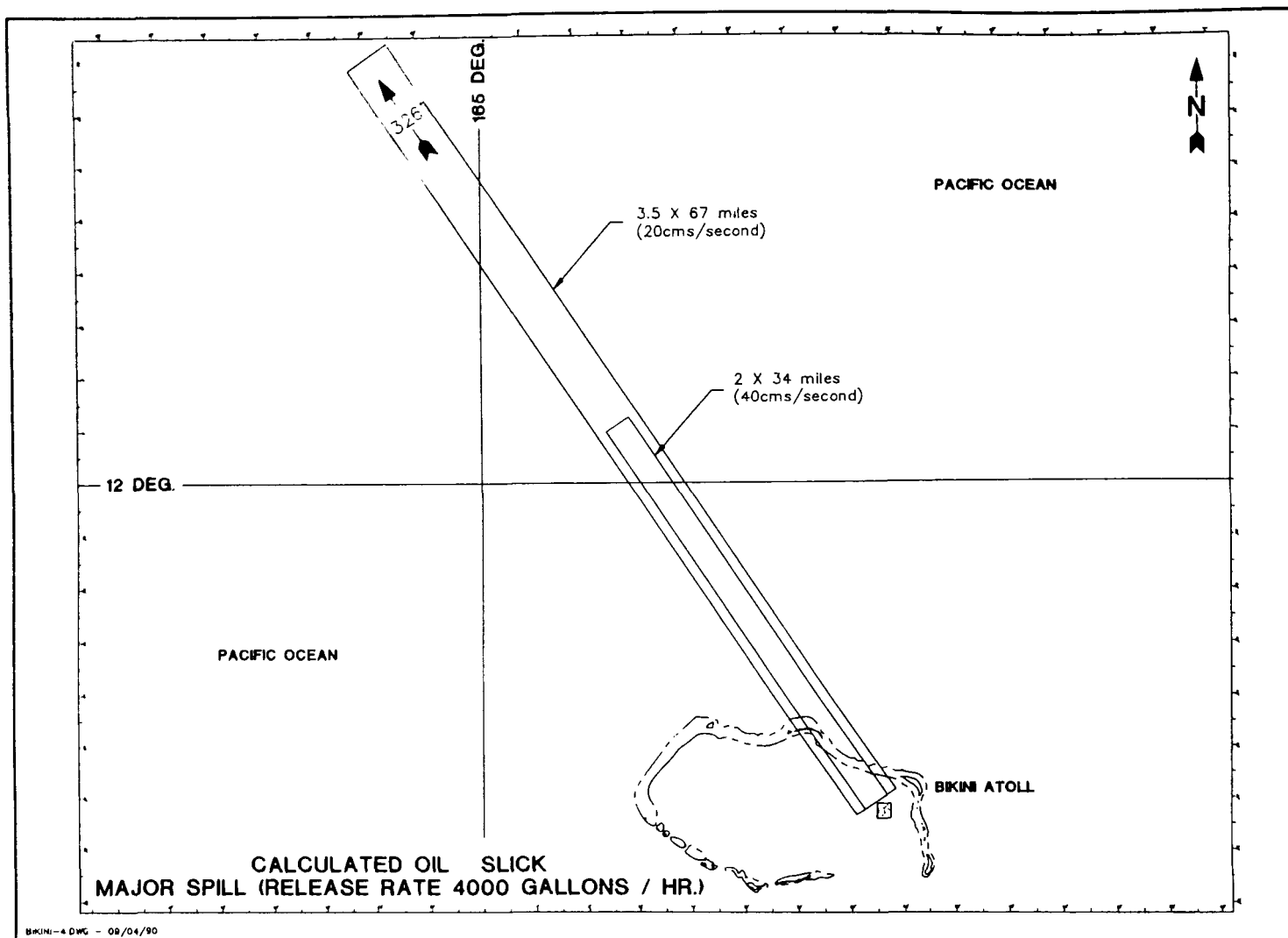
Figure 5
Calculated Dimensions of Oil Slick for Major (4,000 gal/hr) Spill
at Two Surface Current Speeds (20 and 40 cm/sec)

south and southwestern flanks of the Atoll and not in the vicinity of the proposed trajectory of the oil slick. Major reef flat environments, however, are found principally along the northern and northeastern flanks of the Atoll and would be the most impacted by an oil spill.

CONCLUSIONS

Based on historical accounts and site inspection of the sunken ships at Bikini Atoll, it is concluded that the potential for a catastrophic release of product from the sunken ships is extremely low. No remedial action is the recommended alternative for this site.

The vessels already have incurred maximum possible structural damages from nuclear testing. Accelerated deterioration of the vessels could result in an increase in the currently low chronic release rate of product. Historical accounts suggest, however, that a significant amount of fuel was lost from the ships as a result of the BAKER event, thereby greatly reducing the product available for long-term chronic release. The current low rate of release from the ships has not resulted in any apparent environmental degradation. An increased chronic release rate of product could result in impacts to the northern and northeastern flank of the atoll; however, estimated dimensions and duration of even a major spill would be limited in impact.

Fuel recovery would eliminate the long-term risk of chronic oil spill to the environment. This alternative could result, however, in short-

term impacts from the release of fuel during recovery operations. In addition, the deep depth, deteriorating condition of the ships and viscous nature of the predominant fuel, Bunker C, would make this alternative difficult to implement and extremely costly. Furthermore, the highly weathered nature of the petroleum products would probably make the recovered fuel unsalvageable.

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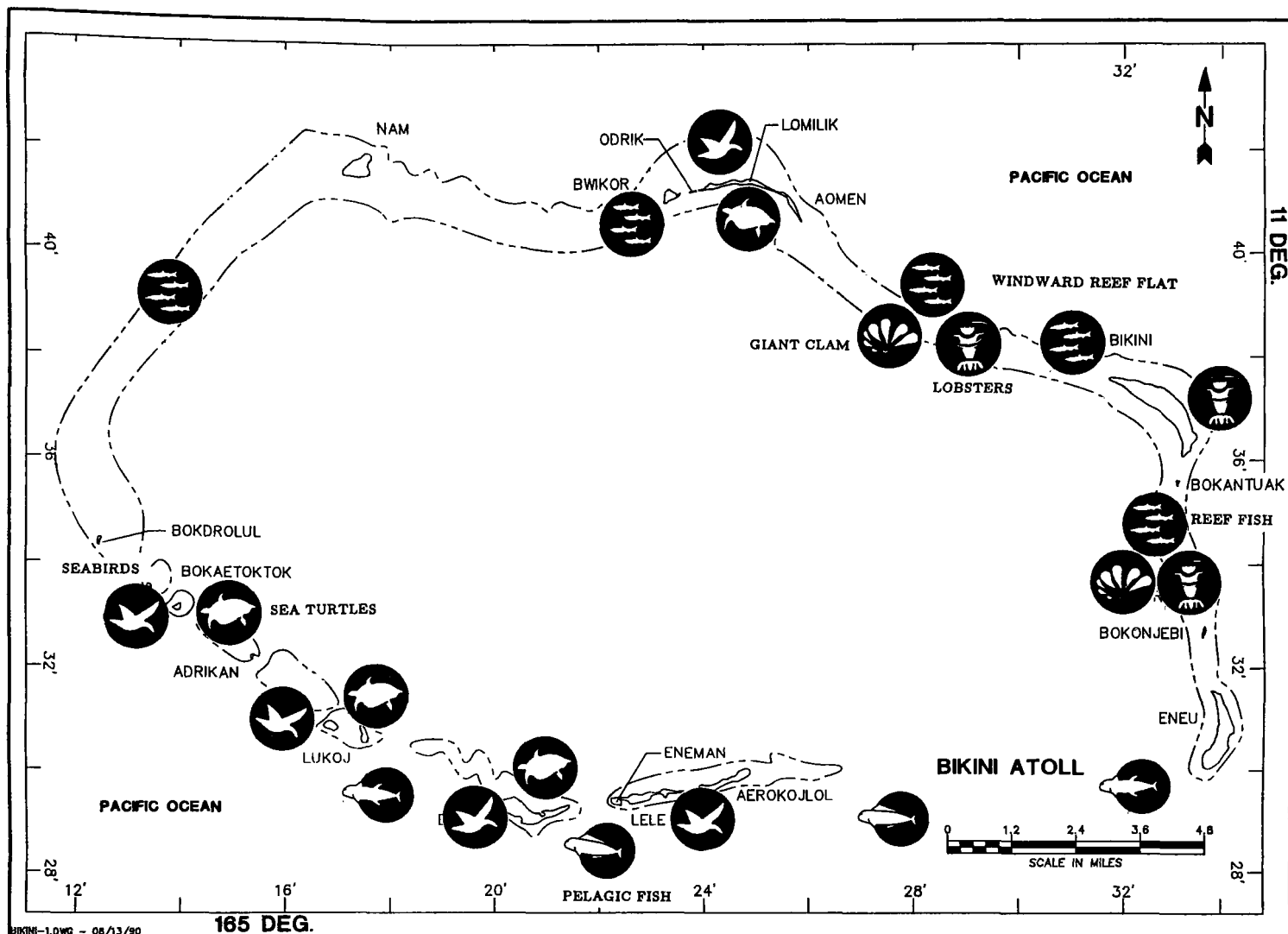
Figure 6
Distribution of Key Ecological Receptors
(Reef Fish, Giant Clams, Sea Birds, and Sea Turtles)
in the Event of an Oil Spill

Consideration of Non-Routinely Monitored Hazardous Substances for the Health Assessment

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ABSTRACT

When conducting Health Assessments of Superfund sites, an attempt is made to determine the specific human health outcomes that might be associated with exposure to site-related contamination. The possible human health outcomes are important for a variety of reasons, such as: (1) worker and public safety during remediation, (2) identifying sensitive subpopulations, (3) targeting specific health effects for the evaluation of health outcome data and (4) determining the need for a health advisory or other action. Therefore, information on the presence of nonroutinely monitored hazardous substances would increase the ability of the health assessor to identify public health problems.

This information can be obtained by examining various factors. The Massachusetts Department of Public Health (MDPH) has identified additional hazardous substances by reviewing information on the chemicals used at a site, chemical impurities and natural and unusual degradation processes. The four cases presented provide examples of how each chemical was identified, how exposure might occur, the possible health outcomes and the resulting public health recommendations or activities.

INTRODUCTION

The Massachusetts Department of Public Health (MDPH) was one of the original participants in ATSDRs Cooperative Agreement Program to conduct Health Assessments at Superfund sites. This paper describes, in part, the MDPHs approach when conducting Health Assessments.

The Health Assessment process considers: (1) the important contaminants at a site (2) the environmental fate and transport of those substances (3) the possible human exposure scenarios and (4) the public health implications (based on available medical and toxicological information) associated with a site. Emphasis is placed on the specific human health effects that might result from exposure to site-related contaminants. Two important parts of the Health Assessment are the evaluation of health outcome data and addressing community health concerns. Ideally, information on the possible human health effects is used in these analyses. The health outcome data analyses can target the health effects to better assess the possible impact of the site on local health; therefore, a thorough understanding of the contaminants present at a site would aid this process. Information on the contaminants present usually is obtained from the Remedial Investigations prepared as part of the cleanup effort as well as other site-specific documents. Most of the substances monitored during the Remedial Investigation are contained within the Superfund Target Compound List (TCL).

A TCL is a media-specific list of compounds that can be detected by a specific analytical method. The Superfund TCL is a list of compounds detected in soils, water and sediment by the analytical methods entailed in the Routine Analytical Services for the U.S. EPA Contract Laboratory Program. This list is periodically revised and, currently, contains 125 organic compounds and 24 inorganic compounds. Depending on site-specific factors and following U.S. EPAs preparation of a Special Analytical Request, other media and compounds can be monitored. Remedial Investigations frequently contain data from special analyses.

The TCL is designed as a tool for remediation purposes and not for determining the potential human health effects. Therefore, the health assessor should consider what other hazardous compounds might be present. Following this process, the findings might include: (1) the need for additional environmental monitoring or other information (2) the potential need for a health advisory or other public health intervention strategies and (3) the specific human health effects to be examined during the evaluation of health outcome data. These findings could be important later in the Health Assessment.

While preparing Health Assessments, the MDPH has used monitoring data for non-TCL hazardous substances contained within the Remedial Investigations and has shown the potential presence of other non-TCL hazardous substances. Selected non-TCL substances have included polychlorinated dibenzofurans, polychlorinated dibenzo-p-dioxin, phenoxy herbicides, methyl mercury compounds, arsine and methylarsines, naphthylamines and benzidine and its analogs. The following four cases are examples of the MDPHs experiences. Information presented includes: (1) the presence or potential presence of a non-TCL substance (2) the site-specific environmental and human exposure pathways (3) the possible human health outcomes or other toxicological information and (4) the conclusions and recommendations or the results of follow-up activities.

CASE EXAMPLES

Case 1: Polychlorinated Dibenzofurans

Site "A" is a granite quarry that was used as an industrial landfill for approximately 30 years. Waste deposited in the landfill included capacitors, transformers, organic solvents and tires. Contamination at the site consists of PCBs, VOCs and other chemicals. In particular, Aroclor 1254, a commercial mixture of PCBs, was detected in the sites soils at levels up to 2,200 mg/kg. Extensive fires occurred at the site, and the tires, solvents and various debris burnt for days before the fire was brought under control.

Laboratory investigations have determined that PCBs can be converted to polychlorinated dibenzofurans (PCDFs) by thermal processes.[1-5] PCDFs are more potent carcinogens than are PCBs. Based on laboratory experiments, the proportion of PCBs transformed into PCDFs is dependent upon PCB and oxygen concentrations as well as temperature and time of reaction, but, under certain conditions, can result in a conversion in the percent range.[1,4] A real life situation (i.e.,

the explosion and fire of an electrical transformer at the Binghamton State Office Building in Binghamton, New York) confirms that a percent range conversion to PCDFs can occur.[4] Although PCDFs are common trace contaminants of commercial mixtures of PCBs, the proportion (roughly 0.0002% for Aroclor 1254[4,6]) is much smaller than that from some thermal processes.

A limited amount of polychlorinated dibenzo-p-dioxin (PCDD) monitoring occurred at Site "A". No PCDDs (specifically 2,3,7,8-tetrachlorodibenzo-p-dioxin) were detected in the soil samples above the method detection limit of 1 ug/kg. PCDDs do not normally form from the heating of PCBs, but thermal reactions of polychlorinated benzenes result in the formation of both PCDFs and PCDDs.[4] The transformer in the Binghamton accident contained 65% Aroclor 1254 and 35% polychlorinated benzenes;[7] hence, the detection of PCDDs in the soot of this fire is not surprising. The level of total PCDDs (20 ppm) detected in the soot was approximately 100 times lower than the level of total PCDFs (>2,000 ppm) detected.[4] Whether polychlorinated benzenes are present at Site "A" is unknown; however, PCDD monitoring would not be an appropriate surrogate for determining if PCDFs might be present.

Whether conditions at the time of the on-site fires were appropriate for PCB conversion to PCDFs is unknown. However, because of the toxicity of PCDFs and the actual PCB levels detected in on-site soils, the possibility of past PCDF formation is of public health concern. No information is available for PCDF occurrence in the soils and sediments associated with the site. Based on a limited amount of experimental animal data and on in vitro studies of structure/activity relationships, PCDFs appear to express PCDD-type toxicity.[8] Like the PCDDs, the 2,3,7,8-congeners of the PCDFs are the more potent toxins and have been estimated to be 0.33 to 0.02 times (a 0.1 relative potency rate most frequently estimated) as potent as 2,3,7,8-TCDD.[8] Congeners other than the 2,3,7,8-PCDFs have been estimated to be 1,000-fold less potent than the 2,3,7,8-PCDFs.[8] The relative proportion of each PCDF formed is difficult to predict; thus, the following 2,3,7,8-congeners are of interest:

2,3,7,8-tetrachlorodibenzofuran
1,2,3,7,8-pentachlorodibenzofuran
2,3,4,7,8-pentachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzofuran
1,2,3,7,8,9-hexachlorodibenzofuran
1,2,3,4,7,8-hexachlorordibenzofuran
2,3,4,6,7,8-hexachlorodibenzofuran

A recommendation was made within the Site "A" Health Assessment that soil and sediment monitoring be conducted for the 2,3,7,8-congeners of the PCDFs listed above. This additional monitoring will be implemented during a future remedial investigation.

Case 2: Naphthylamines and Benzidine and its analogs.

At Site "B," azo and anthraquinone dyes were produced for approximately 70 years. From the review of the company's purchasing and product lists and information from the Colour Index,[9] large quantities of benzidine, naphthylamines and related aromatic amines were known to have been purchased for the production of azo dyes. Both 2-naphthylamine and benzidine are human bladder carcinogens.[10-12] Other aromatic amines and benzidine-based dyes have been associated with bladder cancer in animals or humans.[10] However, at this site, monitoring data for these compounds did not exist.

Waste products and sludges were disposed on a hill and effluent was discharged into nearby wetlands and a brook. The soils, wetlands and water in the brook were often vividly colored. The brook discharges into an off-site river. Based on anecdotal information, the river was discolored until the early 1980s. In addition, the groundwater migrating from the site is highly contaminated with organics used in the manufacture of dyes. At various times, particulates, aerosols and vapors were emitted from the facility into the ambient air. As a result, nearby residents complained about: (1) dye-flecked belongings; (2) pitted automobiles, (3) noxious odors, and (4) irritated and burning eyes, noses and throats. The site also was a popular play area for neighborhood children, who often returned home with discolored clothes and skin.

Benzidine may be resistant to transformation and degradation, especially in anaerobic conditions, but microbial degradation can be substantial following acclimatization. However, high concentrations of benzidine are toxic to microorganisms.[12] Reduction of the azo bond(s) in benzidine-based dyes results in the release of benzidine.[12] Reduction can occur in the gut, on the skin surface and in the environment. Benzidine is more readily absorbed through the gut and skin than are the benzidine-based dyes.

Environmental monitoring for these compounds was recommended because: (1) there was a lack of monitoring data (2) benzidine and related compounds may be persistent in the environment (3) these compounds were purchased and dyes were produced (4) benzidine and 2-naphthylamine are human bladder carcinogens (5) waste disposal and emissions were extensive and (6) contaminants are transported to populated areas and human exposure occurred both on-site and off-site. Because remediation is currently occurring, on-site soils and sludges were not monitored for these compounds. However, groundwater and the rivers sediments and surface water were monitored. The preliminary data indicate the presence of benzidine in groundwater at levels exceeding 100 ug/L. None of these compounds were detected in the rivers surface water or sediment ten years after the facility closed.

An analysis of the cancer incidence and mortality data for the nearby community indicated a statistically significant elevation of male kidney cancer and a possible clustering of male kidney and bladder cases. A case series investigation was conducted to determine if the site or some other environmental exposure factor might have played a role in the etiology of disease among these individuals. The results of the investigation and the review by an expert panel are pending.

Case 3: Phenoxy Herbicides and Polychlorinated Dibenzo-p-dioxin.

Site "C" is the location of a former mixing and batching facility that operated for approximately 70 years. Products mixed, packaged and stored include herbicides, insecticides, disinfectants, soaps, floor waxes and wood preservatives. The herbicides processed at this facility were 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), the two components of Agent Orange. Both compounds are known to contain polychlorinated dibenzo-p-dioxin (dioxin) impurities, although only 2,4,5-T contains the potent toxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

Dioxins and phenoxy herbicides are not currently on the Superfund TCL; however, during the Remedial Investigation of this site, monitoring was conducted for these three compounds. TCDD was detected mostly in on-site surface soils at levels to 48 ug/kg. Both 2,4-D and 2,4,5-T were detected in on-site subsurface soils and groundwater. In addition, 2,4-D was detected at a nearby municipal wellfield in the groundwater and in the subsurface soils below the water table. Because both herbicides are readily biodegraded in aerobic conditions,[13] their nondetection in surface soils was not unexpected.

The municipal wellfield operated from 1959 until 1982. The exact chemicals intercepted by the municipal wells are unknown as are the time period each chemical was intercepted and the concentrations delivered to the distribution system. However, a minimal amount of monitoring of the municipal wells indicated the presence of "phenols" as early as 1959 and of VOCs in 1980. No monitoring was conducted of the municipal well water for herbicides, insecticides, acid/base/neutral extractable compounds, inorganic compounds and certain volatile organic compounds. No aquifer test to determine the capture zone has been conducted.

By 1959, the soils beneath the water table of the wellfield were contaminated. In the 1985 Remedial Investigation, monitoring of subsurface soil borings and groundwater indicated the presence of site-related contaminants below the water table (pesticides, herbicides, creosote constituents and arsenic). Any of the site-related contaminants may have been captured by the municipal wells. The possible exception is 2,3,7,8-TCDD, which binds tightly to soils[14] and has been detected mostly in the surface soil.

The exact area receiving potable water from this wellfield is not known due to a lack of detailed information on: (1) the municipal distribution

system, (2) the relative contribution of the three existing water supply sources at any given time and (3) the effect of demand at any given time. Three observations were used to identify the consumers likely to have received water from this wellfield. First, the water flow within the pipes would tend to follow the path of least resistance; therefore, water from this source would not tend to travel towards the input of the other two water sources. Second, one of the other water sources contained high levels of manganese and iron, which would result in poor aesthetic qualities. This water source elicited strong complaints from the impacted consumers; as a result, the general area that received this water is known. Third, this community shares two water distribution system interconnections with a neighboring town. Because these two towns have the same water sources and treatment plants, the interconnections tended to remain open. The two towns have a total of five census tracts. Two census tracts (one from each town) are more apt to have received drinking water from the contaminated wellfield.

The carcinogenicity of 2,4-D and 2,4,5-T has not been classified by the U.S. EPA or IARC because inconclusive information is available.[13-15] However, based on occupational studies, 2,4-D may be associated with development of non-Hodgkins lymphoma and, to a lesser extent, soft tissue sarcoma and 2,4,5-T with soft tissue sarcoma and, perhaps, non-Hodgkins lymphoma and Hodgkins Disease. These studies cannot determine the relative contribution of the dioxin impurities to the toxic effects. Other site-related contaminants have been associated with non-Hodgkins lymphoma (benzene and arsenic) and Hodgkins Disease (benzene).[16,17] The cancers of the hematological system have been associated with various risk factors, including immuno-deficiency.[18] For example, primary, acquired and therapeutic immunodeficiency disorders have been shown to increase the risk of developing non-Hodgkins lymphoma. Site-related contaminants that may impair the immunohematopoietic system or depress immunity include chlordane, DDT, dieldrin, hexachlorocyclohexanes, 2,3,7,8-TCDD, benzene and arsenic. Whether the chemicals affecting immunity and those chemicals implicated in hematologic cancers interact in a synergistic manner to increase the risk of developing non-Hodgkins lymphoma or Hodgkins Disease is unknown.

Soft tissue sarcoma, non-Hodgkins lymphoma and Hodgkins Disease were added to the primary cancers usually considered by the MDPH for the health outcome study, because: (1) a number of site-related compounds have been associated with these cancers and (2) human exposure to a large population may have occurred via the municipal water distribution system. The two census tracts most likely to have received the water were targeted in the analyses of health outcome data. The health outcome analyses indicated statistically significant elevations in non-Hodgkins lymphoma incidence in the two targeted census tracts, but not in the three bordering census tracts. Statistically significant elevations in Hodgkins disease and soft tissue sarcoma incidences were not observed. As a result of these findings, physician and community education programs will be implemented. Currently, Site "C" is being evaluated by ATSDR for appropriate follow-up with respect to these potential health effects.

Case 4: Arsine and Methylarsines.

Another compound processed at Site "C" was sodium arsenite. Aqueous solutions of this compound were prepared for use as a potato top and weed killer. Arsenic has been detected in the sites soils, sediments, groundwater and surface water at levels to 380,000 mg/kg, 1,290 mg/kg, 3,850 ug/L and 87 ug/L, respectively. The on-site wetlands contain arsenic-contaminated soil at levels to 5,700 mg/kg.

Wetland soils tend to be relatively anaerobic, reducing environments and, under these conditions, arsenic could be reduced and methylated by microbial organisms to volatile species. The predominant forms found in similar environments (e.g., swamps and bogs) are methylarsines, arsine and elemental arsenic.[16] This process also could occur in other anaerobic/reducing environments, such as river or lake sediments and flooded areas. The species of arsenic present are dependent upon the physical and chemical characteristics of the soils and groundwater and the presence of microflora. The species present would change as con-

ditions change. Speciation of arsenic was not conducted during monitoring and, therefore, the presence of arsine and methylarsines has not been confirmed. However, volatilization of arsine and methylarsines should not be a factor unless soils are disturbed, such as during remediation.

Hemolytic anemia is known to occur following inhalation of arsine and, to lesser extents, methylarsines.[16] This disease is also known to occur in humans following oral, inhalation, dermal and transplacental exposure to naphthalene.[19] Naphthalene has been detected in the sites soils and groundwater at levels to 3,400,000 ug/kg and 13,000 ug/L, respectively. Individuals deficient in erythrocyte glucose-6-phosphate dehydrogenase (G-6-PD), an X-chromosome linked recessive trait, are susceptible to hemolytic anemia from exposure to naphthalene. Because this trait is X-linked, males express this disorder more often than females.[20] The severity and frequency of the deficiency varies between ethnic groups. Susceptibility of developing hemolytic anemia exists because reduction of NADP (and also GSSG) does not readily occur; thus, a challenge by an oxidant can result in depletion of GSH, oxidation of hemoglobin and hemolysis.

Whether individuals with G-6-PD deficiency are also susceptible to arsine- and methylarsine-induced hemolytic anemia is unknown, but appears probable. Both naphthalene and arsine act by depleting GSH and causing the oxidation of hemoglobin and hemolysis. In addition, symptoms of naphthalene and arsine toxicity are the same, i.e., jaundice, anemia and renal damage.[16,20]

Excavation of soils and wetland areas during remediation could result in the release of naphthalene and arsine/methylarsines, respectively. Without the proper safeguards, susceptible individuals could develop hemolytic anemia. Because arsine and methylarsines are oxidized to nonvolatile forms once released to the atmosphere,[16] human exposure and health effects from these chemicals are unlikely in off-site areas. Due to the concern from hemolytic anemia, a recommendation in the Health Assessment was to identify whether individuals who will be present during remediation have G-6-PD deficiency. To minimize the possibility of developing hemolytic anemia, particular care is needed to provide the appropriate personal protection equipment to any individual with this deficiency.

DISCUSSION/CONCLUSION

To predict the presence of non-TCL substances, a review of many factors is appropriate. The following factors have been examined by the MDPH, and examples are presented in the cases described above: (1) the chemicals used, made or disposed at a site, (2) the by-products or impurities of specific chemicals, (3) the natural degradation and transformation processes for specific chemicals, including microbial processes, and (4) the occurrence of fires at a site, which might result in chemical transformations.

By incorporating this review in the Health Assessment process, the MDPH has determined concern for specific cancers, including rare cancers and other adverse health outcomes. These cancers were then targeted in the review and analysis of health outcome data contained in each health assessment prepared by the MDPH. Another paper to be presented at this conference expands this idea and presents a case example.[21] In addition, the inclusion of non-TCL hazardous substances has led to various conclusions and recommendations in the Health Assessment, such as: (1) recommended environmental monitoring for specific non-TCL compounds, (2) the potential existence for specific cancers and other human health outcomes, (3) the potential existence of a sensitive subpopulation and recommended further identification of that population and (4) recommended worker and public safety precautions relative to specific non-TCL substances.

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Ecological Assessment and Modeling of a Contaminated Wetland

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ABSTRACT

Disposal practices at the Sullivan's Ledge Superfund Site in New Bedford, Massachusetts, have resulted in the transport of contaminants including PCBs to wetland areas downstream of the landfill. An ROD was signed on June 29, 1989 which outlined the remedial action to be undertaken at the site. However, there is concern that, if a portion of the PCB-contaminated sediments in wetland areas within the site are not excavated, they may continue to pose a long-term threat to a variety of aquatic and terrestrial organisms that inhabit the wetland areas. U.S. EPA has determined that additional studies, including biological testing, are needed before a final remedial action decision on the wetlands areas is given.

Determining appropriate remedial action in wetlands is complicated because of the need to: evaluate existing potential wildlife and other wetland values; identify ecological risk due to exposure to contaminated wetlands; and define the transport and distribution of contaminants in the wetland. For this site, additional wetland, hydrologic and ecological studies and soil/sediment sampling have been conducted to further define the nature and extent of contamination of wetlands areas within the site, with particular emphasis on a 12-acre wetlands area named Middle Wetland. These investigations indicate that the highest sedimentary PCB concentrations are located in low lying, frequently inundated areas of the wetland.

The ecological risk assessment indicates that there may be unacceptable ecological risk in the wetland as a result of exposure of organisms to contaminated sediments which support an aquatic food chain as well as exposure of associated terrestrial and semiaquatic food systems to contaminated soils. In order to identify cleanup levels for remediation of wetlands which are protective of the environment, numerous remediation criteria will be developed based on different ecological systems (aquatic vs. nonaquatic and exposures and associated risks). Finally, to evaluate appropriate remedial alternatives for the remediation of wetlands, a thorough examination of sediment and soil removal techniques will be performed to determine remedial options which shall achieve the cleanup objectives while, to the extent feasible, minimizing reduction of the existing wetland values.

INTRODUCTION

The U.S. EPA is conducting, through a contract with Metcalf & Eddy, a remedial investigation and feasibility study of Middle Wetland, a 13-acre palustrine forested wetland downstream of the Sullivan's Ledge landfill Superfund site in New Bedford, Massachusetts. The study area includes Middle Wetland and associated wetlands areas adjacent to the stream (Fig. 1). The landfill site is a quarry that was used between the 1930s and the 1970s as a disposal area for a variety of industrial wastes including capacitors and transformers. The Sullivan's Ledge landfill site

has been the subject of Phase I and Phase II RI/FS completed in January 1989.[1,2] These investigations revealed that contaminants, including PCBs, were present in high concentrations in the disposal area. Furthermore, soils and contaminated groundwater have migrated from the landfill to the adjacent stream.
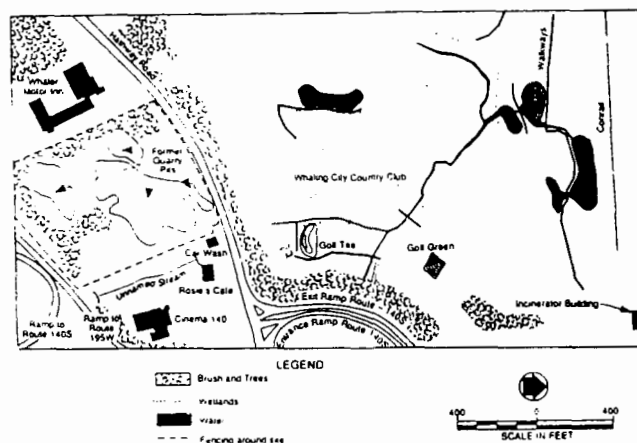
Figure 1
Middle Marsh Study Area

The 1989 ROD which addressed the landfill and the unnamed stream further specified that the U.S. EPA would conduct additional wetlands, hydrologic, ecological and sediment/soil studies in Middle Wetland to determine whether the contaminants in the wetland posed a significant ecological threat warranting destruction of the valuable habitat in the wetland. These supplemental studies are the focus of this paper.

CONTAMINANT TRANSPORT HYPOTHESIS

The first step in conducting the additional studies was to develop a testable hypothesis concerning the transport of PCBs to and within the wetland. Once the hypothesis was confirmed, the distribution of PCBs could be understood and the areas of maximum contamination and thus greatest potential ecological risk, could be delineated with an efficient sampling program. An understanding of the transport and behavior of PCBs within the different media in the wetland (i.e., soil, sediment, pore water and standing water) would be useful in documenting the ecological risk and assessing various remediation strategies.

The unnamed stream adjacent to the disposal area appeared to be the most likely vehicle for transport of PCBs to Middle Wetland. The

transport would occur by erosion of contaminated soil particles, particularly smaller-sized particles, in the disposal area and then overland flow to the stream during rain events. Immediately adjacent to the disposal area, the stream gradient and thus the velocity, is great, and deposition of contaminated soils seemed reduced. However, once the stream enters Middle Wetland the topography flattens out and particles kept in suspension by the water velocity settle out. A transport hypothesis explaining how the PCBs got to Middle Wetland was posed based on this scenario.

A similar logic was used to develop a hypothesis for the mechanics of PCB distribution within the Wetland. During most hydraulic conditions the channel within Middle Wetland contains most of the flow, but during storms the channel overflows, inundating much of the wetland area. It seemed likely and initial observations confirmed, that when the channel overflowed, the suspended load was deposited in areas of the wetland. It appeared that there were two likely areas of deposition: one was immediately outside of the channel and in immediately adjacent low areas where the suspended load would be deposited in small frequent storms; the other area was at the inland boundary of inundated areas where, during larger storms, advective flow would cease and the remaining suspended load would be deposited. The first area would receive deposition relatively frequently and thus could have high concentrations of PCBs. The second area would receive less frequent deposition events, but because they would occur during larger storms carrying a greater suspended load, they also could have high PCB concentrations.

TESTING THE HYPOTHESIS

A program consisting of three critical elements was conducted to evaluate the PCB transport and distribution hypothesis. The first step was to define and reproduce the hydraulic conditions in the Middle Wetland watershed. The second step was to use this description and other information to predict areas of high deposition and, thus, potential PCB contamination. The final step was to measure PCB concentrations in the areas of predicted elevated PCB levels. The approach for each step is described below. The study is ongoing and not all results are available, but some general observations based on preliminary results are presented.

Middle Wetland Hydraulic Conditions

Preliminary baseline hydrology data were collected under the previous RI. These data, however, were limited with respect to the description of hydrologic conditions downstream of Hathaway Road. In order to support a detailed hydrologic and hydraulic analysis of Middle Wetland and the upstream wetland area, previous data were supplemented with additional hydrologic data collected during three wet weather events using the methods described below. Wet weather events were monitored on January 25, February 10 and April 3-4, 1990. The most definitive data were collected during the storm of April 3-4, when a storm of 3.17 inches of rainfall were measured from start to finish including measurements of peak flow. The April storm was approximately equal to the storm with a 1-year return frequency and resulted in flooding of most of Middle Wetland and golf course areas adjacent to the ponds between Middle Wetland and Apponagansett Swamp. Hydrologic measurements included flow velocity, stage or elevation and depth at preestablished stations in the unnamed stream. Field reconnaissance was conducted during December 1989 to plan the hydrologic surveys and to select cross-sections and flow monitoring stations. Fifteen cross-sections were selected in the unnamed stream for input to the hydraulic model.

During the hydrologic surveys, flows were measured at nine cross-sections. All measurements were taken within the effective cross-section (i.e., shallow areas of bank overflow were not considered). Elevation or stream stage measurements were collected by measuring the distance from the top of a stake of known elevation to the water surface. A rain gage was used to collect information on amount of rainfall. Readings were taken approximately every two hours during the sampling event in order to develop a hydrograph for the storm. These data were supplemented with data collected by the National Weather Service.

As soon as possible after the onset of each wet weather event, the survey crew commenced monitoring stream flow and elevation. Measurements were conducted at established cross-sections until stream flow and elevation had increased and stabilized for a significant period of time or until stream flow and elevation rose and subsided substantially. Monitoring of each cross-section station included measuring flow width and depth and recording observed water quality. The objective of the surveys was to measure peak wet weather flow data with which to calibrate the hydrologic model.

A detailed land survey was conducted focusing on the 13-acre wetland area known as Middle Wetland as well as extensive adjacent golf course areas and a previously unsampled upstream wetland area. The principal technical components of this survey included: (1) development of a 1-foot contour map of the areas described above, (2) surveying of 16 stream cross-sections located at all hydraulic control structures and in open and forested areas to support hydraulic modeling of the unnamed stream, (3) location of numbered perimeter wetland delineation and internal habitat delineation markers, (4) location of previous and planned sediment/soil sampling stations, (5) placement of surveyed stakes adjacent to the unnamed stream to enable measurement of water elevation and (6) establishment and field marking of a 100-foot grid to enable location of selected sediment/soil sampling stations in the field by triangulation. Data collected during the survey were used to produce detailed topographic mapping of the study area at horizontal scales of 1 inch equals 80 feet and 1 inch equals 40 feet, at a contour interval of 1 foot, annotated with numerous spot elevations. Subsequently, digitized contour data were downloaded into a geographic information system (ARC-INFO) and a detailed basemap was generated.

As stated above, the objective of the wet weather stream monitoring was to help describe the hydrologic characteristics of the study area. Stream flow data collected during this study were used, along with drainage catchment and culvert data, to develop a hydrologic model of wet weather surface run-off from subcatchments tributary to the study area. This model was used to predict flow in the unnamed stream for 24-hour storms with return periods ranging from less than 1 year up to 100 years.

Flow predictions in the previous RI were made using TR-55. For this study, TR-20 was used. TR-20 is capable of providing a more detailed approach involving the analysis of separate subcatchments and discrete reaches of stream. The input requirements of these two programs are compatible, thus some of the basic drainage basin and culvert data developed during the previous RI were verified or refined and then reused during this study. Storm distribution, times of concentration and curve numbers were developed using guidance set forth in the Soil Conservation Service National Engineering Handbook. Areas of subcatchments, hydraulic lengths and slopes were developed from the most recent USGS map of the area and city drainage plans.

TR-20 was calibrated using stream flow and rainfall data collected during the April 3-4, 1990 wet weather (storm) event. This storm was used because it was the largest storm monitored and because of the volume of data collected. In addition, data collected for this storm included distinct peak flow measurements. The calibrated model was then used to develop hydrographs for more severe, less frequent storm events with return periods between 1 and 100 years. Peak flows calculated for the 1, 2, 5, 25, 50 and 100 year 24-hour storms were 114, 181, 253, 420, 471 and 555 ft^3/sec, respectively. The flow of 555 ft^3/sec calculated for the 100-year 24-hour storm was used in the hydraulic analysis to determine the extent of the 100-year floodplain within the study area.

A qualitative hydraulic analysis of normal and flood conditions was conducted for the stream reach adjacent to the Sullivan's Ledge disposal area during the previous RI. However, the normal hydraulic regime and flooding within the study area downstream of Hathaway Road were not addressed in detail. Accordingly, a detailed analysis of normal and wet weather hydraulics, as well as extreme flooding, was conducted for the area downstream of Hathaway Road.

A one-dimensional hydraulic model was developed for the area between Hathaway Road and the Conrail railroad embankment. Although Middle Wetland comprises a relatively small part of this area,

the hydraulics within it are controlled by the response of the entire area. HEC-2 (published by the U.S. Army Corps of Engineers[3]) was used to simulate normal and wet weather hydraulics within the entire area. This model assumes gradually varied flow conditions.

HEC-2 requires the development of detailed cross-sections of the stream and overbank areas as well as for all culverts, weirs and bridges. Detailed stream cross-section and topographic mapping of overbank wetland and low-lying golf course areas were used to develop cross-section input data for HEC-2. Flow input to the model was developed from monitoring data collected during wet weather events and TR-20 hydrologic modeling predictions for 24-hour 1, 2, 5, 25, 50 and 100 year design storms.

One objective of the hydraulic modeling was to determine the frequency and extent to which different areas of Middle Wetland are flooded. This information was needed as the basis for selecting sediment/soil sample locations within the range of elevation intervals in the wetland to identify correlations between contaminant levels and elevation or flooding frequency. However, following an analysis of the 1, 2, 5, 25, 50 and 100 year storm flows, it was revealed that the majority of Middle Wetland flooded during all storms analyzed. Thus, it was necessary to evaluate smaller storms with return periods between 0 and 1 year. Since there are no established literature values for storms below a 1 year return period, various storms of less than a 1 year return period were selected by extrapolating from a plot of rainfall versus return frequency on log-probability paper. Peak flows calculated for the 3 month, 6 month and 9 month storms were 30, 68 and 90 ft³/sec, respectively. The results were used to evaluate the frequency with which the unnamed stream overtops its banks and floods depressed wetland areas near the bank of the unnamed stream.

Flood elevations for the 3, 6 and 9 month and the 1, 25 and 100 years storms were superimposed on the basemap of the Middle Wetland area. This analysis revealed that due to the low flat topography of Middle Wetland, the banks of the unnamed stream overflow at least once every 3 months for a 24-hour storm, flooding extensive areas of Middle Wetland. The 3 month storm floods areas below elevation 63 encompassing approximately 6 acres of the wetland extending into the extremities of the area on both sides of the unnamed stream. The 6- and 9-month 24-hour storms flood to elevations 63.92 and 63.34, respectively, encompassing smaller increments of the wetland due to the rising topography at the edges of the wetland, resulting in flooding of a 0.5 acre area not inundated by the 3 and 6 month storms. With a flood elevation over 64 feet, the 9 month storm also results in inundation of approximately 3 acres of golf course fairways adjacent to the hazards or ponds between Middle Wetland and the railroad embankment. The 25 and 100 year storms inundate the entirety of Middle Wetland and significantly larger areas of the golf course.

Prediction of Contaminated Areas

The objective of predicting contaminated areas was to follow the logic of the transport and distribution hypothesis and identify likely areas of contamination. Also, as an evaluation of the hypothesis, areas that could be contaminated as a result of alternative transport mechanisms were identified. Each area identified as potentially contaminated by the primary or alternative hypotheses was then slated for sampling.

As described above, the hydraulic modeling identified areas that were frequently inundated and thus potentially contaminated. It could be demonstrated that several of the areas were flooded due to run-off from the margins of the drainage basin and not from overflow of the unnamed stream channel. In these cases, contamination was not expected and they were not selected for intensive sampling. Some such areas were sampled and, if high concentrations of PCBs were found, the hypothesis tested would not fully explain the distribution and transport of contaminants.

The modeling predicted frequent inundation of a wetland area just upstream from Middle Wetland. Although there was no previous documentation of contamination in this wetland area, under the transport and distribution hypothesis, it met the conditions for potential contamination. Consequently, it was identified as a potentially contaminated area.

There were areas within Middle Wetland that supported different vegetation types indicating differences in elevation and thus frequency and extent of inundation. In several of these areas, the detailed topographic survey conducted for the hydraulic modeling did not identify the small differences in elevation and hydrology that can produce such vegetative differences. Also, areas that were historically low could have received significant deposition (and thus potential contamination) over time. Such areas might not now be active depositional areas now but the historic deposition could support different vegetation and these areas were identified as potentially contaminated areas.

A topographic high spot on the northern side of Middle Wetland is an example of an area supporting different vegetation that could be contaminated even though inundation from the stream channel was not predicted for the area. This area supports a stand of the Common reed *Phragmites* and is adjacent to a water hazard on the golf course just beyond Middle Wetland. Previous studies and observations have documented that the sediments in the water hazard are contaminated. Since the Common reed frequently grows in disturbed soils, such as dredged material, the presence of the reeds in this area could indicate potentially contaminated dredged material.

The final category of potentially contaminated areas was previously identified "hot spots." Neither the persistence or the cause of the areas of elevated PCB concentrations had been fully documented. If the "hot spots" correlated with predicted depositional areas and they were consistently higher in PCB concentration than surrounding areas, then the transport hypothesis would be advanced. Other results could indicate a different transport mechanism and/or a secondary source of contamination.

Measurement of PCB Concentration in Potentially Contaminated Areas

To evaluate the potentially contaminated areas, 42 stations were sampled (Fig. 2). At 12 stations, two-foot core samples were taken in four six-inch fractions to examine the vertical extent of contamination. As PCBs are hydrophobic and tend to adhere to organic soils, each sample was analyzed for total organic carbon. To examine partitioning of contaminants between the sediments and water, a pore water sample was extracted using a well point and bailer. If standing water was present at the station, a surface water sample also was collected.
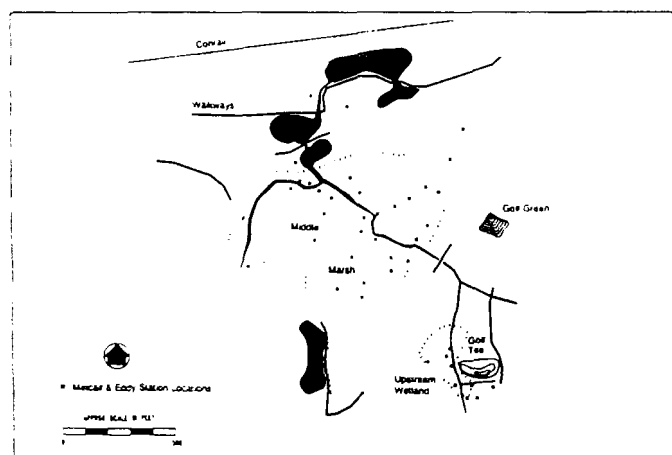
Figure 2
Middle Marsh Soil/Sediment Sampling Stations

This sampling protocol allows not only the identification of contaminated areas, but also provides information which will aid in interpreting the transport and distribution mechanisms. The information also will be useful in understanding the potential bioavailability of the PCBs and thus lend insight into the ecological risk.

The data validation and interpretation are ongoing, but some preliminary results allow for some general interpretations. Sampling results showed a strong correlation between PCB concentrations and

frequency of flooding and supported the hypothesis that deposition occurs mostly in areas close to the stream and in the most upgradient areas of the wetland where stream flows heavy in sediment are expected to meet quiescent areas of Middle Wetland formed during periods of flooding. There is some indication that the most upstream areas of Middle Wetland, which would receive a higher proportion of sediments from Sullivan's Ledge disposal site, have the highest concentration of PCBs (Figs. 3 and 4).

The highest concentrations of PCBs were found in the wetland area upstream from Middle Wetland (Figs. 3 and 4). Subsequent observations during a major storm event indicated that under very high flow conditions the stream overflows the channel in this area and, thus, it is the first area where suspended particles can be deposited. This information lends strong support to the primary contaminant transport and distribution hypothesis. This finding has prompted additional investigations in the area to further define the extent and degree of contamination.
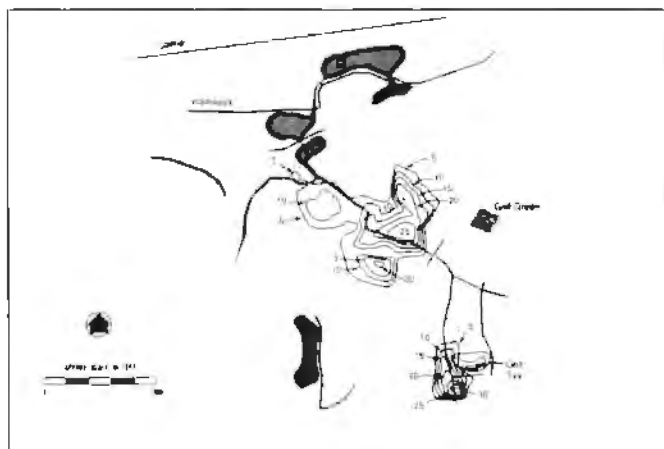
Figure 3
PCB Concentrations (mg/kg) in Marsh
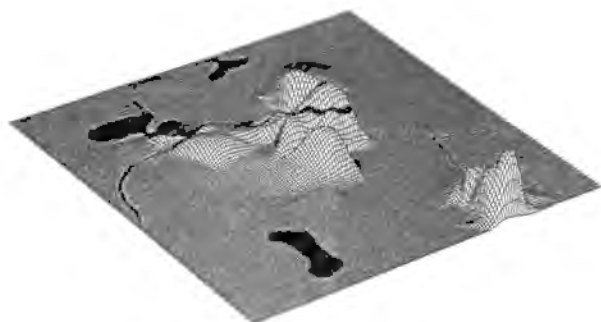
Figure 4
Perspective of PCB Concentration

REMEDIATION APPROACH

There are two elements of the Middle Marsh remediation that must be considered in a site-specific manner. The first remedial element is defining the ecological risk in Middle Marsh as it relates to contaminant concentrations, and the second element is alternative remediation techniques that minimize disruption to existing wildlife and other wetland values of Middle Marsh. Each of these element is discussed below.

Defining Ecological Risk

A critical element in defining the ecological risk is the development of appropriate remediation criteria. Potential criteria designed to pro-

tect biota include sediment quality criteria which are based on the equilibrium partitioning method and accumulation factor-based criteria developed from ecological modeling and estimates of bioaccumulation. In Middle Marsh, both of these approaches may apply and we are investigating the details and application of each process.

Sediment quality criteria are used to estimate sediment toxicity and the biological impact of in-place contaminated sediments. They are intended to be protective of the presence and uses of benthic organisms.[4] The method of calculating sediment quality criteria is based on: (1) the pore water concentration being controlled by partitioning between the liquid phase and the solid phase and (2) the fact that toxicity and exposure of benthic organisms are a function of the pore water concentration rather than the total concentration in the sediment. Partitioning is dictated by a partitioning coefficient that allows calculation of pore water concentration from known sediment concentrations. Organic contaminants, like PCBs, sorb to organic carbon in the sediments. The partitioning coefficient is based on the contaminant characteristic, the octanol-water partioning coefficient and the carbon fraction in the sediment. Hydrophobic chemicals tend to bind to colloidal organic particles. Thus, there is an inverse relationship between the organic content of soils and the bioavailability of PCB. Use of this method depends on the assumption that benthic organisms are as sensitive to contamination as are water column organisms.

Contaminant-specific criteria for sediments are derived from water quality criteria[5] through use of the partitioning coefficient. These data allow back-calculation of safe sediment levels in pore waters that will not exceed water quality criteria. These criteria are intended to protect benthic organisms from long-term exposure and bioaccumulation in higher levels of the food chain. For PCBs, the chronic water quality criterion for freshwater initially set forth by the U.S. EPA in 1980 is 0.014 ug/L and is based on protection of wildlife from long-term consumption of benthic organisms and their predators. Such benthic organisms exposure and accumulation of PCBs is based on intimate contact with the contaminated sediments and associated pore waters. This occurs in true benthic organisms through cutaneous or gill breathing as well as feeding. Many of the freshwater organisms are filter feeders and pump large volumes of water (or use currents for the same purpose) in the process of feeding.

In Middle Marsh, there are areas which support benthic organisms, and there are consumers of such organisms. Therefore, the exposure pathways and assumptions used to develop sediment criteria exist. In these areas the application of sediment quality criteria may be the appropriate method to establish remediation criteria. Efforts are currently underway to delineate areas that could support such aquatic communities. The delineation is being performed by evaluating the hydraulic information to define areas that support standing water most of the year. This information is being supplemented by observations of benthic organisms during the drier part of the year in the identified areas.

In much of Middle Marsh, conditions are not likely to support a self-sustaining aquatic community. In these areas, the hydraulic information does not indicate extended periods of standing water, the vegetation is not reflective of open water environments and the densely vegetated substrate inhibits a self-contained aquatic food chain. In these areas, there may not be the exposure pathway of true aquatic systems because the mechanisms do not exist to allow for the transport of PCB through the aquatic biotic environment to the sensitive wildlife species. In these areas, an ecological model is being considered to evaluate the potential ecological risk.

This model is being developed to investigate the potential for movement of contaminants through the ecosystem and to assist in documenting the importance of various areas in the wetland. Using species observed in the wetland and species expected to occur based on a habitat evaluation, a food chain model is being constructed. The model is being used to facilitate an understanding of the relationship between the biotic and abiotic components of the wetland such as the water and soil matrix. An extensive literature search was conducted to identify analogous studies and toxicity data and bioaccumulation factors for the species used in the food chain model.

Alternative Remediation Techniques

One of the critical elements of remediation in Middle Marsh is to access and remove contaminated material with minimal damage to existing wildlife and other wetland functions. This is being addressed by examining innovative removal techniques including:

- In-place capping to seal contaminated sediments particularly by increasing elevation to eliminate inundation and erosion during storm events
- Hydraulic flushing to remove contaminated surface soils with only minimal disruption of root systems
- Vacuum removal to minimize damage to plants
- Immediate replacement of clean soils to minimize exposure and damage to root systems

- Use of small equipment to minimize destruction of plants and the associated habitat

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Modification of the Persistence Factor in the Hazard Ranking System

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ABSTRACT

The purpose of this paper is to show how the persistence factor in the Hazard Ranking System was modified to reflect the retention of hazardous substances in bed sediments by the process of sorption. The persistence factor is used to stratify chemicals on the basis of their anticipated losses during transport in the water column by decay mechanisms such as volatilization, hydrolysis, photolysis and biodegradation. Chemicals that are rapidly eliminated from the surface water system pose fewer risks to humans and ecological receptors and receive low persistence scores. Compounds that do not decay appreciably in the water column receive high persistence scores.

An assumption inherent in the definition of persistence is that a hazardous substance enters the water column in a dissolved state and remains there. Although this assumption is valid for highly water-soluble compounds, constituents with low water solubility sorb to suspended and shallow bed sediments and have reduced water-phase concentrations.

Steady-state models were used to understand the differences among chemicals and the relationship between degradation in the water column and retention in bed sediments. An exponential decrease in concentration between the source and target distance exists as a function of travel time and decay rate. Because the sediments and water are in equilibrium under steady-state conditions, the sediment concentration profile reflects the same first-order decrease as that of the water column.

This paper illustrates how the relative mass of a hazardous substance in the surface water system is a function of half-life and K_{ow} and how a substances' K_{ow} can be related to its persistence score.

INTRODUCTION

Persistence is the capability of a substance to resist reduction of its concentration despite the several decay processes imposed on it by the environment. The persistence factor is included in the surface water pathway to account for any reduction in concentration of a hazardous substance during transport from its source to a specified target distance. This factor is used to stratify hazardous substances and allows the calculation of the effective concentration at the target distance.

During the field testing of the Revised Hazard Ranking System (Revised HRS), it was discovered that several hazardous substances known to be extremely persistent in surface water (such as PCBs) were rated as being of low to moderate persistence. CH2M HILL was asked to review the persistence values assigned to hazardous substances to determine whether there is a need for changes in the method of scoring these substances, producing a support document for the changes made to the persistence factor leading to the scoring scheme promulgated in the current draft final rule.

The persistence of a substance is a function of its decay rate and travel time. In the original HRS, the persistence value for a hazardous substance was based solely on its biodegradability. However, the Revised HRS recognizes that decay processes other than biodegradation also affect the persistence of a substance; these processes are hydrolysis, volatilization, photolysis and free-radical oxidation. Sorption of hazardous substances onto particulates or sediment also is considered a decay process, but it is not included in the Revised HRS because the hazardous substances still could be available to ecosystems through uptake by benthic organisms or by resuspension.

The technical analysis of the Revised HRS persistence factor focused on the importance or contribution of each decay process to overall half-life, the actual travel time or residence of a hazardous substance in a water body and the effect that sorption to particulates or sediment has on persistence. Also, attempts were made to simplify the persistence scoring process by basing the values on factors other than the decay processes. This paper focuses on sorption. Instead of considering sorption to particulates or sediment solely as a decay process, it was studied as a process that can also enhance the persistence of hazardous substances. This possibility was investigated by looking at the relationship between degradation in the water column and retention in bed sediments.

PERSISTENCE IN THE HRS

The relative change in concentration of a pollutant downstream from its source determines its persistence. After discharge to surface water, the concentrations of many contaminants are reduced by decay mechanisms such as volatilization, hydrolysis, photolysis and biodegradation. Chemicals that are rapidly eliminated from the system pose fewer risks to humans and ecological receptors.

The persistence value assigned to a hazardous substance is based on the effects of decay processes and on the predicted time for the hazardous substance to travel from the source to the target 15 mi downstream. Only substances with half-lives much shorter than the travel time will decay significantly over the target distance. A hazardous substance with a half-life greater than the predicted travel time, or a decay rate of 0 to 50%, is scored as "persistent"; a hazardous substance that decays 50 to 90% is rated as moderately persistent; a hazardous substance that decays 90 to 99.9% is rated as having low persistence; and a hazardous substance that decays more than 99.9% is rated as nonpersistent. These ratings correspond to numerical persistence values (on a linear scale) of 1, 0.4, 0.07 and 0.0007. A travel time of 1.5 days was selected for use in scoring persistence as best representing the median stream velocity in the United States.

SORPTION

The retention of hazardous substances by suspended particulates or bed sediments by the process of sorption will result in changes in the

persistence scoring of these hazardous substances. Hazardous substances that sorb to suspended and shallow bed sediments will have reduced water-phase concentrations. Sorption not only decreases the rate of decay of a hazardous substance, but it also decreases mobility when the substance is retained in bed sediments. The hazardous substance is retained between the discharge point and the downstream 15-mi target for a longer period and typically releases slowly from sediments after the pollutant source is eliminated.

An assumption inherent in the definition of persistence is that a contaminant enters the water column in a dissolved state and remains so. Although this assumption is valid for highly water-soluble compounds, constituents with low water solubility sorb to particulates. Compounds that sorb to suspended and shallow bed sediments have reduced water-phase concentrations. Sorption not only decreases the rate of decay of a constituent, but it also decreases mobility when the substance is retained in bed sediments. The contaminant is retained between the discharge point and the downstream exposure point and typically releases slowly from sediments after the pollutant source is eliminated.

Examples of highly hydrophobic compounds that sorb to particulates are DDT, PCBs and many phthalates and polynuclear aromatic compounds. Hydrophobic compounds generally are carried with particulates into surface water from run-off or deposition and may, in some cases, be strongly bound to these particulates. Compounds such as acetone do not sorb to particulates and are present predominantly in the water phase.

The half-lives are relatively short for many chemicals with low water solubility, which typically are perceived as being persistent in surface water bodies because of their retention in sediments. The half-lives of hydrophobic chemicals appear short, in part, because of their rates of volatilization. Volatilization from water is a function of both vapor pressure and water solubility. Therefore, compounds with relatively low vapor pressures have enhanced rates of volatilization from water as a result of their low water solubility, as illustrated in Table 1.

Table 1

Compound	Estimated Volatilization Half-Life* (days)	Vapor Pressure (mm/Hg)	Water Solubility (mg/l)
Chloroform	1.2	151	8,200
Acetone	17.8	270	miscible
PCBs	2	7.7E-5	0.031

*Rivers.

The compounds with low water solubility, however, typically are reported in sediments that are not in the water column. Sedimentation was not considered a removal mechanism in previous analyses because of potential resuspension, dissolution and ecological impacts, including benthic uptake.

The sequence of instream events after the introduction and then the elimination of a source of hazardous substances has been described by the U.S. EPA[1] If a hazardous substance is discharged to the water column, pollutant concentration in the sediments at the bottom increases due to (1) the partitioning of the water and the sediments, and (2) the exchange between bed sediments and water column sediments. After a period of time, the net exchange diminishes as equilibrium is achieved. If the source is eliminated, the water column concentration decreases and the pollutant is desorbed from bed sediments.

Benthic organisms retard the burial of contaminated sediment fractions, and, according to Burns,[2] lacustrine oligochaete deposits can be active to a depth of 10 to 15 cm. In models presented by Neely and Mackay,[3] bottom sediments were represented by a completely mixed, active layer that overlays the inactive deep sediments.

Although surface water bodies are dynamic, steady-state models can be used to understand the differences among chemicals and the relationship between degradation in the water column and retention in bed sediments. The U.S. EPA model *Exposure Analysis Modeling System*

(EXAMS) describes the concentration profile for the continuous release of a constituent to a surface water body. The concentration profile results for steady-state conditions are illustrated in Figure 1 for two compounds with different first-order decay rates in the water column. An exponential decrease in concentration between the source and target distance exists as a function of travel time and decay rate. Because the sediments and water are in equilibrium under steady-state conditions, the sediment concentration profile reflects the same first-order decrease as that of the water column.

CONCENTRATION PROFILE - STEADY STATE
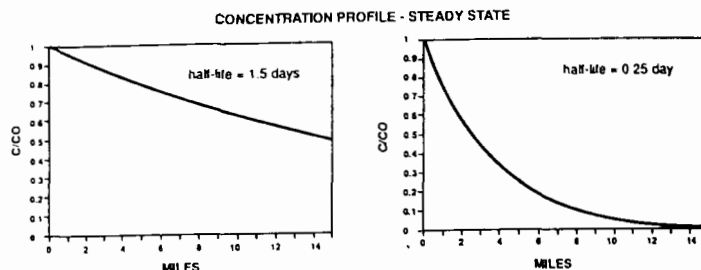
Mass of Containment in Surface Water
- Steady State Conditions -

● No decay, no sorption

$$M_o = C_o\,A\,X$$
where $X = 15$ miles

● Decay, no sorption

$$M = CoA\int_{x=0}^{x=15} e^{-kx} = CoA\left(\frac{e^{-kx_{15}}}{-k} - \frac{e^{-kx_{15}}}{-k}\right)$$

or:

$$M/Mo = (1 - e^{-kx_{15}})/15k$$

● Decay, sorption

$$M/Mo = ((1 - e^{-kx_{15}})/15k)\cdot(1/fw)$$

TERMS:
Co = initial concentration
A = Cross-sectional area of water body
X = distance
k = decay rate (1/mile)
M = mass of contaminant
fw = fraction of mass in water column

Figure 1
Surface Water Sorption and Decay

The relative concentration at the target distance (C/Co at 15 mi) depends only on the decay rate in the water column, and not on the sorptive properties of the contaminant. Once the bed sediments are in equilibrium with the surface water, there is no further net exchange and the sediments have no further influence on the decay processes in the water column. This calculation assumes negligible losses of contaminant from the bed sediments via biodegradation of the sorbed contaminant or burial to deep sediments.

Although the fraction of the total mass in the water phase (fw) is a function only of the partition coefficient and sediment/water ratio, the total mass accumulated in the sediments under steady-state conditions also is a function of the aqueous concentration. Thus, for two contaminants with the same source concentration (Co), the contaminant with the higher decay rate will have a lower overall mass in both the water column and the associated sediments.

The equations that describe mass in a river system are presented in Figure 1. The reference mass (Mo) is defined as the total mass of contaminant in the river from the source to the target distance with no decay and no sorption [that is, the river volume multiplied by the input concentration (Co)]. For constituents that decay in the water column, the mass in the river is reduced as a function of the concentration profile. The relative mass (M/Mo) is greater than the relative concentration

at the target distance (C/Co). As the rate constant (k) goes to zero, M/Mo approaches 1.

Sorption increases the mass retained in the system by the factor 1/fw or ($K_p S/W$ +1), where K_p is the partition coefficient, S is the mass of solids and W is the volume of water. For compounds that sorb and degrade, as k goes to zero, M/Mo approaches 1/fw, which is related to the equilibrium ratio of contaminant between solids and water phases. The relative mass (M/Mo) is shown in Figure 2 as a function of half-life and K_{ow}. This illustrates that sorption has a smaller effect on the retention of mass in the water body for compounds that decay rapidly relative to their travel time in the water body.
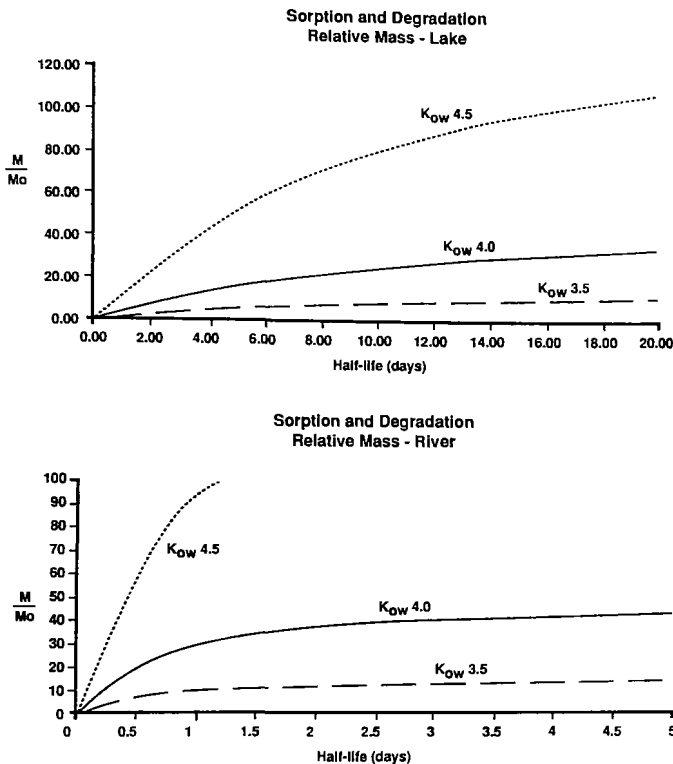
Figure 2
Sorption and Degradation
Relative Mass—Lake and River

Table 2 illustrates the relationship between K_{ow}, the increase of mass in the system at steady state (M/Mo) and the maximum increase (1/fw) for a compound at that K_{ow}.

Compounds are listed in order of decreasing partition coefficient, which corresponds to decreasing values of 1/fw. The relative mass (M/Mo) is also a function of the decay rate relative to the travel time in the system.

Several compounds have rapid decay rates relative to lake travel times. The M/Mo for hexachlorocyclopentadiene and heptachlor illustrate that highly sorbing compounds may not accumulate due to their high degradation rates.

SORPTION AND ADJUSTED HALF-LIVES

The half-life estimates in the HRS data tables are based on presence of the contaminant in the dissolved phase in the water column. It is generally assumed that the first-order decay processes degrade only this dissolved solute. Sorption reduces the water-phase concentration and decreases the rate of loss.

The partition coefficient describes the ratio of the concentrations of constituents in the phases; however, the distribution of mass also depends on the solids concentration. Suspended solids concentrations in surface waters are generally less than 500 mg/L. At this concentration, a contaminant with a K_{ow} of 4.13 would have 90% concentration in the

Table 2

Chemical Name	Log K_{ow}	River M/Mo	Lake M/Mo	1/fw	Sed %
Bis(2-Ethylhexyl)Phthalate	9.60	1.84E+07	1.47E+07	18805501	100.0
DI-n-Octyl Phthalate	9.20	7.46E+06	7.41E+06	7465501	100.0
DDD	6.20	5969	4888	7490	100.0
DDT	6.19	6828	5358	7319	100.0
Benzo(a)pyrene	6.06	3630	470	5426	100.0
Pentachlorophenol	5.86	3412	3360	3424	100.0
DDE	5.69	2234	1713	2315	100.0
Chrysene	5.61	1768	751	1926	99.9
Benz(a)anthracene	5.60	1881	1869	1882	99.9
Aldrin	5.30	788	645	944	99.9
Hexachlorobenzene	5.20	585	426	750	99.9
Pyrene	5.09	401	55	582	99.8
Hexachlorocyclopentadie	5.04	99	7	519	99.8
Hexachlorobutadiene	4.78	206	128	286	99.6
2,3,5-Trichlorophenol	4.56	145	36	173	99.4
Phenanthrene	4.46	129	79	137	99.3
Anthracene	4.45	92	13	134	99.3
Heptachlor	4.40	50	4	120	99.2
Dieldrin	4.32	98	85	100	99.0
Fluorene	4.18	55	32	73	98.6
1,2,4-Trichlorobenzene	4.12	47	26	63	98.4
3,4,5-Trichlorophenol	4.01	48	40	49	98.0
Acenapthene	4.00	41	23	48	97.9
Lindane	3.90	37	38	39	97.4
PCB'S	3.90	30	24	39	97.4
Acenapthylene	3.70	22	7	25	95.9
2,3,6-Trichlorophenol	3.40	12	8	13	92.2
1,4-Dichlorobenzene	3.39	9	6	13	92.1
Chlordane	3.32	10	7	11	90.8
Napthalene	3.30	7	4	10	90.4
Toxaphene	3.30	8	7	10	90.4
m-Xylene	3.20	6	4	8	88.2
Ethylbenzene	3.15	1	0	8	87.0
Chlorobenzene	2.84	3	2	4	76.6
Carbon Tetrachloride	2.83	3	2	4	76.2
2,4-D	2.81	4	4	4	75.3

dissolved phase. Thus, the increase in half-life as a result of sorption to suspended solids is significant only for chemicals with high partition coefficients.

Half-life also can be calculated based on the total mass of contaminant in the system, including bed sediments. This adjusted term is used in the EXAMS model. It reflects the losses resulting from degradation processes in a static system and can be used with advective losses in modeling the dynamics of the surface water system. Using the assumption of 10 cm of bed sediments with an f_{oc} of 0.04, adjusted degradation half-lives (Table 2) illustrate the apparent increase in half-life as a result of sorption to bed sediments. However, under steady-state conditions, the mass of contamination in the bed sediments is a constant and the adjusted half-life does not appropriately reflect the decrease in concentration at the target distance. Thus, this adjusted half-life cannot be directly compared with travel time.

A nonsteady-state condition results when the source of a contaminant is eliminated. In addition to the extra mass in the system for the more strongly sorbing contaminants, the time it takes to purge the system of contaminant once the source loadings cease varies according to the partition coefficient.

A method of estimating desorption of hazardous substances from a river bed as presented in *Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water*[1] is shown in Table 3. This equation illustrates that the time required for removal is directly proportional to the partition coefficient. Therefore, an increase by a factor of 10 in the partition coefficient will also lengthen the time required for removal by a factor of 10.

SUMMARY OF EFFECTS OF SORPTION

Based on this evaluation, sorption has several effects. Sorption delays the arrival of contaminants; lower concentrations may arrive at the receptor over a longer time period. Sorption to bed sediments does not affect the mass reaching the receptor if degradation occurs only in the water column. If contaminants biodegrade in the sediments, the mass of the chemical reaching the receptor will be reduced.

Table 3
Estimating Desorption of a Hazardous Substance from a River Bed

Calculation:

$$T_d = K_p \, (x_L \, M_s / U \, d)$$

where

T_d	=	time required to desorb the hazardous substance
K_p	=	partition coefficient
x_L	=	length
M_s	=	mass of contaminated sediment/unit area
U	=	stream velocity
d	=	equivalent depth of water in sediment

Estimated removal times based on a stream velocity of 15 miles in 1.5 days and a contaminant depth of 10 cm.

Log K_{ow}	Time (years)
2.0	0.1
3.0	1.1
3.3	2.1
3.5	3.3
4.0	10.5
4.5	33.0
5.0	105.0

Sorption to suspended sediments increases the concentration reaching the receptor; however, since the concentrations of the suspended sediments is low, the effects will be minimal. Contaminants that sorb to sediments may be retained near the source and may not reach the receptor at a specified downgradient location. The presence of these constituents can result in exposures along the 15-mi distance of concern.

Contaminants retained in sediments are typically of low mobility or immobile in groundwater. The mechanism by which these constituents are released and distributed into the surface water body will differ from that of highly soluble components. According to relative mass calculations, the increase in mass (M/Mo) in lakes is lower than in rivers as a result of longer retention time relative to the half-life in the water column.

ESTABLISHING PERSISTENCE SCORES FOR SORPTION TO SEDIMENTS

The foregoing discussion indicates that compounds with higher partition coefficients retain a greater contaminant mass in the system. A ranking system for stratifying the persistence of chemicals found in sediments is proposed based on the previously discussed sorption effects.

Retention in sediments may be reflected by increasing the persistence factor for chemicals with high K_{ow}. However, some compounds would be ranked as persistent based on these criteria even if the relative mass retained in the system (M/Mo) would be low. These compounds include hexachlorocyclopentadiene, anthracene and heptachlor.

The following Log K_{ow} values are proposed to reflect the tendency to persist in sediments:

Log K_{ow}	Effect on Ranking
>4.5	1
4.0–4.5	0.4
3.5–4.5	0.07
<3.5	0.0007

If a higher persistence value can be assigned using this relationship between Log K_{ow} and persistence value, the higher value should be used as the score.

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Estimating Cleanup Levels at Hazardous Waste Sites

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ABSTRACT

An important component of feasibility studies for hazardous waste sites is the development of remediation goals (cleanup levels) for contaminated soils. Ideally, these cleanup levels should be based on site-specific data and protective of human health and the environment. However, these levels often are arbitrarily related to the analytical detection limit, various federal and state water quality criteria, or natural background levels. Often such cleanup levels are much more stringent and, hence, more costly to implement than risk-based cleanup levels.

This paper describes methods for computing site-specific cleanup levels that are protective of human health and are based on an acceptable level of risk. Acceptable concentrations at the exposure point are determined from the site-specific exposure scenarios (i.e., ingestion of water, inhalation, dermal adsorption, etc.) and the chemical-specific toxicity. Contaminant transport models are then used in the "backward" mode to compute the cleanup level at the contaminant source. Two case studies are presented to illustrate the procedure.

INTRODUCTION

The goal of remediation is to clean up hazardous waste sites to a level that is protective of human health and the environment. Achievement of this goal requires the determination of the concentration of chemical that can be left in the environment without posing undue harmful effects to humans, i.e., the determination of "How clean is clean?" This maximum concentration level, defined as the cleanup level, has a direct impact on the selection, design and cost of remedial alternatives.

Although cleanup levels are conceptually defined in terms of human health, they are in practice often set to arbitrary levels such as the background concentration or the analytical detection limit. Both of these methods have serious limitations. Cleaning to background may be consistent with the concept of restoring contaminated sites to their pre-existing condition, but involves prohibitive costs. Detection limits depend upon the sample matrix and change over time as analytical methods improve. Thus, use of the detection limit as a cleanup goal can result in cleanup levels that differ from site to site. Further, there is no guarantee that either the background concentration or the detection limit is protective of human health.

This paper describes a risk assessment-based procedure for estimating cleanup levels that are protective of human health and the environment. Allowable concentrations are related directly to target risk levels, and contaminant transport models are used to back-calculate the corresponding cleanup level at the contaminant source. The paper presents a discussion of the method, including general considerations for calculating risk-based cleanup levels and guidelines for allocating risk among multiple chemicals. This is followed by a description of two case studies involving: (1) cleanup levels for a contaminated shallow aquifer and (2) cleanup levels for contaminants in the unsaturated zone.

ESTIMATING CLEANUP LEVELS TO MEET A SPECIFIED TARGET RISK LEVEL

Given a target risk level for a chemical, the cleanup level (or concentration) can be estimated using risk assessment procedures such as those recommended by the U.S. EPA.[1] These procedures are used in the "backward" mode to estimate allowable concentrations, as opposed to the usual "forward" mode to estimate risk. The procedure consists of the following steps:

- Compute the allowable chemical dose based on the target risk level
- Back-calculate the allowable concentration at the receptor location, based on the exposure scenario and chemical uptake parameters
- Back-calculate the corresponding source concentration (cleanup level) using a contaminant transport model in the "backward" mode

Estimating Allowable Dose

The allowable dose is related to the target risk level by the potency factor for carcinogens or the reference dose for noncarcinogens. For carcinogens, the allowable dose (assuming a linear dose-response model) is calculated by dividing the target risk by the potency factor:

$$D = TR/PF \tag{1}$$

where

D = the allowable dose (mg/kg-day)
TR = the target individual excess lifetime cancer risk (dimensionless)
PF = the chemical-specific potency factor (mg/kg-day)$^{-1}$

For noncarcinogens, the allowable dose is equal to the reference dose (RfD).

Estimating Allowable Receptor Concentrations

The allowable concentration in the receptor media (e.g. soil, water and air) is computed from the allowable dose and human exposure/uptake parameters. The procedure is dependent upon the exposure pathway, but generally can be applied using equations of the following form:

$$C_r = D/PEF \tag{2}$$

where

C_r = the receptor concentration (e.g., mg/L)
PEF = the pathway exposure factor (e.g., L/kg-day)

The PEF is a pathway-specific factor that is estimated from human uptake and behavioral parameters. For instance, for lifetime exposure to drinking water the PEF is given by:[1]

$$PEF = IR/BW \tag{3}$$

where

BW = body weight (kg)
IR = water intake rate (L/day)

The U.S. EPA[1] presents the relationships that can be used to estimate the PEF for other exposure scenarios. Note that the allowable receptor concentration also may be derived from federal or state action levels, such as drinking water standards or MCLs.

Estimating Cleanup Levels at the Source

Having estimated the allowable concentration at the receptor, the cleanup level at the contaminant source is computed using a contaminant fate and transport model in the backward mode. These models account for the attenuation of contaminants as they migrate from the source to the receptor point, due to advection, dispersion, chemical and biological degradation, volatilization and adsorption. Numerous models have been developed for transport in air, surface water and groundwater. Alternatively, a multimedia model such as EPAMMM[2] may be used.

Typically, analytical and semi-analytical models are used, although numerical models may be applied for complex sites. Application of these models yields an attenuation factor equal to the ratio of the receptor point concentration to the source concentration. Assuming that the receptor point concentrations are linear with respect to the source concentrations, llthe cleanup level is given by:

$$TCL = C_r/AF \qquad (4)$$

where

TCL = the cleanup level (e.g., mg/L)
AF = the attenuation factor (dimensionless)

Using the linearity assumption, the three steps used to estimate cleanup levels can be consolidated by defining the unit risk, or the risk per unit concentration at the source:

$$UR = (PEF)(AF)(PF) \qquad (5)$$

where

UR = the risk per unit source concentration (L/mg)

The cleanup level is then calculated by dividing the target risk level by the unit risk:

$$TCL = TR/UR \qquad (6)$$

The assumption of linearity requires that contamination and cleanup levels be below solubility and saturated vapor pressure levels. This assumption is usually valid for the low concentrations required for protection of human health. However, computed cleanup levels should be compared to solubility limits to verify this assumption.

APPORTIONING RISK AMONG MULTIPLE CHEMICALS

When multiple chemicals present a health hazard at a site, cleanup levels must account for the combined effects of these chemicals. Sufficient information is not available on the synergistic or antagonistic effects of chemicals; it is therefore commonly assumed that the risks from multiple chemicals are additive. Thus, at the cleanup level, the sum of the risks from all chemicals must be less than the acceptable individual excess lifetime cancer risk:

$$TR = \Sigma TR_i \qquad (7)$$

where

TR = the total target risk level
TR_i = the target risk level for chemical i

The total risk among the various chemicals can be allocated in a number of ways, considering at a minimum the type of remediation to be applied, the existing levels of contamination and the potency of each chemical. Examples of algorithms for allocating risk among multiple chemicals include:

- Allocate risk equally among all chemicals. This is the simplest alternative, but can result in prohibitively low cleanup levels for highly potent chemicals.
- Allocate risk proportional to unit risk. This alternative allocates more

risk to the more potent chemicals. If risk is allocated in linear proportion to unit risk, this alternative results in the same cleanup level for all chemicals.

- Allocate risk such that chemical concentrations are in the same proportion after remediation as before. This alternative assumes that all chemicals are remediated in the same proportion, i.e., that all chemical concentrations are reduced by the same proportion. This alternative works well when one or more chemicals occur at significantly higher levels than others, or when the chemicals respond equally to the remediation technology.

Each of the above processes has its own advantages; it often is useful to apply all three and compare the resulting cleanup levels. It also may be appropriate to allocate risk differently depending upon the remedial alternatives selected. For instance, if vapor extraction is proposed, target risks would be allocated such that volatile chemicals would have lower cleanup levels than nonvolatile chemicals.

CASE STUDY 1: CLEANUP OF A SHALLOW AQUIFER

The first case study illustrates the application of the above procedures to a contaminated shallow aquifer in the Midwest. The aquifer lies in glacial till below a former liquid incineration site and receives approximately 0.05 m/yr (2 in./yr) of vertical recharge. Chemicals of concern in the aquifer include trichlorethylene (TCE), vinyl chloride and benzene.

For this analysis, cleanup levels were developed for a hypothetical residential well exposure scenario. Ingestion of water was evaluated as the primary exposure route. To estimate the allowable concentration, realistic average exposure parameters were selected from the U.S. EPA's Exposure Factors Handbook.[3] A water intake rate of 1.4 L/day was used, based on the average total fluid intake rate minus intake of milk and other fluids not derived from tap water. Residents were assumed to stay on-site for 20 years out of an average 70-year lifetime and spend 73% of their time at home.

In this case, the aquifer was both the source of contamination and the receptor location. Thus, there was no attenuation between the source and the receptor. However, concentrations in the aquifer do reduce during the 20-year period due to flushing by natural recharge. Assuming that only the dissolved phase is leached out of the aquifer and no biological decay, concentrations will decrease exponentially over time, and the average concentration for the exposure period is:

$$C_{avg} = TCL [1 - \exp(-kt)] / [kt] \qquad (8)$$

where

C_{avg} = average concentration over the exposure period (mg/L)
TCL = the target cleanup level, i.e., the concentration at the beginning of the exposure period (mg/L)
t = the exposure period (years)
k = leaching constant (years^{-1})

The leaching constant k quantifies the rate at which chemicals are flushed out of the aquifer and is expressed as follows:

$$k = I/H(p_b K_d + n) \qquad (9)$$

where

I = the recharge rate (m/yr)
H = the aquifer thickness (m)
p_b = aquifer bulk density (g/cc)
K_d = soil-water partition coefficient (cc/g)
n = porosity (cc/cc)

The total allowable individual excess lifetime cancer risk for the exposure scenario was 10^{-6}. Table 1 shows the resulting cleanup levels for TCE, vinyl chloride and benzene. Cleanup levels are shown for all three of the risk allocation procedures discussed above and are driven by the high unit risk for vinyl chloride. Thus, the first alternative (equal risk for all chemicals) results in a very low cleanup level for vinyl chloride, and high cleanup levels for TCE and benzene. The second alternative (target risk proportional to unit risk) results in the highest cleanup level for vinyl chloride, but the lowest for TCE and benzene. The final alternative (all chemicals reduced by the same percentage)

results in perhaps the most realistic distribution of cleanup levels.

Table 1
Cleanup Levels for the Shallow Zone Aquifer,
Case Study 1

Chemical	Cleanup Level (ug/l)		
	Alternative 1	Alternative 2	Alternative 3
TCE	0.95	0.11	0.48
Vinyl Chloride	0.04	0.11	0.09
Benzene	1.70	0.11	0.39

Alternative 1: Equal Risk for all Chemicals

Alternative 2: Risk Proportional to Unit Risk for each Chemical

Alternative 3: All Chemicals Reduced in Concentration by Same Proportion

CASE STUDY 2: UNSATURATED ZONE CLEANUP

This case study illustrates the use of an unsaturated zone contaminant transport model to back-calculate soil cleanup levels. The site for this case study is a former industrial waste storage facility. As illustrated in Figure 1, the unsaturated zone consists of 15 feet of silty clay underlain by 25 feet of silty sand. The saturated zone lies at a 40-foot depth. Because the area is to be paved as part of remediation, the infiltration rate was assumed to be only 0.3 in./yr (10% of the annual rainfall excess). During the remedial investigation, soils were found to be contaminated with 1,1-DCE, 1,1,1-TCA, TCE and 1,1-DCA throughout the thickness of the unsaturated zone.
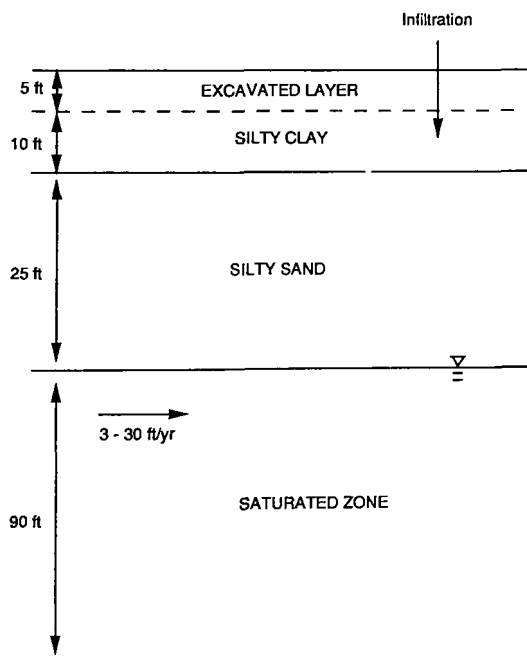
Figure 1
Generalized Cross-Section of the Site for Case Study 2

The exposure scenario for this analysis was ingestion of well water drawn from the saturated zone. Cleanup levels were derived for the unsaturated zone to meet state action levels at the water table, rather than to meet a specified target risk level. Thus, soil cleanup levels were computed as follows:

$$CL_s = (ADS)(AF\ C_{al}) \qquad (10)$$

where

CL_s = soil cleanup level (ug/kg)

AF = attenuation factor for the dissolved phase (unitless)

C_{al} = the state action level in drinking water (mg/L)

ADS = the adsorption factor, for converting dissolved concentrations to total soil concentrations (ug/kg per mg/L)
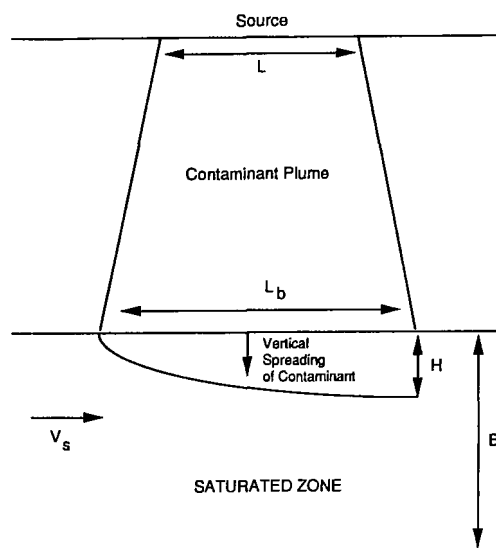
Figure 2
Attenuation of a Contaminant Migrating to the Saturated Zone

Table 2
Soil Cleanup Levels Derived from
Contaminated Transport Model Results

Source I - 5' Excavated Layer

Chemical	With Decay		Without Decay	
	Total Attenuation	Cleanup Level [ppb]	Total Attenuation	Cleanup Level [ppb]
1,1-DCE	1.7E+07	4.7E+04	450	368
1,1,1-TCA	3.1E+09	1.8E+07	500	30719
TCE	2.8E+09	2.3E+05	430	577
1,1-DCA	6.4E+05	4.8E+03	410	157

Source II - Silty Clay Layer

Chemical	With Decay		Without Decay	
	Total Attenuation	Cleanup Level [ppb]	Total Attenuation	Cleanup Level [ppb]
1,1-DCE	1.1E+06	4.7E+04	255	368
1,1,1-TCA	8.4E+07	1.8E+07	315	30719
TCE	3.5E+07	2.3E+05	260	577
1,1-DCA	9.4E+04	4.8E+03	230	157

Source III - Silty Sand Layer

Chemical	With Decay		Without Decay	
	Total Attenuation	Cleanup Level [ppb]	Total Attenuation	Cleanup Level [ppb]
1,1-DCE	1.2E+04	4.7E+04	200	368
1,1,1-TCA	5.9E+04	1.8E+07	230	30719
TCE	3.7E+04	2.3E+05	220	577
1,1-DCA	3.0E+03	4.8E+03	200	157

Based on the remediation alternatives to be evaluated, individual cleanup levels were derived for three distinct soil layers: (1) the top 5 feet of silty clay, to be excavated and treated, (2) the lower 10 feet of silty clay, and (3) the 25-foot silty sand layer. Attenuation factors for each layer and chemical were estimated by simulating the transport of the dissolved phase through the unsaturated zone to the water table. Attenuation by three processes was simulated:

- One-dimensional flow and transport through the unsaturated zone
- Lateral dispersion in the unsaturated zone
- Near-field mixing at the water table

The resulting cleanup levels for the site are shown in Table 2. Results are presented for two cases: (1) base case with decay (assuming a five-

year half-life for all chemicals) and (2) base case with no decay. Because of the slow infiltration rates (and correspondingly long travel times), the attenuation of chemicals is increased by as much as 3 to 4 orders of magnitude when chemical decay is simulated.

Figure 2 illustrates how these processes affect the transport of the chemical to the water table. One-dimensional transport was simulated using the unsaturated flow and transport component of the U.S. EPA's Multimedia Model.[2] This model simulates one-dimensional advection and dispersion, linear, reversible adsorption, source flushing by recharge and exponential chemical decay. An analytical lateral dispersion model[4] was then applied to calculate attenuation due to lateral spreading of the contaminant plume. Finally, a mass-balance mixing model was used to compute dilution of the plume as it is intercepted by the saturated zone flow. The total attenuation factor was the product of the attenuation factors for each of these three processes.

CONCLUSIONS

In the preceding sections of this paper, we have discussed procedures for computing cleanup levels using a risk assessment methodology. Two case studies were presented illustrating the allocation of risk among multiple chemicals and the use of contaminant transport models in the backward mode to estimate source cleanup levels. The following conclusions can be drawn from these case reviews:

- Cleanup levels should be set to levels protective of human health, rather than arbitrary levels such as background or analytical detection limits
- Allocation of cleanup levels among multiple chemicals should consider the type of remediation, the potency of the each chemical and the existing contamination levels
- Analytical contaminant transport models can be readily applied to estimate source cleanup levels

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The National Exposure Registry: A Community's Reaction

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INTRODUCTION

The Agency for Toxic Substances and Disease Registry (ATSDR) was created by the CERCLA of 1980 to assess the health problems of persons living near waste sites and dump sites. The Superfund legislation assigned 10 mandates to the Agency, one of which was the creation of a National Exposure Registry and a National Disease Registry. The National Exposure Registry is currently being constructed and at this time contains more than 5000 registrants. The policies and procedures for the National Disease Registry are under development.

The National Exposure Registry is a listing of persons who have been exposed to selected toxic substances.[1] The purpose of the National Exposure Registry is to help assess long-term health consequences of exposure to Superfund-related hazardous substances. ATSDR is trying to determine whether any long-lasting, adverse health outcomes may be associated with low-level, long-term exposures such as those experienced by persons living near waste sites and dump sites. The National Exposure Registry is designed to facilitate epidemiologic research or health studies by creating files of data that can serve as the basis for these efforts. The Registry files also can be used to facilitate state and federal health surveillance programs and to provide information for assessing the burden of the effects of an exposure or health outcome on a population.

In keeping with the dictates of a public health agency, the registry program will benefit the public by providing current, relevant information to exposed persons on the hazardous substances to which they have been exposed. Information gained from the subregistries will also enable local, state or federal health officials to notify registrants rapidly of any adverse health effects of exposure, preventive measures or therapeutic advances that may not have been known earlier.

The National Exposure Registry is composed of chemical-specific subregistries (subregistries currently exist for trichloroethylene, dioxin and benzene) that list persons (known as registrants) exposed to the selected chemicals. The selection of each chemical for a subregistry is based on its frequency of occurrence and for potential human exposure at waste sites and on its toxicity. Chemical selection also is based on the existing data gaps identified for the chemical and an assessment of whether the data collected for the registry would fill the identified data needs.

CHEMICAL CHOSEN

Trichloroethylene (TCE), the first chemical chosen, was identified at 468 of the then 1177 NPL sites; 368 of the contaminated sites had reported contaminated groundwater; 356 of these sites reportedly depended on this groundwater for drinking water. Some sites had privately owned wells while other were municipally, county, state or federally owned wells. The dioxin subregistry was established to follow a population previously identified as exposed. A subregistry for benzene was established because of the large number of sites with relatively high levels of benzene-contaminated drinking water and the health effects noted in worker populations exposed to benzene. The paucity of data on human populations who have been exposed to benzene, particularly the long-term, low-level exposures found in populations exposed through drinking benzene-contaminated water, was also a factor.

SITE SELECTION

Specific sites for a given chemical subregistry are selected based on the existence of documented contamination of the media, the size of the potentially exposed population, the reporting of potentially chemical-related health problems by the community and the community's level of interest in participating in such a project. The cost of establishing a registry at a given location is approximately $500,000 and the cost of each annual update for that location is approximately $125,000. Given the large expenditure of resources and the potential impact on the communities involved, the sites must be chosen judiciously. One community decided, on the advice of its state health department, not to participate. ATSDR did not pursue the project further because participation in the registry is strictly a voluntary activity and the support of all parties is needed to ensure high participation rates.

EXPOSURE CRITERIA

Three criteria must be met before a potential registrant can be classified as "exposed": (1) valid analytical data must document a contaminated medium, (2) a plausible route of transmission exists from the medium to the individual and (3) evidence exists that transmission occurred from the contaminated medium to the individual. Meeting the first two criteria would make an individual "potentially exposed"; the addition of the third, "exposed." An example of a site meeting all these criteria would be: contaminated groundwater exists; the water is used for drinking; and the individual drank the water. Exposure from all media is considered.

The "potentially exposed" persons are identified at a given site through existing records such as well-water tests, air monitoring results or soil sample test results. The persons are then contacted and asked further questions to confirm their exposure; if their exposure is confirmed, they are asked to participate in the National Exposure Registry. Participation is strictly voluntary.

DATA COLLECTION

A "Core Questionnaire" is administered to each registrant, the first time in a face-to-face interview and after that by telephone. This "Core Questionnaire" consists of basic demographic questions, 25 general health questions, three general reproduction-related questions, ques-

tions related to tobacco use and background questions related to occupational exposure. The "Core Questionnaire" provides the minimum amount of information to be collected on a registrant. Additional questions may be added at some sites if more specific information is available on the health outcomes thought to be related to the chemical of interest there. The same questionnaire is administered annually from then on; all updated information is added to the existing file. The annual updates continue indefinitely until it is determined whether a health problem exists in the exposed population.

The number of persons to be enrolled on a given subregistry depends on the sample size needed to compare a given health outcome to national norms at a specified statistical level of significance. The TCE subregistry has approximately 5000 registrants; the benzene subregistry will contain approximately 7000 registrants.

DATA ANALYSIS

Using data from the National Exposure Registry, ATSDR conducts ongoing trend analyses and comparisons with national norms. These will indicate whether further health studies are needed or whether information already available, when combined with other epidemiologic and toxicologic information, is sufficient to determine that no potentially exposure-related, adverse health outcomes are present. Because of the relatively small number of eligible persons at each site, the small number of cases of any one adverse health outcome and the number of potentially confounding factors, it is almost impossible to conduct epidemiologic analysis for individual sites at an acceptable level of statistical significance. If data from multiple sites could be combined, this process would increase the sample size with the potential for reducing the level for significance testing to a point that would be meaningful for interpretation of results. ATSDR is now exploring the concept of conducting studies across multiple sites.

Although participation in a subregistry is voluntary, the current participation rate does not appear to be a matter of concern or a source of bias. At 13 of the sites where eligible persons have been asked to participate in the National Exposure Registry, the response rates have exceeded 99% (one site had 100%); at four other sites the response rate exceeds 96%. The sites now in the registry represent a broad spectrum of possible conditions—the socio-economic levels vary greatly, the level of community anger at remedial actions that have or have not occurred ranged from outrage to approval and health studies have been conducted at some sites and not at others. None of these factors, however, appears to have any impact on the response rate.

Subregistries

Nearly 5000 persons have been enrolled in the TCE subregistry and 250 in the dioxin subregistry. Data for the TCE subregistry have been collected on persons at three NPL sites in Michigan, two NPL sites in Indiana, two non-NPL sites in Indiana, five NPL sites in Illinois and one non-NPL site in Illinois. All but one of the sites have other chemicals present besides TCE. The persons on this subregistry have lived for more than 30 days in homes for which the private well serving the home was contaminated over a specified time-frame. The time-frame is determined from available information about the responsible polluter and from geographic information about the site location.

A potential registrant may or may not currently living in a home with a contaminated well. Indeed, a concerted effort is made to identify former residents, to locate them and to solicit their participation in the registry.

Registrants of the dioxin subregistry lived near one of the four NPL sites in the Times Beach, Missouri, area and previously participated in one of the health studies conducted there. The site selection process is now taking place for the benzene subregistry.

PUBLIC NOTIFICATION/PARTICIPATION

At each location, the actual data collection process is preceded by activities designed to inform each potential registrant; federal, state, county and local officials and citizen groups—everyone is to be informed! The purpose of the registry, its implementation and what the registry is and is not are discussed at conferences with officials and

meetings with citizen groups, in press releases in the local newspapers and on radio and television stations. Also, both ATSDR and a regional health official, usually the state health commissioner, send letters to each potential participant explaining the registry.

Because anger often results from unfulfilled expectations, it is imperative that the community know what to expect and, equally as important, what not to expect from the National Exposure Registry program. The registry is not an epidemiologic study with measured health variables. Nor is the registry activity a hypothesis-testing effort, although it could be viewed as a potential hypothesis-generating activity.

Community Meeting

A community meeting is held the evening before interviewing begins to discuss the registry and to introduce the interviewers to the community. This process also introduces the community to the interviewers and makes the interviewers feel involved in the project. In most cases, people living in these communities are well-informed about their exposures and the possible health-related consequences. Communities appear to accept the registry approach as not only a viable way to assess the presence of excess adverse health outcomes within their community, but also as a general tool to be applied across the nation. The exceptionally high participation rate indicates this acceptance. We have heard many individual comments that although the information provided will probably not be of benefit to them personally, it may be of benefit to their children and grandchildren.

Data Confidentiality

When the policies and procedures were presented at meetings before their adoption, a concern for confidentiality was expressed repeatedly. At many of the sites, the registrants are involved in ongoing litigation. Other persons were concerned about the potential impact on their insurance (cancellation or rate increases) should the company find out they were registrants on the National Exposure Registry. To address the concern for confidentiality, ATSDR has adopted the policy that no data containing personal identifiers will be released without the written permission of the registrant. Each registrant will be asked in writing whether ATSDR may release personal information to a specifically named researcher for a specific purpose. As an agency of the federal government, ATSDR must respond to Freedom of Information requests, but only for aggregate data with personal identifiers removed. In-house, data-handling procedures strictly limit the persons who have access to the data base with personal identifiers.

ANNUAL UPDATES

ATSDR is now initiating the first annual updates; interviews will be conducted by trained telephone interviewers. We are concerned with maintaining over time the high level of participation we experienced in the initial interviews. We are following the same procedures for disseminating information to the registrants and to all other parties involved in the initial data collection. We hope that the same factors thought to prompt initial participation—a recognition of being "exposed", a promise that ATSDR will remain in the community as long as a problem is thought to exist, the promise of being kept informed and the desire to contribute to science—will remain viable in the follow-up efforts.

CONCLUSION

ATSDR envisions that the registry data base will be used for many research-related purposes. This data base will be available to qualified researchers for their individual studies. If a specific health concern is identified in a subregistry population, ATSDR will make that knowledge public with the expectation that other researchers will conduct further studies. Researchers may access the data base, with personal identifiers, by submitting a study protocol to ATSDR; a panel will then review the protocol to assess its scientific merit and the requestor's ability to maintain confidentiality. If the request meets the established criteria for acceptance, the next step will be to obtain the registrants permission to release the requested data. These procedures will be published in the Federal Register when they are completed.

The information collected for The National Exposure Registry will help answer the question whether adverse health outcomes are associated with waste sites and dump sites. The cost of a registry program and the long-range commitment needed must be considered, however, in making long-term registry plans.

REFERENCE

1. Agency for Toxic Substances and Disease Registry, "Policies and Procedures for Establishing a National Registry of Persons Exposed to Hazardous Substances: National Exposure Registry," Agency for Toxic Substances and Disease Registry, Atlanta, GA, 1988.

The Use of Minimal Risk Levels (MRLs) and Biologic Markers in Evaluating Potential Health Concerns at National Priorities List Waste Sites

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ABSTRACT

People who live near hazardous waste sites are concerned about health outcomes resulting from exposure to hazardous substances. Public health concerns are threefold: is there a possibility of exposure; are adverse health effects occurring as a result of these exposures; and are there exposure levels below which adverse health effects are not expected to occur? In an effort to answer these questions, the Agency for Toxic Substances and Disease Registry (ATSDR) prepares health assessments for each of the sites on the NPL, and where needed, conducts human exposure or health studies.

The tools available to ATSDR when it conducts health assessments or site-specific health studies are limited. One tool is biologic markers which are used in these activities to evaluate exposure to hazardous wastes and effects. Another tool is minimal risk levels (MRLs) which are environmental or external exposure levels below which adverse health effects are not expected to occur. In this paper, we explore biologic markers, MRLs and their uses in evaluating potential health concerns at NPL hazardous waste sites.

INTRODUCTION

Biologic markers are used to evaluate exposure to hazardous wastes and effects. Detecting the parent substance or its metabolites in a biologic tissue or fluid specifically indicates that exposure and absorption has occurred. The health effects that occur as a result of exposure to hazardous substances are usually less specific because many hazardous substances produce similar health effects. Furthermore, health effects may be influenced or caused by many different factors, including exposure to other substances, genetic variability, state of health and socioeconomic status. However, simultaneous detection of both biologic markers of exposure and effect provide suggestive evidence that the adverse health effect is a consequence of exposure to the hazardous substance.

It is generally believed that, for events other than cancer and genotoxicity, a threshold level exists below which adverse effects are not likely to occur. Many thresholds, however, lack precision and repeatability and are inappropriate for human health assessment. In an effort to account for this variability and to meet its mandate, the Agency for Toxic Substances and Disease Registry (ATSDR) is developing Minimal Risk Levels (MRLs). The development of MRLs begins with a determination of the threshold level and incorporates uncertainty factors to derive exposure levels for the general population below which adverse health effects are not expected to occur.

ATSDR is charged with preparing health assessments for each of the sites on the NPL. These assessments include an evaluation of human exposure and a determination of public health implications based on available medical and toxicological information. Questions generally discussed and answered include: are people being exposed to hazardous substances found at these sites? Are adverse health effects occurring as a result of these exposures? Are there exposure levels below which adverse health effects are not expected to occur? The objective of this paper is to investigate the use of biologic markers and MRLs in evaluating potential health concerns at NPL sites.

BIOLOGIC MARKERS

Biologic markers are indicators that signal events in biologic systems or samples.[1] Biologic markers do not indicate whether the event being monitored is adverse or has no known effect; they only indicate that an event has occurred. For evaluating people exposed to exogenous substances, biologic markers can be subdivided into three categories: biologic markers of exposure, effect and susceptibility.

Biologic markers of exposure have been defined by the National Research Council[1] as exogenous substances or their metabolites or the product of an interaction between a xenobiotic agent and some target molecule or cell that is measured in a compartment within an organism. Detecting a substance in a tissue or fluid such as blood, urine, hair or fat indicates that exposure and absorption have occurred. Although attempts have been made using models to correlate tissue or fluid concentrations with exposure levels, a biologic marker by itself is not an indication of the amount of substance to which a person is exposed, the total amount absorbed, the total body burden or the duration of exposure; it only indicates that the substance has been absorbed and is currently present in a tissue or fluid.

ATSDR's Toxicological Profiles contain substance-specific information on hazardous substances found at NPL sites. The profiles include information on biomarkers of exposure. Table 1 presents a survey of the detection limits and accuracy of the most sensitive bioanalytic techniques available for detection of ATSDR's 50 priority hazardous substances. The data are organized by chemical class because, with the exception of a few miscellaneous substances (e.g., dinitrotoluenes, cyanide and isophorone), exposure to each substance can be monitored using class-specific screening methods.

Despite the fact that adequate bioanalytic methods are available for clinical detection and measurement of most of the substances listed in Table 1, almost no useful biologic monitoring data have been published for populations located near waste sites contaminated with these substances. A review of the Toxicological Profiles on the first 50 priority substances indicates that information linking environmental levels with body levels exists for less than 30[4] of the subject substances. In fact, for only one of the substance classes identified in Table 1, volatile organic compounds (VOCs), is such information available for more than 20% of the class (Fig. 1). More studies involving simple, clinically available, noninvasive biomonitoring techniques are needed for populations sur-

Table 1
Medium, Detection Limit and Accuracy of Sensitive
Bioanalytical Methods Available for Substances
Covered in the First 50 Toxicological Profiles

Class/Name	Excreta	Detection Limit	Accuracy	Fluids	Detection Limit	Accuracy	Tissues	Detection Limit	Accuracy
Volatile Organic Compounds									
1,1,2,2-Tetrachloroethane	ND	ND	ND	Blood (whole)	500 ppt	Poor	ND	ND	ND
1,1,2-Trichloroethane	Urine, breath	ND	ND	Blood, milk	ND	ND	ND	ND	ND
1,1-Dichloroethene	Breath	1 mg/m3	Poor	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	Urine	ND	ND	Blood	ND	ND	Soft tissue	10 ug/kg	Fair
1,2-Dichloropropane	Urine	ND	ND	Blood	100 ppt	Poor	ND	ND	ND
1,4-Dichlorobenzene	Urine	0.75 ng/g	Fair	Blood	2 ppb	Fair	Adipose	0.012 ug/g	Good
Benzene	Urine, breath	1 ug phenol /ml, 3 ppt	ND	Blood, milk	0.5 ppb, NA	ND	ND	ND	ND
Bromodichloromethane	Breath, urine	ND	ND	Blood serum	< 0.8 ug/L	ND	Adipose	< 0.8 ug/L	ND
Carbon tetrachloride	ND	ND	ND	Blood serum	< 1.3 ug/L	ND	Adipose	< 1.3 ug/L	ND
Chloroethane	Urine	3 ug/L	Fair	Blood, milk	3 ug/L	Fair	Adipose	ND	ND
Chloroform	Urine	0.1 ug/L	ND	Blood, serum	0.05 ug/L	good	Adipose	ND	ND
Methylene chloride	Urine, breath	0.2 ppm	ND	Blood	0.022 mg/L	Poor	Adipose	1.6 mg/kg	ND
Tetrachloroethylene	Urine, breath	0.15 ppb	ND	Blood	10 ppb	ND	Mixed	ND	ND
Toluene	Urine	2 mg/L	ND	Blood	7.5 ug/L	ND	Brain tissue	ND	ND
Trichloroethene	Urine, breath	75, 0.3 ppb	Good, Good	Blood	2 ppb	Good	ND	ND	ND
Vinyl Chloride	Urine, breath	1 ppt	Good	Blood	ND	ND	Mixed	30 ppb	Fair
Polyaromatic hydrocarbons	Urine, feces	1ug PAH/mmol creatinine	Poor ->fair	Blood	<2X10E-15 mol BDPE/ug DNA	ND	Skin	10E-15 mole BPDE/sample	ND
Halogenated Pesticides and Related Compounds									
Aldrin	ND	ND	ND	Blood serum	ND	ND	Adipose	ND	ND
Chlordane	ND	ND	ND	Blood	10 ng/L	Fair	Adipose	0.1 ppm	Good
DDT, DDE, DDD	ND	ND	ND	Milk	1.6-2.2 ppb	Poor ->good	Adipose	4.32ppm	ND
Dieldrin	ND	ND	ND	Serum	ND	ND	Adipose	ND	ND
Heptachlor	ND	ND	ND	Blood, milk	1 ppb	ND	Adipose	10 ppb	ND
Heptachlor epoxide	ND	ND	ND	Blood serum	1 ppb	ND	Adipose	10 ppb	ND
Hexachlorocyclohexanes	Urine	4.9-19 ug\L	Good	Serum	0.5-0.9 ug\L	ND	Adipose	1 mg\kg	ND
Polychlorinated biphenyl	ND	ND	ND	Blood, serum, milk	0.1 ng/ml	85%	Fat	ND	91-93%
TCDD	ND	ND	ND	Milk, serum	1.25 pg/Kg	Fair	Adipose	< 2 ng/Kg	Fair
Inorganic substances									
Arsenic	Urine	0.5 ug/L per form	Good	Blood	0.5 ug/L As	Good	Adipose, hair, liver, kidney,soft tissue	5 ppb As	Good
Beryllium	Urine, feces	0.01 ug/L	ND	Blood	0.5 ug	ND	Hair,nails,lung,liver	< 1 ug/kg	ND
Cadmium	Urine	0.09 ng/ml	Good	Blood plasma	< 1 ng/ml	Good	Hair, liver, kidney, muscle	0.01 ppm	ND
Chromium	Urine	0.05 ug/L	Good	Blood, plasma, serum	0.05 ug/L	Good	Hair	ND	ND
Lead	Urine	4 ug/L/ml	Good	Blood	0.05 ug/g	Good	Bone	2 ug/g	ND
Mercury	Urine, breath	2 ug/ml, 1 ng/sample	ND	Blood	1 ng/ml	ND	Hair	1 ng/mg	Good
Nickel	Urine	0.18 ug/L	ND	Blood, serum	0.18 ug/L	ND	Liver, lung, kidney, hair, nails	0.18 ug/L	ND
Selenium and compounds	Breath, urine	20 ug\L	Good	Blood, semen	10 ug\Kg	Good	Soft tissues	50 ng\Kg	ND
Zinc and compounds	Breath, urine, feces	0.1 ug/sample	Good	Blood, serum, plasma	0.5 ug/g wet	ND	Soft tissue,bone,hair	0.2 ug\g	Good
Benzidines and Phenols									
3,3-Dichlorobenzidine	Urine	<= 1 ug/L	ND	ND	ND	ND	Soft tissue	<20 ppb	ND
Benzidine	Urine	1 ug/L	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	Urine	10 ppb	Good	Plasma	1 ppb	Good	Adipose tissue	1 ng/kg	Good
Phenol	Urine	0.1 mg/L	Good at 6 mg/L	Whole blood	< 1 mg/L	Good	ND	ND	NO
Phthalates, ethers and nitrosamines									
Di(2-ethylhexyl)phthalate	Urine	ND	ND	Plasma, whole blood	0.345 ug/ml	ND	Lung,liver,spleen, adipose,heart,kidney	0.1 ug/mg	ND
Bis(2-chloroethyl)ether	Urine	ND	ND	ND	ND	ND	ND	ND	ND
Bis(chloromethyl)ether	ND	ND	ND	ND	ND	ND	ND	ND	ND
N-Nitrosodi-n-propylamine	Urine, feces	0.05 ug/L	Poor	Blood, saliva	.05-0.5 ug/kg	Poor	Brain, liver, kidney, pancreas	.6 ng/kg	Good
N-Nitrosodimethylamine	Urine	5 ng/L	Good at 10 ng/L	Blood	< 1 ppb	Good at 2 ppb	Liver, kidney, brain	< 1 ppb	Good at 2.3 ppb
N-Nitrosodiphenylamine	Urine	0.1 ppm	ND	Blood, serum	0.01 ppm	ND	ND	ND	ND
Miscellaneous									
Cyanide, hydrogen	Urine	0.07 ppm	Fair	Blood, plasma	0.07 ppm	Good	Liver	ND	Good
Dinitrotoluenes	Urine	ND	ND	Blood	0.01 mg/L	ND	ND	ND	ND
Isophorone	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND=No data, Poor=<80% recovery, Fair=80-90% recovery, Good=90-100% recovery
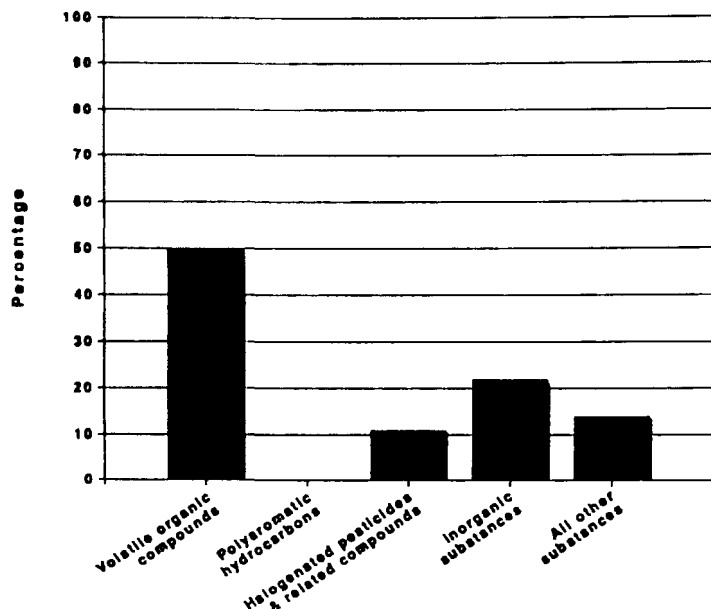
Figure 1
Percentage of Hazardous Substances in Each
Class for which Data on the Relation Between
Body Levels and Environmental Levels has been
Reported in the Toxicological Profiles

rounding waste sites. Without these data, it is difficult to interpret information obtained using biologic markers of exposure.

Many factors confound the use and interpretation of biologic markers of exposure:

- The body burden of a substance may be the result of exposures from more than one source; for example, polyaromatic hydrocarbons (PAHs) exposure can come from waste sites, but significant PAH exposure also can come from cigarette smoking and the consumption of charcoal-grilled meat
- The marker being measured may also be a metabolite of another xenobiotic substance; high urinary levels of phenol can result from exposure to several different aromatic compounds
- Depending on the properties of the substance (e.g., biologic half-life) and environmental conditions (e.g., duration and route of exposure), the substance and all of its metabolites may have left the body by the time biologic samples can be taken
- Many of the substances listed in Table 1 (particularly the essential mineral nutrients such as copper, zinc and selenium) are commonly found in the tissues and fluids of unexposed individuals; such background levels can complicate the correlation of body levels with environmental levels and health effects thereby complicate health assessments

These confounding factors and the existence of data gaps complicate the use of biologic markers of exposure and impede the performance of site-specific health studies. Exposure studies of waste site contaminants, such as the ATSDR-sponsored studies summarized in Table 2, help fill data gaps and establish background levels of these substances in biologic tissues and fluids.

Table 2
A Summary of Results from ATSDR Pilot Exposure Studies

Substance	Location	Source	Major Finding
Arsenic	Anaconda, Montana	Soil, housedust, air	Urine arsenic levels >50 ug/l in children living downwind of an inactive copper smelter
	Tacoma, Washington	Soil, housedust, air	Mean urine arsenic levels higher in children living within 1/2 mile of an inactive copper smelter than in comparison communities, but mean is less than 50 ug/L
	Park City, Utah	Soil from mine tailings	Urine arsenic levels in the normal range for children living on or near mine tailings
Lead	East Helena, Montana	Soil, housedust, air	Blood lead > 25 ug/dl in some children; related to distance from an active smelter
	Kellogg, Idaho	Soil, housedust, air	Blood lead > 25 ug/dl in some children, related to distance from a recently closed smelter
	Park City, Utah	Soil from mine tailings	Mean blood lead of children living on or near mine tailings elevated above control community but still less than 10 ug/dl
PCBs	12 NPL sites in 8 states	Soil, surface water, occupation	High prevalence of elevated serum PCBs >120 ppb in two communities; occupational importance
	Monroe County, Indiana	Soil, surface water, direct contact	High prevalence of elevated serum PCBs > 120 ppb with occupational exposure
	Newport County, Mass.	Food chain, occupation	High prevalence of elevated serum PCBs > 120 ppb with consumption of local seafood
	Fort Smith, Arkansas	Soil, dust	Serum PCBs within normal range
	Paoli, Pennsylvania	Soil, dust	Serum PCBs within normal range
Dioxin*	Missouri	Soil, occupation	Elevated adipose tissue levels in all groups of exposed persons (geometric mean 21.8 ppt compared with 6.4 ppt for controls)
	New Jersey	Occupation	Elevated serum levels in workers compared with controls
Pesticides	Memphis, Tennessee	Soil, surface water, food chain	Elevated serum levels of hexachlorobenzene (geometric mean 0.23 ppb vs 0.17 ppb for controls) and elevated adipose levels of heptachlor epoxide (0.08 ppm vs 0.06 ppm for controls) in persons living near the site, eating fish from contaminated river
	Nashville, Georgia	Soil	No evidence of elevated serum pesticides
VOCs	Doylestown, Pennsylvania	Groundwater, surface water (used for sanitation but not for drinking)	No evidence of elevated serum VOCs
	Uniontown, Ohio	Groundwater, surface water (used for sanitation but not for drinking)	Of 27 VOCs evaluated only tetrachloroethene detected in > 1.96 standard deviations above the mean (two individuals)

* 2,3,7,8-tetrachlorodibenzo-p-dioxin

Biologic markers of effect are defined as measurable biochemical, physiologic or other alterations within an organism that, depending on the magnitude, can be recognized as established or potential health impairment or disease.[1] Biologic markers of effect tend to be nonspecific for any given substance but may be relative within a given chemical class. However, similar hepatic or neurologic abnormalities can be caused by many classes of substances such as VOCs or chlorinated hydrocarbons. Organophosphorus and carbamate insecticides are a class of substances that are known to cause a decrease in red blood cell or plasma cholinesterase levels. Although these effects are specific for this class, they are not specific for any individual substance within the class.

Confounding factors such as diseases, nutritional status, genetic variability, occupation and life style can influence markers of effect. Decreased cholinesterase levels, for example, can be caused by such conditions as parenchymatous liver disease, genetic variability, malnutrition, acute infection, anemias, myocardial infarction and dermatomyositis.[3,4]

In the environmental setting, the use of meta-analysis to study the effects of exposure in a large population pool may help to better define markers of early biologic effects. The National Exposure Registry under development at ATSDR will contain information on health effects resulting from exposure to select priority hazardous substances at waste sites. Although it may not be possible to define markers of early biologic effect(s) that are truly substance-specific, the use of batteries of biologic markers of effect can provide the added information needed to verify public health concerns. A summary of some biologic effects investigated or under investigation via epidemiologic studies funded by ATSDR is presented in Table 3.

Table 3
Summary of Biological Effects Investigated
by Epidemiological Studies Funded by ATSDR

Biologic Effect Investigated	Study Location	Substance	Findings
Blood Pressure	Bristol Co, MA	PCBs	No Observed Effect
	Monroe, Co, IN	PCBs	Self-reported high blood pressure Dose response with serum PCB level
	Memphis, TN	Pesticides (pp'-DDE)	No Observed Effect
Hepatic Function	Quail Run, MO	Dioxin*	Elevated for five liver enzymes Elevated urinary uroporphyrins
	Missouri	Dioxins*	Elevated globulin and decreased albumin/globulin ratio
	Monroe, Co, IN	PCBs	No Consistent Pattern
	Memphis, TN (Hollywood)	Pesticides	No Observed Effect
Immune Function	Quail Run, MO	Dioxin*	Abnormal T4/T8 T-cell ratios - Anergy on DTH skin test in exposed group compared with nonexposed group (11.8% vs 1.1%)
	Quail Run, MO (follow-up)	Dioxin*	No Observed Effect
	Missouri	Dioxin*	No Observed Effect
Reproductive Outcomes	Missouri	Dioxin*	No Observed Effect
	Albany, NY	Multiple Substances	Under way
	Woburn, MA	Multiple Substances	Under way
	Georgia	Multiple Substances	Under way
	St. Gabriel, LA	Multiple Substances	Under way

* 2,3,7,8-tetrachlorodibenzo-p-dioxin

MINIMUM RISK LEVELS

People who live near hazardous waste sites are concerned about health outcomes resulting from exposure to hazardous substances.[4] To address this issue, ATSDR is developing MRLs for substances found at NPL hazardous waste sites. The MRL provides state and local health professionals, scientists and concerned citizens with an estimate of the level of a substance below which no harmful health effects (other than cancer) are expected to occur.

This estimate is intended to provide health professionals with a basis for comparing levels that people might encounter in the environment. These data will help determine the need for further evaluation of the potential public health impacts. Although these values are not meant to support regulatory action, they may be useful to physicians, project managers and public health officials who must take appropriate actions at hazardous waste sites or chemical releases.

An MRL is based on noncarcinogenic effects and is not intended to provide any information on the carcinogenic potential of a substance. The methodology used for MRL derivation is similar to the U.S. EPA's risk assessment methodology for determining reference doses for lifetime exposures (RfDs).[5] In deriving MRLs, ATSDR emphasizes its preference for using data from humans whenever such data are reliable and otherwise appropriate. However, when sound human toxicological data are unavailable or incomplete (insufficient exposure duration, insufficient sample size, poorly documented exposure information, etc.), animal data must be used.

The most sensitive species with the highest no-observed-adverse-effect level (NOAEL), below which there are no adverse effects, is determined from an evaluation of sound toxicological data. This is the end-point from which an MRL may be derived. The lowest level at which adverse effects are observed (LOAEL) is used when all reported levels of exposure have caused adverse effects. The highest NOAEL or the lowest LOAEL are then divided by separate factors of 10 to adjust the MRL for each of the following uncertainties when appropriate:

- Human variability to protect the most sensitive population
- Interspecies variability for extrapolating animal results to humans
- The uncertainty in using a LOAEL to estimate the MRL

Thus, the uncertainty factors (UFs) used by ATSDR range from 10 to 1000.

MRLs derived for priority hazardous substances are based on an assessment of available toxicological and epidemiological data (as mentioned above). Necessary NOAELs and LOAELs are evaluated for the following organs and systems: hepatic, neurologic, developmental, reproductive, respiratory, hematologic, immunologic, dermal/ocular, renal, cardiovascular, gastrointestinal, musculoskeletal and genotoxic. MRLs are then determined for the most sensitive effect.

In a recent ATSDR effort, data from a study subset (a representative sample of 54 of the 225 priority hazardous substances listed to date) revealed that although all organs and systems are evaluated and considered in deriving MRLs, most of the MRLs have been derived from either hepatic (31%), neurologic (20%), developmental (11%) or other (15%) end-points. The "other" category mainly represents changes in body weight and rates of food intake. These four types of effects taken together account for more than three quarters of the MRLs in the sample. Other systemic effects, such as cardiovascular, gastrointestinal, musculoskeletal and genotoxic, are not represented. This pattern suggests that the majority of MRLs are derived from a minority of end-points.

ATSDR classified 225 priority hazardous substances on the basis of extractive or analytical technique.[6] Eleven categories are used: volatile organic compounds; polycyclic aromatic compounds; halogenated pesticides and related compounds; organophosphates and carbamates; phthalates; inorganic compounds, including elemental metals; phenols and phenoxy acids; nitrosamines, ethers and alcohols; benzidenes and aromatic amines; reactive intermediates; and miscellaneous compounds. Three categories contain 60% of the 225 priority substances listed: VOCs (35%), inorganic substances (12%) and halogenated pesticides and related compounds (13%).

The MRLs derived from the study subset are mainly distributed among the same substance categories: VOCs (38%), inorganic substances (15%) and halogenated pesticides and related compounds (11%). This pattern also suggests that the majority of MRLs are derived from a minority of substance categories.

ATSDR derived MRLs for the most sensitive end-point according to route and duration. Routes used to derive MRLs are inhalation and

oral. Exposure via the dermal route is discussed in the Toxicological Profiles, but dermal MRLs are not currently being derived. Duration of exposure is defined as acute (less than or equal to 14 days), intermediate (15 to 364 days) or chronic (greater than 364 days). MRLs compared on the basis of exposure route and duration were generated from the study subset. Reflected in this evaluation is the fact that MRLs from oral exposure are twice as prevalent as those from inhalation MRLs (Table 4) and acute inhalation exposures are used for 13% of the study subset MRLs, half of which were neurologically derived. Chronic exposure MRLs are underrepresented as a whole, thereby identifying a future area for research (Table 5).

DISCUSSION

For biomarkers to be useful in evaluating individuals and popula-

Table 4
Distribution of MRLs Across Route/Duration and Chemical Class

	INHALATION			ORAL		
	A	I	C	A	I	C
VOLATILE ORGANICS	8	7	2	8	5	6
HALOGENATED PESTICIDES/RELATED CPDS	0	1	0	5	5	3
INORGANIC COMPOUNDS	1	1	1	2	3	2
MISCELLANEOUS	0	0	0	1	3	2
REACTIVE INTERMEDIATES	2	1	0	1	1	1
PHENOLS/PHENOLIC ACIDS	0	0	0	2	2	0
NITROSAMINES/ETHERS/ALCOHOLS	0	2	0	1	0	0
BENZIDINES/AROMATIC AMINES	0	0	0	0	1	1
PHTHALLATES	0	0	0	1	1	0
ORGANOPHOSPHATES/CARBAMATES	0	0	0	0	0	0
	11	12	3	21	21	15

ACUTE (A) 32   INTERMEDIATE (I) 33   CHRONIC (C) 18
INHALATION(I) 26   ORAL (O) 57

Table 5
Distribution of MRLs Across Route/Duration and Health Effect Category

	INHALATION			ORAL		
	A	I	C	A	I	C
HEPATIC	1	4	1	6	7	7
NEUROLOGIC	5	1	1	5	3	2
DEVELOPMENTAL	1	1		5	2	
RENAL				1		4
REPRODUCTIVE				1	5	
RESPIRATORY	2	3				
HEMATOLOGIC					2	2
IMMUNOLOGIC	1				1	
DERMAL/OCULAR	1					
CARDIOVASCULAR						
GASTROINTESTINAL						
MUSCULOSKELETAL						
GENOTOXIC						
OTHER		3	1	2	2	

tions, reference values or ranges of normal physiological values must be known. Without this knowledge, it will be difficult to evaluate information collected from people living near NPL sites.

Before biologic markers can be used to evaluate people exposed to hazardous substances, their predictive value must be assessed. Positive predictive value is the probability that people actually have the disease or organ dysfunction when the results of the biologic marker tests are positive. Negative predictive value is the probability that people do not have the disease or organ dysfunction when the results of the biologic marker tests are negative.

Predictive value depends on the sensitivity, specificity and prevalence of the end-point being measured. Sensitivity can be defined as the probability that detection of a biologic marker is not within the range of normal physiological limits. Specificity is the probability that the marker will be absent or within normal limits when exposure has not occurred or is below a level that produces observable effects. If the criteria for defining disease or organ dysfunction are broad, more people who have the disease or organ dysfunction will be detected (increased sensitivity); however, the specificity will be decreased, i.e., more people who do not have any abnormality will test positive. Abnormalities that are prevalent increase predictive value, while those with low prevalence decrease predictive value.

Many difficulties arise in trying to assess whether exposure to toxicants will result in health effects in humans. Exposure may be difficult to demonstrate because the parent substance or its metabolites may not be retained in the body long enough to be measured, or suitably sensitive or specific tests may not be available. The detection of a health effect may be delayed because the biologic capacity in such organs as the liver and kidney is so great that the effects of significant organ damage are not clinically detectable until the toxicant's effects have overcome the repair and reserve capacity of the target organ.

Genetic differences in susceptibility, prior sensitization or preexisting disease may create a situation in which one person exposed to a particular dose of a toxicant will have overt symptoms while another person with an identical dose will have no apparent effect. A toxicant sequestered in fat (e.g., DDT) or in bone (e.g., lead) may be undetectable and possibly innocuous until it is released into the circulation by stress, such as pregnancy or an appreciable loss of body fat. The long latency periods for some health end points make it difficult to correlate human exposure to toxicants at NPL sites with disease or organ-system dysfunction. The heterogeneous, usually small populations of persons affected at most NPL sites create problems for detecting subtle or rare events. Excluding confounders such as unrelated or concurrent diseases, genetic predisposition and changes in laboratory tests caused by aging, sex differences, drug use and smoking remains a challenge to researchers hoping to employ biologic markers as predictors of health outcomes. Despite these limitations, ATSDR has begun an effort to implement the use of preselected batteries of biologic markers in the hope of detecting preclinical differences in exposed vs. unexposed populations.

MRLs ultimately are derived from biologic markers. Hence, an increase in the quality and quantity of biologic markers will result in more accurate NOAELs and LOAELs which will increase the accuracy of the MRLs and, consequently, reduce the uncertainty of health assessments.

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Missouri Dioxin Studies: What Have We Learned?

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ABSTRACT

The Centers for Disease Control (CDC) has conducted nine studies of exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD or dioxin) in Missouri since 1974, when the compound was identified as the possible etiology of a 1971 poisoning episode. In an earlier report, persons who had been exposed to TCDD were observed to have had an increased frequency of anergy, relative anergy and other possible immunologic effects (increased frequencies of abnormal T-cell subsets; T4/T8 [CD4/CD8] cell ratios less than 1; and abnormalities in T-cell function). These findings were not confirmed in other studies of exposure to TCDD in Missouri. In this article, we present the historical events leading up to studies of TCDD in Missouri and selected results of the nine CDC studies.

INTRODUCTION

The Centers for Disease Control (CDC) has conducted nine studies of exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD or dioxin) in Missouri since 1974, when the compound was identified as the possible etiology of a 1971 poisoning episode. Following are the dates and titles of these nine studies.

- 1971 Toxin-Associated Illness
- 1974 2,3,7,8-TCDD Contamination of Salvage Motor Oil
- 1983 Pilot Health Effects Study[1-4]
- 1984 Quail Run Health Effects Study[5,6]
- 1986 Quail Run Followup Health Effects Study[7]
- 1986 Reproductive Outcome Study[8]
- 1986 Adipose Tissue Study[9,10]
- 1986 Adipose Tissue-Serum Correlation Study[11]
- 1987 Adipose Tissue Health Effects Study[12]

As we look back on the studies of TCDD carried out in Missouri, we are prompted to ask, What have we learned? So what? What do we know now about dioxin or hazardous substances in general that we would not have known—or might not have known—if dioxin had not been studied?

The first thing we have learned is that things are not always as they seem. As W.S. Gilbert, the poet, said, "Things are seldom what they seem, skim milk masquerades as cream." The second thing is that we do not yet know all—or even most—of what there is to know about hazardous substances, whether it be their mechanism of action or the adverse human health effects they cause. Third, even some good can come from an unfortunate event. As many of us heard in our childhood, "It is an ill wind that does not blow someone some good." First, a summary of the story of dioxin contamination in Missouri.

BACKGROUND

In August 1971, the St. Louis Division of Health, the Missouri Division of Health (DOH) and the Centers for Disease Control (CDC) investigated a toxic illness in St. Charles, Missouri (Epi-Aid 72-13-2, Atlanta, Georgia: Centers for Disease Control, Aug. 14, 1972). CDC reported that 54 of 57 horses exposed to a horse arena had died of an illness characterized by skin lesions, severe weight loss and hepatotoxicity. Birds, dogs, cats, insects and rodents also were found dead in and around the arena and one 6-year-old girl who was exposed developed hemorrhagic cystitis. Urine cultures for the girl were negative for bacterial and viral pathogens. Immediately before onset of these illnesses, the horse arena had been sprayed with salvage motor oil for dust control.

Although a phosphorus-containing compound was found in samples taken from the affected animals and the one human, results of the investigation were considered inconclusive. The authors considered PCBs, triorthocresyl phosphate, tri-butyl phosphate, zinc dithiophosphate compounds or other organophosphorus compounds as the possible etiologic agents.

The first report of dioxin contamination in the published literature was an article by Dr. Arthur A. Case, a veterinarian, from the University of Missouri.[13] In his 1972 article, Dr. Case summarizes:

> "This preliminary report of the complex and deadly sequence of events that followed the use of discarded motor oil to settle dust in a riding arena and horse stable should alert horse owners, veterinarians and physicians to a common, but potentially dangerous practice. Waste oil collected from service stations and other sources in a large midwestern city was used in June 1971 to settle the dust in a large riding arena next to a prominent stable housing valuable Quarterhorse breeding stock.
>
> As of September 1971, the loss of horses and pets and the illness of two children had already become an economic disaster with the potential of tragedy for the children's family. The girls, aged 6 and 10 years, were affected by an apparently volatile toxic agent present in the waste crankcase oil. The children played with their ponies and pet dogs and cats in the arena and collected dead sparrows as they fell from the top of the arena during the week after the application of the oil. The jury is still out on the accident, but the toll is high enough that warnings to protect others from such hazardous situations are in order."[13]

It was not until July 1974 that the possible etiology of the outbreak was determined. Until that time, there was no reason to suspect that 2,3,7,8-tetrachlorodibenzo-p-dioxin was involved. In July 1974, after the Missouri DOH was informed that the samples collected at the horse

arena had 31,800 to 33,000 ppb TCDD, Missouri invited CDC to participate in a renewed investigation (Epi Aid 75-17-2, Atlanta, Georgia: Centers for Disease Control, Mar. 31, 1975). In its Aug. 24, 1974, issue of the Morbidity and Mortality Weekly Report, CDC reported finding the TCDD.[14] The editorial for the article stated:

"TCDD is a very persistent chemical and a potent contact poison. Its acute oral LD-50 for rabbits, mice, guinea pigs and other species is in the microgram-per-kilogram range. TCDD may cause chloracne and liver damage in humans, chickedema disease in chickens and porphyria cutanea tarda in animals and perhaps man. It has been shown to be teratogenic in some mice strains and has also a general embryotoxic effect."

An investigation in August and September 1974 traced the St. Charles wastes to a chemical plant in Verona, Missouri. A tank containing 4300 gallons of wastes contaminated by TCDD concentrations of up to 343 ppb still existed at the plant. In its report, CDC acknowledged that the expected half-life of dioxin was 1 year and recommended that: (1) inaccessible contaminated soil remain undisturbed, (2) soil in residential fills be removed to a landfill, (3) the contents of the storage tank at Verona be properly incinerated, (4) the tank be marked and deep buried (5) and symptomatic persons be followed up (Epi Aid, 75-17-2, Atlanta, Georgia: Centers for Disease Control, Mar. 31, 1975).

Given the expected half-life of dioxin in soil, soil levels of dioxin were expected to approach the minimum detectable limits by 1975. The decision was made not to remove residential soil but to resample it in an effort to confirm the anticipated degradation rate of dioxin. Visits to residential sites in September 1976 confirmed that the soil was not eroding and that vegetation had been established.

From 1974 to 1977, many discussions were held about the best way to dispose of the wastes in the tank at Verona. In September 1979, a final decision was made to use a new photolysis process that could detoxify dioxin. The project was completed in August 1980. Almost immediately, the U.S. EPA received an anonymous telephone call alleging that other sites in southwest Missouri had received wastes from the Verona plant. This led to the discovery of several other sites. Cleanup of these sites was carried out between October 1979 and 1981.

Subsequently it was estimated that approximately 29 kilograms of TCDD-contaminated sludge wastes, which had originated as a byproduct of hexachlorophene production, had been mixed with other waste oils and sprayed for dust control at approximately 250 residential, recreational and commercial sites throughout Missouri.

In May and June 1982, samples were taken again from TCDD-contaminated soil. The samples were analyzed and the results were made public in Aug. 18, 1982. When TCDD was unexpectedly found in these soil samples, the issue of dioxin was raised again. This report led to further dioxin studies in Missouri.

DIOXIN STUDIES IN MISSOURI

Pilot Health Effects Study

The Pilot Health Effects Study[1-4] was carried out in 1983. It compared the health effects in 68 persons who lived, worked or played in areas with TCDD-contaminated soil with the health of 36 persons who lived, worked or played in areas without TCDD-contaminated soil. No clinical illness was associated with TCDD exposure. No cases of chloracne or porphyria cutanea tarda were seen. In-vitro lymphocyte proliferative responses, overall cell-mediated immune responses and delayed-type hypersensitivity skin testing were not statistically different between the two groups. However, one exposed person and one unexposed person were anergic (defined in the study as having less than 2 millimeters of induration to all seven skin test antigens on the Multitest CMI produced by Merieux).

The Quail Run Health Effects Study

The Quail Run Health Effects Study[5,6] was carried out in 1984.It compared health effects in 135 persons who lived in a trailer park with TCDD-contaminated soil to the health of 142 persons who lived in three trailer parks without TCDD-contaminated soil. The study showed no

consistent differences between the two groups on medical history, physical examination, serum and urinary chemistry studies and neurologic tests. However, exposed persons did have a statistically significant increased frequency of anergy and relative anergy (defined as having less than 2 mm of induration on six of the seven antigens on the Multitest CMI). Exposed persons had nonstatistically significant increases in abnormalities in T-cell subsets, T4/T8 cell ratios less than 1.0 and abnormalities in T-cell function. Although it was not possible to put a value judgment on which of these findings was most important, we were very concerned about the findings of anergy and relative anergy, which we felt could indicate a deficit in immune function that could have grave clinical consequences of infectious disease or cancer.

The Quail Run Followup Health Effects Study

The Quail Run Followup Health Effects Study[7] was carried out in 1986. It examined results of delayed-type hypersensitivity skin tests for all persons from the Quail Run Study with anergy or relative anergy who agreed to be retested. Twenty-eight exposed participants and 15 unexposed persons who had previously tested as anergic or relatively anergic agreed to participate in this followup study. Only one exposed and one unexposed person were relatively anergic and none was anergic. This finding made the results of the Quail Run Study seem questionable. This followup study was carried out 18 months after the Quail Run Health Effects Study and TCDD was thought to have a serum half-life of several years. Multiple peer reviewers believed that the differences in skin test findings from the Quail Run Study and the followup study were unlikely to be due to TCDD exposure—especially because so many unexposed persons found to be anergic or relatively anergic in the first study were not anergic in the second.

The Reproductive Outcome Study

The Reproductive Outcome Study[8] in 1986 compared birth records from 402 women who lived in areas with TCDD-contaminated soil with such records for 804 women who lived in areas without TCDD-contaminated soil. There were 17 birth defects in neonates of exposed women and 42 in neonates of the unexposed women. Fifteen of the 17 and 35 of the 42 were classified as major birth defects. No abnormalities were significantly elevated in the neonates of exposed women. Although risk ratios ranged from 1.33 to 3.00 for the categories of infant, fetal and perinatal death, low birth weight and several of the defects, the 95% confidence intervals always included a risk ratio of 1.0.

The Adipose Tissue Study and the Adipose Tissue-Serum Correlation Studies

In the Adipose Tissue Study[9-11] carried out in 1986, 51 persons who worked, lived or played in areas with TCDD-contaminated soil and 128 persons who worked, lived or played in areas without TCDD-contaminated soil donated adipose tissue samples that were assayed for TCDD. The results showed that unexposed persons' adipose tissue levels of TCDD ranged from 0 to 20.2 ppt and exposed persons' levels ranged from 3.7 to 750 ppt. Of the exposed group, 22 (43%) had adipose tissue levels of 20.2 ppt TCDD or less. Even though these 22 persons were considered exposed to TCDD using an epidemiologic definition of exposure, when a quantifiable objective laboratory measure of exposure was used, they were found to be unexposed. A following study, also performed in 1986 and designed to assess the correlation between adipose tissue and serum levels, found that the levels did correlate.

The Adipose Tissue Health Effects Study

The Adipose Tissue Health Effects Study[12] performed in 1987 examined 40 persons, classified as exposed, who had participated in the adipose tissue study in Missouri and who agreed to be retested for health effects, including delayed-type hypersensitivity skin testing. No specific patterns associated with TCDD exposure were noted in medical histories or physical examinations—for example, chloracne, abnormal vibratory sensation or abnormal reflexes. After adjustments were made for gender and age in multivariate analysis, only globulin and albumin/globulin

ratios were associated with adipose tissue levels of TCDD. No participants were anergic or relatively anergic, confirming the findings of the Quail Run Followup Health Effects Study.

Selected Serum Chemistry and Immunologic Results

The number of exposed and unexposed persons and selected results of the Pilot Health Effects Study, the Quail Run Health Effects Study, the Quail Run Followup Health Effects Study and the Adipose Tissue Health Effects Study are shown in Tables 1, 2 and 3.

- No significant difference was found in the number of reported cases of cancer between the exposed and unexposed study participants in the four studies (Table 1).
- In the two studies where serum globulin levels were measured, no clear pattern emerged of association with TCDD levels (Table 1).
- Similarly, in the same two studies, no clear pattern appeared in the albumin to globulin ratio, although the ratio was lower in exposed participants in the Adipose Tissue Health Effects Study. This finding is consistent with the increased globulin levels reported in this group (Table 1).
- The number of persons reported to be relatively anergic in the four studies is shown in Table 2. Although relative anergy was associated with TCDD exposure in the Quail Run Health Effects Study, no such association was reported in the Pilot Study, the Quail Run Followup Health Effects Study, or the Adipose Tissue Health Effects Study.
- Similarly, only the Quail Run Health Effects Study showed an association of anergy with TCDD exposure (Table 2). Twice as many exposed as unexposed persons were anergic, but the number of exposed and exposed participants was approximately the same.
- No consistent pattern was noted of association of the number of positive delayed-type hypersensitivity skin test antigens with TCDD exposure (Table 2).
- Only the Quail Run Health Effects Study shows an association of a decreased number of millimeters of induration with TCDD exposure (Table 2).
- No clear pattern was found of association with the number of T4 cells/mm³ and TCDD exposure. In none of these studies was the number of T4 cells significantly associated with TCDD exposure (Table 3).
- With T8 cells, both the Pilot Study and the Adipose Tissue Health Effects Studies showed an association with TCDD exposure. However, a review of the four studies showed a pattern of a slightly increased number of T8 cells in exposed persons compared with unexposed persons (Table 3).
- For the four studies, no overall pattern emerged of differences in T4/T8 cell ratios associated with TCDD exposure. However, a nonstatistically significant tendency was found for an association of T4/T8 ratios less than 1 in exposed persons. This association seems to be related to the slightly increased number of T8 cells in exposed persons, causing the T4/T8 ratio to decrease below the magic level of 1 in more exposed than unexposed persons (Table 3).

When the phytohemaglutinin, concanavalin A, pokeweed mitogen, tetanus toxoid and allogeneic T-cell cytotoxicity percent lysis for the four studies are reviewed, the only statistically significant finding was an increase of the pokeweed mitogen response in exposed persons.

CONCLUSION

In conclusion, we found no overall pattern to date of abnormal health effects associated with TCDD exposure in studies involving medical history, physical examination and laboratory findings including neurologic abnormalities, dermatologic abnormalities, reproductive abnormalities, routine hematology, serum chemistry, liver function and porphyrin metabolism.

The only suggested laboratory finding associated with TCDD exposure was the tendency of exposed individuals to have a few more T8 cells than unexposed individuals. Whether this finding is real and whether it will have any clinical significance, must be answered with the study of TCDD-exposed workers currently being carried out by the National Institute for Occupational Safety and Health.

Table 1
**Number of Participants and Results
for Exposed and Unexposed
Persons in Four TCDD Studies in Missouri**

	Pilot Health Effects Study	Quail Run	Quail Run Followup	Adipose Tissue
Number of Participants				
Exposed	68	135	28	24
Unexposed	36	142	15	16
Total	104	277	43	40
History of Cancer				
Exposed	3	2	0	0
Unexposed	2	4	0	0
Total	5	6	0	0
Globulin (g/dl)				
Exposed	2.6	ND*	ND	2.6
Unexposed	2.6	ND	ND	2.4
Albumin/Globulin Ratio				
Exposed	1.8	ND*	ND	1.7
Unexposed	1.8	ND	ND	1.9

*ND—Not done

Table 2
**Delayed-Type Hypersensitivity Skin Test Results
for Exposed and Unexposed Persons
in Four TCDD Studies in Missouri**

	Pilot Health Effects Study	Quail Run	Quail Run Followup	Adipose Tissue
Relatively Anergic				
Exposed	NR*	50	1	0
Unexposed	NR	27	1	0
Total		77	2	0
Anergic				
Exposed	1	22	0	0
Unexposed	1	11	0	0
Total	2	33	0	0
Average Number of Positive Antigens				
Exposed	3.0	2.3	4.4	6.0
Unexposed	3.5	3.1	3.9	5.6
Average Millimeters of Induration				
Exposed	13.4	8.6	17.3	25.8
Unexposed	14.8	11.2	15.0	22.5

*NR—Not Reported

Table 3
**T-Cell Related Results
for Exposed and Unexposed Persons
in Four Studies in Missouri**

	Pilot Health Effects Study	Quail Run	Quail Run Followup	Adipose Tissue
T4(CD4) cells/mm³				
Exposed	652	1,021	974	1,080
Unexposed	588	1,033	982	1,084
T8(CD8) cells/mm³				
Exposed	425	592	663	726
Unexposed	388	578	584	562
Mean T4/T8 Cell Ratios				
Exposed	1.8	1.9	1.7	1.8
Unexposed	1.8	1.9	2.0	2.1
Number of Persons with T4/T8 Ratios <1				
Exposed	9	11	4	3
Unexposed	2	9	0	1

What then, have we learned from these studies? As we mentioned at the beginning, things are not always what they seem. Clearly, illness occurred at the time of the original use of TCDD-contaminated wastes for dust control. But to date, we have not been able to document acute health effects even in persons known to have elevated levels of adipose tissue TCDD. Studies under way by the National Institute for Occupational Safety and Health may shed additional light on possible long-term health effects associated with TCDD exposure, including cancer.

Second, 19 years after the TCDD-contaminated wastes were used for dust control in Missouri, we still do not have all the answers on the adverse health effects caused by exposure to TCDD.

And third, the interest in dioxin has stimulated laboratories to develop expertise in measuring substances in the ppt and ppq (parts-per-quadrillion) range. The current national interest and expertise in hazardous substances has resulted in a large part from events such as those that occurred in Missouri.

ACKNOWLEDGMENTS

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Methods for Characterizing Populations Residing Near Hazardous Waste Sites

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ABSTRACT

In this paper, we describe the actions the Agency for Toxic Substances and Disease Registry (ATSDR) is taking to evaluate methods for obtaining demographic information about populations who reside near uncontrolled waste sites and who may be potentially impacted by releases or potential releases of hazardous substances from these sites. Door-to-door surveys represent the preferred method for obtaining such data; however, such surveys are not practical for most of the 1200 sites currently listed on the NPL. Thus, we propose to use one or more methods to obtain reliable estimates of total numbers and other demographic characteristics for populations potentially affected because of their proximity to hazardous waste sites.

Four approaches for obtaining estimates of critical demographic information about NPL sites were identified and are being evaluated. These four methods were given the following descriptive names: (1) ZIP Code Method, (2) Population Centroid Aggregate Method, (3) Block/Enumeration District Method and (4) Geographic Information System (GIS) Method.

Five NPL sites in Georgia were selected as part of a pilot project to evaluate and compare each of the methods. Total population was used as the initial demographic criterion for evaluation. Field surveys were conducted to determine base line populations for each site. Total population estimates obtained by each of the four methods are being compared against the field survey (base line) data. Data from the GIS Method were not available for this report.

Using these findings, we will apply one or more of the methods to a larger pilot of 30 NPL sites. In addition to total population, other demographic data — including information on racial and ethnic composition for populations residing near the sites — will be estimated.

INTRODUCTION

Valid demographic data are necessary to characterize populations whose health is potentially impacted because of their proximity to hazardous waste sites. Such data are critical to public health professionals and researchers who design and conduct studies to investigate possible relationships between human exposure to environmental contaminants at hazardous waste sites and adverse health effects. Human populations who live near sites that are listed on or proposed for the NPL are of particular interest.

Door-to-door surveys would provide the most accurate method for obtaining these data. However, such surveys of potentially affected residents are not practical for most of the 1200 NPL sites. Thus, we intend to use one or more methods to obtain reliable estimates of total numbers and other demographic characteristics for populations that are potentially affected because of their proximity to hazardous waste sites.

Various approaches for obtaining demographic data are being used by environmental regulators and private marketing firms.[1-6] However, these methods have limited utility for environmental health researchers because the demographic data they provide pertain to large geographic areas that are not easily linked to sources of environmental contamination at hazardous waste sites.

Four methods were identified as potential approaches for obtaining estimates of critical demographic information about NPL sites. These methods were given the following descriptive names: (1) ZIP Code Method, (2) Population Centroid Aggregate Method (also referred to as the centroid assignment technique),[6-10] (3) Block/Enumeration District Method and (4) Geographic Information System (GIS) Method.[4]

We describe an ongoing pilot project and future activities being planned by the Agency for Toxic Substances and Disease Registry (ATSDR) to evaluate and compare the utility of the above four methods for obtaining demographic data for populations near NPL sites.

METHODS

Selection of Sites

Five NPL sites located in Georgia were selected for the initial pilot project. The sites were designated as Sites 1, 2, 3, 4 and 5. Accessibility for field surveys was a criterion used to select the sites. An attempt was made to include sites that were representative of small urban and rural population areas. Sites 1 and 3 were considered to be located in rural population areas; Sites 2, 4 and 5 were considered to be located in urban population areas.

Selection of Base Line Criterion Used in Initial Evaluation

Total population was selected as the initial demographic criterion for evaluation. For these five sites, door-to-door surveys were not practical; estimates of total population for each site were determined through field surveys, which consisted of identifying and counting all houses located within one-mile radii of the sites. The estimates were made for each site by multiplying the number of residences observed by the average number of persons per household reported in the 1980 census for that county or geographic area.[11] The total population estimates were used as the population base lines against which similar estimates derived by each of the four methods were compared.

Methods for Estimating Population

ZIP Code Method

The method involved merging three computer data files: (1) the U.S. EPA NPL file, which contained addresses including ZIP Codes for all NPL sites; (2) the U.S. EPA Comprehensive Environmental Response, Compensation and Liability Information System (CERCLIS) file, which

contained similar but not identical information as the NPL file; and (3) the U.S. Bureau of the Census Master Area Reference File 3b (MARF 3b) and extract of the Summary Tape File 3b (STF 3b), which included 1980 census population data for ZIP Code areas.[12]

In merging the CERCLIS and NPL files, we noted some discrepancies between files for individual site addresses and ZIP Codes. When discrepancies were noted, the ZIP Code given in the U.S. Postal Service 1988 National Five Digit ZIP Code and Post Office Directory[13] was regarded as the actual ZIP Code. Four sites were located in one ZIP Code area and one site was located in two ZIP Code areas. Population data were retrieved from the 1980 census MARF 3b for the Zip Code areas in which the sites were located.

Population Centroid Aggregate Method

With the Population Centroid Aggregate Method, site latitude and longitude coordinates reported in the U.S. EPA CERCLIS file were used. The coordinates were used to locate sites on digitized maps for 1980 census tract, block group (BG) and enumeration district (ED) geographies. Concentric circles of one-, two- and three-mile radii were drawn around each site; the smallest concentric circle to include at least one BG or ED population center (centroid) was used to estimate the total population in 1988. Population data were derived by distributing the 1988 census tract population among the constituent BGs and EDs according to the population reported in the 1980 Census Summary Tape File 1 (STF 1) for these areas. Total population estimates were defined for each site by summing the populations for all BGs and EDs whose centroids were included within the concentric circle about the site. Total population estimates in 1988 of persons residing within one-mile radii were available for one of the five sites and within two-mile radii for four of the five sites.

Block/Enumeration District Method

The Block/Enumeration District Method involved the use of U.S. Geological Survey topographic maps to define actual site locations, which were then transferred to U.S. Census maps for 1980 census tract, block and ED geographies. One-mile radii were defined around each site and 1980 census population data were summed for all or portions of blocks and EDs that were included within the area.

Geographic Information System (GIS) Method

The GIS Method involves converting U.S. Census MARFs 1 and 3 into map coverages for each site. The coverages are generated by computing Thiessen polygons to approximate the boundaries of census blocks where the geographic centroid of each block is defined by latitude and longitude coordinates. Population densities at the corners of the Thiessen polygons and at the centroids are interpolated from the block population estimates.

U.S. Geological Survey topographic maps will be used to define actual site locations, which will then be transferred to the map coverages. One-mile radii will be defined around the sites. Total population estimates will be derived for each site by summing the population data for those blocks, BGs and EDs (and portions thereof) included within the one-mile area around the sites. The population data will be retrieved from the Census MARFs 1 and 3 and corresponding STFs 1 and 3. Areas surrounding the site that are known to be uninhabited, such as water bodies, forests and parks, will be designated as exclusion areas; population data for these areas will not be included in the total population estimates.

The GIS Method is currently being applied to the five Georgia sites. Use of this method will generate estimates for total population for geographic areas included within one-mile radii of the sites. The method can be applied to any lateral distance from the sites.

RESULTS AND DISCUSSION

The total populations for the five Georgia NPL sites that were derived using the proposed methods are shown in Table 1. Demographic data derived by the GIS Method were not available for this report. Base line estimates of total population, determined by field surveys, are included for comparison purposes.

Table 1
Total Population Estimates for Five Georgia
Sites: Results Using Three Methods[a] Compared
with Field Survey Values

Total Population

Site	Field Survey	ZIP Code	Pop Centroid	Block/ED
Site 1	980	18,512(+19)[b]	1,389(+1.4)	4,323(+4.4)
Site 2	8,087	18,512(+2.3)	1,389(-5.8)	14,377(+1.8)
Site 3	466	198(-2.3)	2,570(+5.5)	652(+1.4)
Site 4	632	54,096(+86)	40(-15.8)	2,974(+4.7)
Site 5	1,776	36,027(+20)	434(-4.1)	3,071(+1.7)

a   The three methods consisted of the ZIP Code Method (ZIP Code),
    Population Centroid Aggregate Method (Pop Centroid), and
    Block/Enumeration District Method (Block/ED).
    For the ZIP Code Method, the estimate for total population for Site 4
    includes population data for two ZIP Code areas.
    For the Population Centroid Method, the estimates for total
    population include a two-mile area for Sites 1, 2, 3, and 4, and a
    one-mile area for Site 5.
b   Numbers in parentheses indicate the difference from the field survey
    values.

ZIP Code Method

The ZIP Code Method was easy to implement and involved readily accessible computerized data files that could be cross-referenced to identify and correct inconsistencies in geographic descriptors (ZIP Codes). However, the total population estimates obtained using this method varied significantly from their respective field survey values. Estimates for four of the five sites were above the field survey levels and varied from approximately 2 to 85 times greater than these base line values. Only the estimate for Site 3 was less than the field survey value. The overestimates of the total population probably occurred because the ZIP Code areas were geographically much larger than the areas surrounding the sites and were not defined relative to site boundaries.

The population estimates generated using this method were identical for Sites 1 and 2. The two sites are reported in the CERCLIS and NPL files as being located in the same town and county; however, the sites are physically located one mile apart and Site 1 is located in a rural area and Site 2 in an urban area.

Population Centroid Aggregate Method

Total population estimates obtained using the Population Centroid Aggregate Method also varied from the field survey values, but to a lesser extent than when the ZIP Code Method was used. Three of the five estimates were less than their respective field survey values. The largest difference was a 16-fold underestimate of the population for Site 4. The population estimates for Sites 1 and 2 were identical.

The observed differences in population estimates may be attributed to several factors. First, BG geographies were large; concentric circle areas had to be extended beyond one mile in order to identify a single BG centroid. This resulted in an overestimation of total population for sites in more rural areas (Sites 1 and 3) and an underestimation of total population for sites in more urban areas (Sites 2, 4 and 5).

Second, the method relied on site latitude and longitude coordinates reported in the U.S. EPA CERCLIS file. Many of these coordinate data have not been validated and are incorrect. Last, census tract, BG and ED geographies did not conform to the one- and two-mile concentric circles defined around the sites. Rather, the concentric circles transected BG and ED boundaries and included portions of individual BGs and EDs. Population data were obtained only for those census tracts, BGs, or EDs whose centroids were included within the concentric circle; population data for the entire BG and ED area were counted in the site population estimate provided that the centroid was included within the concentric circle.

The method used population data for BGs and EDs that were derived from data reported for 1988 census tract geographies. Changes in population distributions within census tracts and constituent BGs and EDs may have occurred between 1980 and 1988. The 1988 population estimates derived using this method may not be reliable for sites whose

residential population distribution had changed during that period.

Previous work conducted by the ATSDR attempted to estimate populations residing near hazardous waste sites and at potential risk of exposure to environmental contaminants.[10] The method used to obtain demographic data was identical to the Population Centroid Aggregate Method evaluated in this pilot project. Based on population data for 725 NPL sites, an estimated 4.1 million persons were identified as living within one-mile radii of the hazardous waste sites.

Block/Enumeration District Method

The population estimates obtained using the Block/Enumeration District Method were more consistent with the field survey population values than with the estimates obtained by the other two methods. For all sites, the estimates for total population were higher than those obtained by field survey. None of the overestimates were greater than 4.7 times higher. No obvious differences between estimates for urban and rural sites were noted. The population estimates for Sites 1 and 2 were markedly different. The population for Site 2, which is located in an urban area, was 3.5 times higher than that for Site 1, which is located in a rural area.

The comparatively high level of correlation was attributed to the fact that population data for small geographic areas (blocks, EDs) defined relative to the sites were used. In addition, actual site locations were defined using topographic and census maps so that portions of census geographic areas (blocks, EDs) located within the areas surrounding the sites—and the corresponding population data for those areas—were included in the population estimates. However, manual plotting of sites on topographic and census maps and interpretation of census descriptive and geographic map codes[14] was time-consuming and resource-intensive.

GIS Method

Demographic information is currently being obtained using the GIS Method and was not available for this report. On a conceptual basis, the GIS Method combines the strengths of the Block/Enumeration District Method with those of the Population Centroid Aggregate Method. Demographic data will be obtained for small geographic areas (blocks, EDs) defined relative to the sites and will include population data for portions of blocks and EDs that are included within areas surrounding the sites. Manual plotting of sites on topographic and census maps and interpretation of census geographic and descriptive codes will not be required.

Comparison of Preliminary Data

The total population estimates varied significantly depending on the method used. In general, the largest estimates were obtained using the ZIP Code Method, and the smallest estimates were obtained using the Population Centroid Aggregate Method. This was an unexpected finding for the Population Centroid Aggregate Method, since 1988 population data were used with this method; 1980 population data were used with the other two methods. Information reported by the U.S. Bureau of the Census on population changes between 1980 and 1988 indicated that county and city population estimates increased by as much as 8.1% for four of the sites and decreased by 9.9% for one site.[15]

From the preliminary findings, demographic information obtained using the Block/Enumeration District Method correlated most closely with the field survey population estimates. For each method, the highest level of variation was observed for Site 4. The reason for this is not clear. No other patterns were obvious for the data evaluated in this pilot project.

The findings of the pilot are preliminary and should be reviewed cautiously. Only a few of sites were evaluated. A larger pilot of 30 NPL sites is planned. The larger pilot will again evaluate total population, but other variables including racial and ethnic composition will be incorporated. Field surveys similar to those for this pilot project will be conducted. After the demographic data for all 35 sites are reviewed, we will determine the preferred method or combination of methods for obtaining demographic data on total numbers and demographic characteristics for populations residing near hazardous waste sites.

The demographic information will be essential to ATSDR researchers conducting possible health investigations for these sites. The site-specific demographic information will be correlated with environmental data on contaminant concentrations and information on human exposures (e.g., biological indicators) and adverse health outcomes in order to better define possible relationships between exposure to environmental contaminants and the occurrence of adverse health outcomes.

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Health Risk Assessment for Complex Mixtures of PAHs

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ABSTRACT

Although most health-based risk assessments have been performed on individual toxic chemicals, hazardous waste sites contain mixtures of individual chemicals. The importance of quantitatively estimating the human health risk from exposure to such mixtures for cleanup purposes cannot be overstated. However, several less obvious benefits exist, including: (1) priority assessment of waste sites, facilitating decision-making regarding the expenditures of time, money and man-hours; (2) development of selective remediation techniques for the most hazardous component(s) of the mixture; and (3) a realistic basis for exposure assessment.

Typically, the exposure risks of only a few components in a mixture have been adequately characterized from human or lifetime animal bioassay data. Risks from mechanistically or structurally related components must be estimated using acceptable alternatives. For carcinogens, the most widely used alternative involves calculation of a relative potency or the anticipated strength of a tumor response for a poorly understood candidate chemical relative to the response from a well-studied standard. Potency ratios comparing the candidate compound to the standard typically are based on short-term bioassay end-points believed to be related to the carcinogenic response. The final product of the relative potency calculation is a risk estimate of the standard and all the candidate compounds in the mixture expressed in "toxicologically equivalent" units of the standard.

The U.S. EPA recently developed a relative potency procedure for mixtures of polycyclic aromatic hydrocarbons (PAHs) based on mouse skin painting studies. The authors of the present paper discuss the adequacy of these studies as predictors of human carcinogenic risk for six structurally similar PAHs. We also consider the appropriateness of relative potency calculations based on mechanistic experiments. Because PAH metabolism to the ultimate carcinogen depends on organismic variables, we have incorporated physiological parameters to account for interspecies variation and use default values when such data are sparse.

Our model indicates that, as a whole, the candidate compounds are considerably less potent than the standard, benzo[a]pyrene (B[a]P). Therefore, compared to an approach in which all mixture components are considered equipotent with the standard, the relative potency model can reduce cleanup costs while assuring continued compliance with health standards.

INTRODUCTION

When analyzing complex mixtures of potential environmental carcinogens, health risk assessors traditionally have used a surrogate approach to describe excess risk. According to this approach, the carcinogenic potencies of mechanistically similar but poorly studied substances are considered equivalent to the potency of a congener that has been adequately assessed for carcinogenicity in lifetime animal bioassays or epidemiological studies. Excess risk is defined as the product of the total concentration of all congeners in the environmental sample, in some standard unit, and the potency determined for the well-studied substance, or standard, minus the background risk. Because the standard is often considerably more toxic than its congeners, use of the surrogate approach can lead to serious overestimations of carcinogenic risk.

An alternative approach involves the calculation of a relative potency. Relative potency is most frequently determined as the ratio of the magnitude of an effect resulting from exposure to an empirically data-sparse substance with the magnitude of the same effect, in the same experiment, resulting from exposure to a mechanistically similar and better understood standard. Effect ratios are calculated at equal exposure (or, alternatively, equimolar) concentrations and typically are based on short-term results that, by themselves, would be insufficient to support a potency estimate. The legitimacy of the relative potency approach is strengthened if effects ratios based on different experimental conditions are approximately consistent. If such consistency is demonstrable, then the environmental concentrations of the data-sparse substances can be converted to "toxicologically equivalent" concentrations of the standard for use in the subsequent risk and exposure assessments.

For polycyclic aromatic hydrocarbons (PAHs), substances formed during incomplete combustion, the standard has been benzo[a]pyrene (B[a]P). B[a]P has been studied extensively in both oral[1] and inhalation[2] animal bioassays. Based on these studies, the U.S. EPA[3] cited unit risk estimates of 11.53 and 6.11 (mg/kg day)$^{-1}$, respectively, for oral and inhalation exposure. Although a comparable data base does not exist for mechanistically similar PAHs, results of short-term studies clearly indicate that B[a]P is considerably more potent than most of these related substances.

The fallacy of the surrogate approach can be illustrated by comparison of the cancer risks from cigarette smoking and occupational exposure to roofing materials.[4,5,6] Based on face mask residues, the amount of B[a]P inhaled daily by roofers ranged from 16.7 ug to approximately 30 ug. Daily B[a]P intake from mainstream cigarette smoke in individuals smoking two packs a day was estimated as 1.4 ug. Despite these differences, the excess lung cancer risk in smokers is considerably greater than in nonsmoking roofers. These findings indicate that a simplistic surrogate approach based on controlled animal experimentation does not always accurately reflect the cancer risks experienced by heterogenous human populations exposed to a variety of potentially interacting parameters.

The authors of the current paper will identify some of the many variables that impact on the human health risk of exposures to com-

plex mixtures, with specific reference to PAHs. Five high molecular weight PAHs, all structurally similar to B[a]P and considered by the U.S. EPA as possible or probable human carcinogens, will be considered. Using B[a]P as a standard and these five substances as comparison compounds, the robustness of the relative potency approach will be addressed. Next, some of the variables affecting the significance of the both the animal and the human B[a]P potency estimates will be considered. These variables include the appropriateness of experimental design and modeling parameters, the importance of the statistical model used to extrapolate from high, experimental exposure levels to more environmentally realistic levels, the effects of physical and chemical characteristics on risk determination and the issue of interspecies extrapolation. The ensuing sections will include an analysis of the interactive nature of other mixture components and a discussion of a recent exposure assessment for combustion sites. The paper will conclude with an analysis of the adequacy of the relative potency approach for risk characterization and a consideration of those factors that most significantly impact risk estimation.

VALIDITY OF THE RELATIVE POTENCY APPROACH FOR PAH

Common Mechanism of Action

An essential tenet of the relative potency approach is that the standard and the data-sparse substances show a common mechanism of action. For high molecular weight PAHs, the common mechanism involves metabolism to one or more short-lived, reactive ultimate carcinogens.[7] Most investigators believe that the ultimate carcinogen is a diol (or triol) epoxide that is formed adjacent to the so-called "bay-region" of the molecule. As depicted in Figure 1, all alternant PAHs (those consisting strictly of fused ring structures) have one or more true bay regions. Nonalternant PAHs, such as the cyclopentenyl-containing benzo[b]fluoranthene (B[b]F) and indeno[1,2,3-c,d]pyrene (IP), may or may not contain a true bay region. As discussed below, these latter substances contain other metabolically active sites that may influence carcinogenic potential.
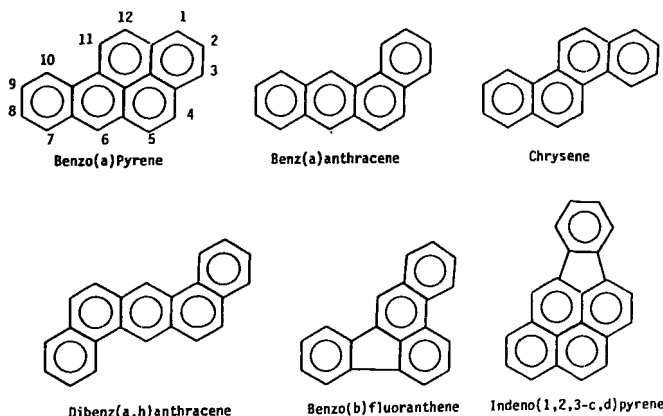
Figure 1
Structures of Six High Molecular Weight PAHs[8]

Studies in newborn mice[9,10] have added support to theories about B[a]P's mechanism of action. In this paradigm, the experimental substance is intraperitoneally injected into mouse pups for 3 days, and the mice are observed for tumors for up to 40 weeks. If the substance is carcinogenic, the mice develop lung adenomas, liver tumors and/or malignant lymphomas. Using this model, Kaputilnik and his coworkers[10] determined that a specific stereoisomer, (+)7,8-diol-9,10-epoxide-2, is the putative ultimate carcinogen (Fig. 2). Rodent studies indicate that the formation of this stereoisomer is metabolically favored. Other investigators,[11,12] using the newborn mouse model, demonstrated similar metabolic reactivity for benz[a]anthracene (B[a]A) and chrysene (Ch). Although the available evidence[13] in-

dicates that bay region epoxide formation is essential for tumor expression after B[b]F or IP administration, other molecular sites may have contributory roles. Silverman and Lowe,[14] for example, discussed evidence indicating that diol epoxide formation on the phenylic ring of these nonalternant substances may impact on the carcinogenic response. To date, however, no empirical evidence for diol formation on this portion of the molecule has been found.

NOTE: Heavy arrows indicate favored metabolic pathway.
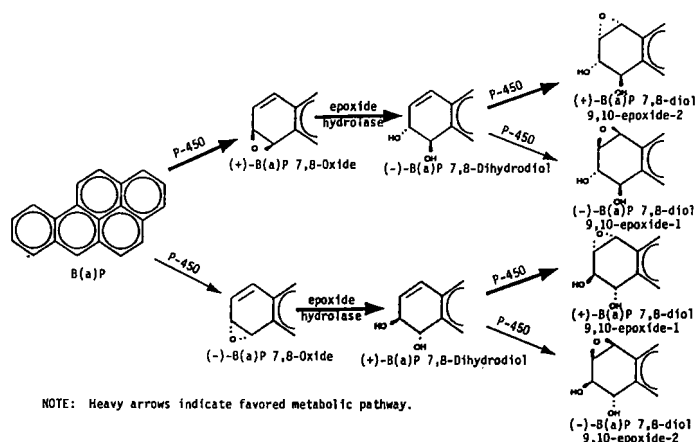
Figure 2
Metabolic Conversions in the Bay Region of Benzo(a)pyrene[18]

Dose Additivity

The relative potency approach assumes that toxicologically equivalent doses can be summed to produce an overall response. This assumption ignores the possibility of both toxicant interaction and cocarcinogenesis induced by the presence of similar congeners. Interactions (synergisms or antagonisms) could occur because other mixture components induce enzymes that either detoxify the standard or accelerate metabolism to a carcinogenic precursor. Several investigators[15,16] have found synergistic relationships between cigarette smoking (which involves exposure to high PAH levels) and other environmental hazards.

A study by Schmahl et al.[17] may provide the only data that address the issue of low PAH exposure levels and dose additivity. NMRI mice received twice weekly skin applications of PAH mixtures that were representative of concentrations in automotive exhaust. Some mice were treated with a mixture consisting of 4.0, 6.8 or 12.0 ug of B[a]P, B[a]A, B[b]F and dibenz[a,h]anthracene (DB[a,h]A). Skin carcinoma incidences at these exposure levels were adequately predicted by a relative potency approach[18] of which dose additivity was an essential component. A second group of mice received higher concentrations of a mixture containing different PAHs. In this instance, the relative potency approach overestimated risk, implying that interactions at these higher exposure levels may have reduced toxicity. Although these results support the use of the relative potency approach at low exposure concentrations, further validation in a number of test systems is needed.

Relative Potency Ratios Across Test Systems

Table 1 illustrates carcinogenic potencies, relative to B[a]P as unity, of the five high molecular weight PAHs that are the subject of this report. Although these data are from different study designs in a variety of animal models, order-of-magnitude consistency is apparent for DB[a,h]A, B[b]F and Ch. The ratios for both IP and B[a]A vary by an order of approximately 20. In general, the results indicate that a geometric mean average of the relative potencies of each compound would provide a fair to excellent estimate of tumorigenic risk in animal models. Furthermore, use of the relative potency approach may provide a more reasonable estimate of risk than the surrogate approach, which would overestimate risk in four out of five cases.

SIGNIFICANCE OF THE POTENCY ESTIMATES

Relevance of the Experimental Model

In the absence of standard lifetime bioassays for most PAHs, some researchers have calculated relative potency values on the basis of mouse skin painting studies. These studies are of two types: complete carcinogenicity assays, in which the test substance is applied repeatedly and without further stimulation from other substances, and initiation-promotion assays, in which the test substance (initiator) is applied for a limited duration, and carcinogenicity is not expressed until the repeated application of a known tumor promotor.

IARC[24] has commented on the appropriateness of mouse skin bioassays as estimates of carcinogenic risk. They noted that certain PAHs initially established as mouse skin carcinogens have subsequently been shown to produce malignancies by other routes of administration. Moreover, the skin is a functionally autonomous organ. Tumor (primarily site papillomas and carcinomas) incidence after dermal application of PAHs is dependent on the inducing activity of local enzymes, rather than the more complex induction and repair mechanisms occurring after systemic administration.

The newborn mouse model has provided considerable insight into the metabolic reactivity of various stereoisomers of alternant PAHs. Because this experimental protocol results in multiple site tumors, site relevance becomes an important factor for relative potency calculations. For example, LaVoie et al.[23] administered B[a]P and B[b]F to male and female newborn CD-1 mice on Days 1, 8 and 15 after birth. Both compounds induced hepatic tumors in male mice, but were inactive in females. Based on the hepatic tumor incidence in males, B[b]F was slightly more potent than B[a]P. However, B[b]F was much less potent than B[a]P in inducing lung adenomas. Because the liver is not a target organ for PAH activity, and the male mouse shows unusually high spontaneous hepatic activity, the pulmonary tumor response was chosen for relative potency calculations (Table 1).

Table 1
Carcinogenic Potencies of Five High Molecular Weight PAHs Relative to B[a]P

| Basis for Relative Potency | | | |
Compound	q_1*[1]	ED_{10}[2]	2-Stage Model[3]	Neonate Model
DB[a,h]A	0.69	2.26	1.11[5]	--
B[b]F	0.08	0.29	0.14[4]	0.48[6]
Ch	0.0012	0.0041	0.0044[5]	0.011[7]
IP	0.017	0.011	0.23[4]	0.035[6]
B[a]A	0.013	0.20	0.14[5]	0.30[7]

[1] Slope estimate of the carcinogenic potency. Relative potency calculated as the ratio of potencies of the data-sparse PAHs to B[a]P in mouse skin painting studies, multiplied by the oral potency of B[a]P determined by the linearized multistage model. (19)

[2] Dose associated with an excess risk in 10% of the exposed population. Relative potency calculated as the ratio of ED_{10}s of the data-sparse PAHs to B[a]P in mouse skin painting studies, multiplied by the oral potency of B[a]P determined from the linearized multistage model. (19)

[3] Relative potencies calculated from the ratio of the transition rate parameters for the data-sparse PAHs and B[a]P, calculated from a restricted 2-stage model. (18)

[4] Intrapulmonary instillation. (20)

[5] Complete carcinogenicity skin painting studies. (21, 22)

[6] Comparative incidences of tumor bearing animals with lung adenomas, adjusted for total dose administered. (23)

[7] Comparative potencies of the metabolically active stereoisomers. (7)

In general, mutagenicity assays are not adequate for the assessment of risk for complex mixtures. These assays typically require exogenous activation, which contributes variability to the test system.[7] Moreover, with the exception of the cell transformation assay, short-term in vitro studies detect only initiation activities. Rice et al.[25] have observed that the active mutagenic metabolites of B[a]P and IP in the Salmonella typhimurium assay show little tumorigenic activity.

The U.S. EPA is currently reevaluating B[a]P unit risk factors based on oral[1] and inhalation[2] exposure. Although these re-evaluations, which would probably lead to lower risk values, would not affect relative potency calculations, they would affect the human unit risk estimates for these two exposure routes.

Low-Dose Extrapolation Modeling

Regulatory agencies have traditionally used values of 10^{-4} to 10^{-7} as acceptable levels of carcinogenic risk. Animal experiments would require millions of animals per exposure group to statistically detect treatment-related effects at these arbitrarily-defined levels. To avoid this problem, experimenters typically expose smaller groups of animals to relatively large doses and then use mathematical extrapolation models to estimate low-dose risk. Because various models can predict markedly different risks at the same exposure level, the choice of a model has been a source of continuing controversy.

In the absence of a more complete understanding of the carcinogenic process at low doses, the U.S. EPA uses the multistage linearized model[26] for extrapolation purposes. This model provides a conservative, stable upper bound estimate of risk. However, the model is statistically, rather than biologically, based, and the risk estimate depends largely on experimental design rather than the actual potency of the test compound.

Researchers at ICF-Clement Associates[18] proposed an alternative extrapolation model based on a two-stage approach (Fig. 3). According to this approach, nondifferentiated stem cells may divide into daughter cells, terminally differentiate, die or undergo mutations that result in a premalignant cell. The premalignant cell may in turn undergo any of the first three processes or mutate to a cancer cell and undergo tumor formation. The numbers of premalignant and malignant cells are assumed to be random variables, while the numbers of normal cells at risk of transformation are assumed to be known. Based on experimental data,[27] researchers have concluded that a restricted form of the two-stage model was appropriate for assessment of the carcinogenic risk of B[a]P. According to this model, response probability is a function of three empirically-derived parameters: the growth rate of preneoplastic cells, the background tumor rate and interstage transition rates. Using the restricted two-stage model, a unit risk of 5.74 (mg/kg day) for oral exposure to B[a]P was calculated. Empirically-determined transition rate parameters between other carcinogenic PAHs were used to calculate potencies relative to B[a]P (Table 1). These calculations were based on intratracheal instillation[20] and complete carcinogenicity skin painting[21,22] studies.

The two-stage model provides a biologically-based, maximum likelihood estimate of risk that is applicable to the study of exposure to multiple carcinogens. It apparently can be used only with genotoxic substances.

Physico-Chemical Considerations

Other factors affecting carcinogenic risk after PAH exposure include physical properties of the mixture and matrix effects. For example, Mahlum et al.[28] studied the initiating activity of three coal distillate fractions applied to mouse skin. The boiling points for two of the distillates were in the 800 to 850°F range, while the boiling point of the third was 850+°F. Each distillate was further fractionated into aliphatics and olefinics, neutral PAHs, nitrogen-containing polycyclic aromatic compounds and hydroxy-PAHs. For each distillate, the neutral PAH fraction was the most carcinogenic. Although the neutral PAH fraction of one of the 800 to 850°F distillates had the same B[a]P content as the 850+°F sample, the latter had greater biological activity. Furthermore, the presence of noncarcinogenic PAHs in the distillate fractions had a significant effect on the expression of a carcinogenic response. The results indicate that B[a]P is not the determinant factor in the carcinogenicity of these mixtures.

When adsorbed to particulate complexes, B[a]P is not subject to photo-degradation and can reach the human lung more easily than unbound B[a]P.[29] Warshawsky et al. demonstrated that the co-administration of B[a]P and crude particulate matter to the isolated perfused lung increased

the rate of dihydrodiol formation and depressed the formation of non-toxic, water-soluble conjugates.

Finally, DeCaprio et al.[30] showed that soil type was the determining factor in the toxicological activity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), a substance that is mechanistically similar to the PAHs. The soils differed markedly in TCDD binding affinity. Although each of two TCDD-containing soil samples induced cytochrome P-450 enzyme activity, only loosely-bound TCDD, after extraction, was capable of inducing toxicity in rats and guinea pigs. The differences in toxicological activity are a function of bioavailability, which can range from 0.1% in tightly bound matrices to 85% in loosely bound matrices.
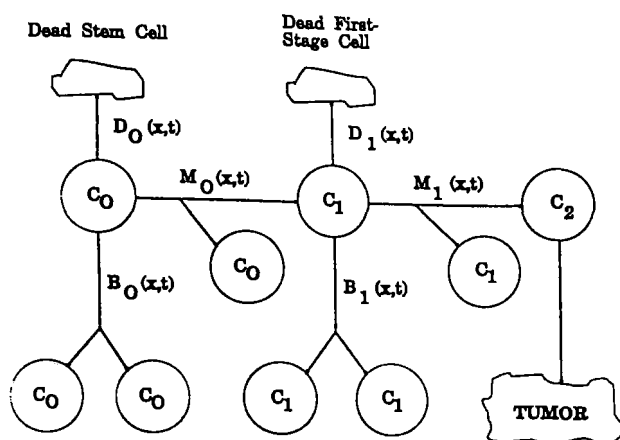
C_0 is a normal, susceptible stem cell.
C_1 is a transformed, first stage cell, that can proliferate into a premalignant clone.
C_2 is a cancerous cell that will eventually develop into a detectable tumor.
$D_0(x,t)$, $B_0(x,t)$, and $M_0(x,t)$ are the exposure- and time-dependent death, birth, transition or mutation rates for the normal stem cell.
$D_1(x,t)$, $B_1(x,t)$, and $M_1(x,t)$ are the exposure- and time-dependent death, birth, and transition or mutation rates for the first-stage cell.
x is the exposure level, which is assumed to be constant over time.
t is the age of the subject.

Figure 3
Biological Schematic of the Two-Stage Carcinogenicity Process[18]

Interspecies Extrapolation

One major issue in quantitative risk assessment is the development of a general formula describing equipotent doses between species, with particular emphasis on dose extrapolation from experimental animals to man. The U.S. EPA has adopted a multiplicative conversion factor based on the 2/3 power of the ratio of the human to the animal body weight. This ratio is equivalent to extrapolation based on surface area. Mouse, rat and human data for a variety of chemicals[31] support the validity of this conversion factor.

Recently, O'Flaherty[32] has recommended a body weight ratio exponent of 3/4, based on dose equivalency at the receptor, or target organ, level (effective dose). O'Flaherty provided data indicating that this approach would be appropriate for substances, such as high molecular weight PAHs, that bind covalently to DNA and/or produce reactive metabolites. In practice, the use of the 3/4 exponent, compared to the 2/3 exponent, would not have a significant impact on risk determina-

tion. For example, based on a "standard" 30-gram mouse and a 70-kg human, conversion to the less conservative 3/4 factor would only reduce the risk estimate by a factor of 2.

More importantly, humans are exposed to genetic and environmental variables that have great influence on the expression of a carcinogenic response, and that will result in far greater variability than the controlled laboratory situation. These variables, including heterogeneity in the rate of enzyme induction, smoking and dietary habits and proximity to combustion sites, can have complex and variable effects on an initiated cell. The variability in the uncontrolled human environment is a primary reason why human carcinogenic potency is difficult to accurately determine from laboratory animal data.

INTERACTIONS WITH OTHER MIXTURE COMPONENTS

Several researchers[21,33] have studied solvent effects on the carcinogenic activity of B[a]P in skin painting studies. The data show that carcinogenicity is amplified by co-administration of C10 to C14 straight-chain alkanes, catechol, pyrogallol, pyrene, benzo(e)pyrene and fluoranthene. Carcinogenicity was increased over a thousand-fold when n-dodecane, rather than decalin, was administered with B[a]P. The results suggest cocarcinogenicity (enhancement of a carcinogenic response by simultaneous administration of a noncarcinogen), possibly through the presence of functional groups that increase hydrogen bonding and/or metal chelation. Bingham et al.[34] further demonstrated that pretreatment with n-dodecane increased 9,10-diol formation in B[a]P-treated isolated rabbit perfused lungs, compared to B[a]P treatment alone.

Although cocarcinogenicity is a putative factor for some of these compounds, other possibilities remain. The solvents may directly injure the skin, causing modifications in uptake. Dermal absorption will be also be affected by the lipophilicity of the PAH-solvent complex. For example, in the Van Duuren and Goldschmidt[33] studies, the aromatic hydrocarbons pyrene, benzo[e]pyrene and fluoranthene may have shown cocarcinogenic activity by alteration of epoxidizing enzyme activity. However, the inhibitory effect of several phenolic compounds probably involved decreased absorption efficiency.

EXPOSURE ASSESSMENT

Even after allowance for interspecies extrapolation, risk estimates based on controlled laboratory studies have little direct relevance to the "true" risks to humans resulting from environmental exposure. Although exposure assessment is one of the major components of the risk assessment process, it is often the least well characterized.

The U.S. EPA[35] conducted an environmental assessment of health risks associated with indirect exposure to combustor emissions. B[a]P was chosen as a representative carcinogenic constituent of these emissions. Indirect sources included intake from soil, the terrestrial food chain, dust resuspension, drinking water and fish. The U.S. EPA determined risk on a modeling scenario involving an individual (child, then adult) who spends 30 years within 5 kilometers of a combustion site that has been in operation for 60 years and consumes food grown within that 5-kilometer radius.

The U.S. EPA calculated risk levels for each of the exposure pathways and found that exposure through the terrestrial food chain constituted the only significant source of intake. For children and adults combined, the EPA calculated an excess risk of 5.93×10^{-5} based on the total daily B[a]P intake, a measure of absorption efficiency and the human oral cancer potency factor.[1] An uncertainty analysis for human soil ingestion and terrestrial food intakes indicated that the estimated daily B[a]P intake was probably within two orders of magnitude of the true intake.

CONCLUSIONS

Table 2 is a rating system for the various factors that impact the quantitative risk assessment for complex mixtures of PAHs. The number of check marks accompanying each factor defines the extent to which additional field, laboratory and/or literature research can refine and improve health-based risk estimates. The following descriptions accompany each rating.

Table 2
Authors' Ranking of Research Needs for Reducing Uncertainty in Quantitative Health Risk Assessment of Complex Mixtures

Research Needs	Relative Importance
Validity of the Relative Potency Approach	//
Relevance of the Experimental Model	//
Relevance of the Low-Dose Extrapolation Procedure	/
Physicochemical Factors	////
Interspecies Extrapolation	///
Effects of Other Mixture Components	/////
Exposure Assessment	////

Validity of the Relative Potency Approach

The data in Table 1 suggest that the relative potency approach is a useful tool for assessing risk of mixtures of similar hazardous substances and provides a reasonable alternative to the surrogate approach. Furthermore, preliminary evidence substantiates the possibility of dose additivity at low exposure levels. The conditions that distinguish "mechanistically similar" substances need clarification. In general, results from studies with differences in experimental design and carcinogenic end-points support the validity of the relative potency concept for PAHs. Based on these studies, a unit risk factor for groups of high molecular weight PAHs can be calculated and, after modification by the factors described below, can be incorporated into the exposure assessment.

Relevance of the Experimental Model

Both the mouse skin complete carcinogen assay and the newborn mouse models appear to be adequate predictors of the oncogenic potential of PAHs and should be used for additional comparative studies. The relevance of the oral route of exposure to human risk assessment needs to be carefully re-assessed, and, if necessary, a new unit risk factor needs to be derived.

Relevance of the Low-Dose Extrapolation Procedure

Because of uncertainties regarding the carcinogenic process, the use of a conservative extrapolation model is recommended. Although both the linearized multistage model and the restricted two-stage model provide an adequate fit of tumor incidence data in the observable dose range, the latter appears to be more consistent with the biological mechanism of action.

Physico-Chemical Factors

The physical properties and physico-chemical form of the mixture components have a great impact on quantitative risk estimation. Nevertheless, these factors are consistently overlooked in most risk characterizations. A more systematic effort to correlate these factors with toxicological findings is required. Risk estimates from similar mixtures with different physical properties can vary by several orders of magnitude.

Interspecies Extrapolation

Metabolic and physiological processes are similar across mammalian species. Nevertheless, numerous idiosyncracies in biotransformation and repair rates exist. Extensive analysis of these idiosyncracies in both experimental humans and animals is unfeasible. A general formula based on the body weight ratio has received some empirical support and is recommended for complex PAH mixtures. In addition, further study of the factors that influence base line PAH levels in humans may help reduce the uncertainty of the extrapolation procedure.

Effects of Other Mixture Components

The available data indicate that the noncarcinogenic components in the mixture have a profound effect on the expression of tumorigenicity. The interactive effects of low molecular weight PAHs can be studied through structure-activity relationships. A thorough literature review

should be conducted to assess specific solvent effects on dermal absorption. Modifying factors based on the physical composition of mixtures should be incorporated into the risk assessment.

Exposure Assessment

Exposure assessments should be customized for individual sites. Because extensive surveying of regional populations is not cost-effective, the best approximations of exposure parameters from recent data compilations (such as the FDA's NHANES reports) should be used. Whenever possible, actual data from these reports, rather than results of modeling studies,[35] are preferable.

The average human daily intake of the high molecular weight PAH fraction of the mixture should be estimated based on environmental concentrations and appropriate exposure parameters. The total intake of these PAHs can be converted to toxicologically equivalent units of B[a]P and multiplied by a unit risk factor adjusted for interspecies extrapolation, physico-chemical considerations and the interactive effects of other mixture components. The final result is an estimate of the human carcinogenic risk attributable to the high molecular weight PAH component of the mixture.

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Application of the Expanded Health Assessment: The Massachusetts Experience

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ABSTRACT

In 1986 SARA was passed calling for a variety of environmental in-itiatives, among them health assessments at each of the NPL sites in the United States. The Agency for Toxic Substances and Disease Registry (ATSDR) developed a methodology for these health assessments (HA) and in 1987 requested proposals from state health departments wishing to enter into cooperative agreements to perform HAs.

The Commonwealth of Massachusetts responded to this request by proposing the use of a methodology Department of Public Health uses in its community health investigations. This methodology involves the evaluation of actual community health outcomes. The rationale for this approach is that if we are to suggest a variety of health outcomes which may be expected with the types of exposures a community has suffered, we should see if easily retrievable information may exist which would indicate the health outcomes that are being observed in an affected com-munity. By including such information, it would then be possible to discuss the plausibility of an association between environmental exposures and health outcomes that may be of concern to the community. This has proven to be an effective approach to community-specific health assessments in Massachusetts. ATSDR is currently developing a methodology for including health outcome data in an expanded health assessment.

Besides this additional health analysis section, considerable effort and emphasis is placed upon public education as well as cancer and environmental awareness campaigns. These types of activities aid the affected community in better understanding the work that is done, in addition to fostering communication and building trust and credibility in the health assessments. This approach has been the most effective and efficient procedure for addressing all environmental and health con-cerns posed by an NPL site. An actual case study of a Massachusetts NPL site will be presented.

INTRODUCTION

It is no secret that for a long time environmental epidemiologists and toxicologists did not have the closest working relationship. It was dif-ficult for either group to understand where the other was coming from in terms of the best methods for assessing health outcomes in relation to environmental exposures.

The toxicologists seemed to resent the "Texas sharpshooter approach" that the environmental epidemiologists took when they first identified a "cluster of disease" and then looked for a nearby environmental culprit upon which to blame the occurrence. At the same time, epidemiologists were never pleased with the fact that toxicologists often suggested that the health outcomes of interest for a particular exposure were not those that were easily measured, if measured at all.

As a result, the community often has been left in a state of confu-sion. This confusion usually has led to mistrust and/or credibility problems when environmental investigations are completed but ques-tions remain. These problems are not always easy for state environmental health officials to deal with. It is important to stress, however, that the people left with even greater problems are usually the local officials and the community. This type of situation does not occur often, but it is important to provide an example of this type of problem in order to clarify why the expanded health assessment can solve some of these problems. In order to do this, we will take an actual case study of a recent environmental health assessment in Massachusetts.

As part of a community investigation, several individuals living in close proximity to each other were diagnosed with the same primary site of cancer. Some of the exposures that might have occurred given the industry that formerly occupied this site were suggested to be associated with the cancer of interest. Naturally the community and state environmental health officials were concerned, so a more in-depth investigation began. This involved looking closely at the environmen-tal contamination present and taking into consideration environmental fate and transport of the chemicals involved. Unfortunately, the answers to all of the questions were not readily available and the local health official felt pressured to find quick answers to complex questions. He therefore began to try to find a possible explanation for each individual that had been diagnosed with cancer (e.g., smoking status) as opposed to waiting for more information regarding occupational exposures, routes of environmental exposures, etc.

As a result of these types of problems, the Massachusetts Depart-ment of Public Health established the Community Assessment Unit two years ago. This unit is housed within the Division of Environmental Health Assessment. The Division itself is set up in the form of a triage system (Fig. 1) with the community assessment unit logging in more that two dozen requests for environmental health information and assistance on a weekly basis. Questions often are answered over the telephone and do not require extensive followup. These calls warrant simple public health education regarding cancer and/or environmental awareness.

A large number of calls, however, require what we refer to as level I investigations. The level I investigation is always initiated with a com-munity meeting. The purpose of this meeting is two-fold. The first reason is to learn more about the community's concern(s). The second, and perhaps more important purpose, is to establish a working relation-ship and plan of action with both the concerned citizens and the local officials. The expanded level I investigation is what we consider the Massachusetts approach to the ATSDR health assessment.

METHODS

As can be seen, Figure 2 presents the series of steps involved in con-

ducting the expanded health assessment. The first step in the health assessment process involves receipt of existing data from the U.S. EPA. Oftentimes, Agency for Toxic Substance and Disease Registry (ATSDR) regional staff have assisted and been extremely helpful in the transfer of these data packages.
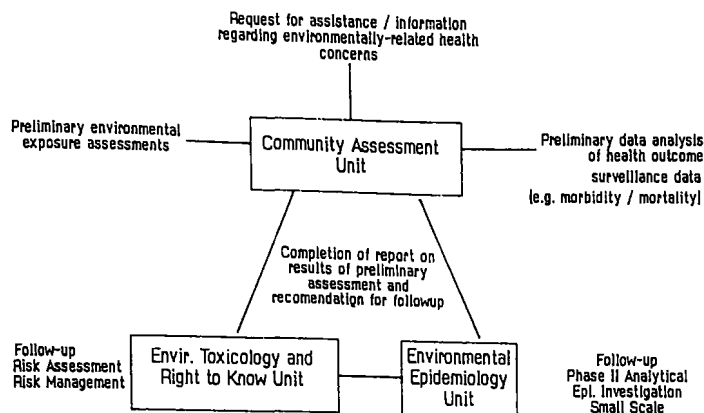
Figure 1
Division of Environmental Health Assessment
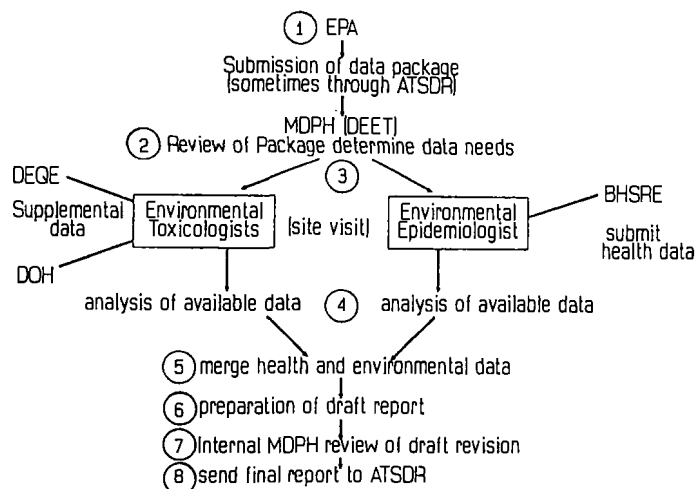
Figure 2
Department of Public Health Responsibilities

Step 2 involves the preliminary review of the data package to adequately determine additional data needs. At this point in the process (Step 3), the epidemiologists and toxicologists meet to determine individual supplemental data needs such as information available from the State Department of Environmental Protection and local water departments.

The toxicologists define health outcomes of interest and the epidemiologic research staff begin to collect appropriate health outcome data. As part of this step, the staff assigned to a site also perform a site visit. They are accompanied by ATSDR regional staff and the U.S. EPA Regional Project Manager (RPM) for the site as well as the local health officials and a citizen representative should there be a person so designated.

At this point, a public meeting with the community also is held to determine any special concerns that the residents may have. This is the final step in the information/data gathering process and the analysis of health and environmental data begins.

When the analyses have been completed, the staff once again meet to merge the health and environmental data and draft one report for

internal review and then submission to the ATSDR Technical Project Officer and the U.S. EPA and Massachusetts Department of Environmental Protection (DEP) officials. Soon after, a community meeting is scheduled to present an overview of the public health implications and to officially solicit comments.

We believe that this is the best possible approach we can take to provide a final document that is both scientifically sound and accepted by the affected community. The actual application of these methods at an NPL site in MA will be discussed here.

APPLICATION OF ASSESSMENT METHODS

The site of interest was the home of a chemical mixing company. The company began operating in the early 1900s and operated until 1982, during which time it produced formulations of disinfections, soap, floor wax and pesticides.

Basically, chemicals were mixed in large vats. Waste disposal consisted of direct discharge of wastewater into nearby wetlands and brooks, cesspools, sumps, and unlined lagoons. The company closed in the early 1980s when forced out of business by the local board of selectmen and was then placed on the U.S. EPA'S proposed NPL list.

Contaminant monitoring has been extensive at the site. A total of 102 chemicals have been detected on-site, including numerous pesticides (e.g., chlordane, DDT, dieldrin), the herbicides 2,4-D and 2,3,5-T, the dioxin 2,3,7,8-TCDD, arsenic, and creosote. Extensive contamination is present in the site's soils, groundwater, wetlands and sediments.

After initial review of the data was completed, a site visit was scheduled. The site visit included both an afternoon trip to the site and an evening community meeting. At the evening meeting, a great deal more was learned concerning the nature and extent of public contact with the site.

The site visit is an important phase of the expanded health assessment approach. It is here that we gain significant insight into the nature and extent of public contact with the site. What we learn about are the community concerns regarding pathways for exposure and potential health implications. In this example, the citizens were particularly concerned about drinking water quality.

We decided that it would be prudent to meet with representatives from the local water departments to learn more about several issues. Most important were where drinking water was distributed in the two affected communities and what part of the population was consuming it.

We learned that operation of a municipal wellfield resulted in the induced infiltration and capture of contaminated groundwater by the wells. The wells operated from 1958 until 1982 when closed because of contamination. As early as 1959, phenols were detected in one of the wells and strong evidence of 2,4-D also was documented. These wells were one of only three sources of drinking water for the two Massachusetts communities. A nearby river also was contaminated by the site. Water from the river was diverted to a reservoir which was used as a supplemental source of water for the towns. Several interim remedial measures have been conducted to contain the hazardous waste condition. At present, remediation is in the design and test stage.

The contaminants of interest and potential health outcomes of interest are presented in Table 1. Among the diseases caused by the contaminants that have been identified, the health outcomes of greatest interest included non-Hodgkins lymphoma (NHL) and soft tissue sarcoma (STS). It is important to stress that we have established, to the extent possible, that 2,4-D was highly likely to have been present in two particular municipal drinking water wells.

After establishing the likelihood of human exposure and the health outcomes of particular interest, the next phase of the expanded health assessment is initiated.

In this phase, we review existing health outcome data bases for information on the outcomes of interest. This is to establish if there is existing evidence for unusual occurrences of the health outcomes.

We reviewed the overall distribution and standardized incidence rates (SIR) for both diseases of concern in the two affected communities. The overall rates of NHL and STS are 22 observed and 13.4 expected with an SIR of 165 for NHL, and 3 observed and 2.7 expected with an SIR of 113 for soft-tissues sarcoma. As we look more closely at these

outcomes, NHL appears to suggest the strongest potential association.

The geographic distributions of NHL cases for the areas that were likely to have received the greatest amount of 2,4-D contaminated drinking water are presented in Figure 3. As can be seen, the majority of cases appear visually to be concentrated in census tracts 4211 and 4203. The incidence rates for NHL in these areas of greatest potential impact are 5/3.2 = 156 and 17/10.2 = 167, respectively.

What we have gathered here is some very interesting information that may suggest a potential association between historical, but fairly recent, environmental exposures and adverse health outcomes in these two communities. It is important to note that while the evidence that may link these two events is rather circumstantial, it does provide us with a more stable base for appropriate public health intervention and follow up actions.

CONCLUSION

Through the expanded health assessment approach, we believe that the communities feel the health assessments are more of a collaborative effort. We can then be responsive to community concerns that local government officials, for example, need to address on a daily basis.

It has been our experience that by using this approach we develop a document which best describes the environmental public health picture of communities affected by NPL sites. Perhaps more importantly, the document represents a document that is accepted by everyone concerned.

We feel that the expanded approach permits us to make more informed conclusions and recommendations regarding the mitigation or preven-

tion of adverse health outcomes from potential exposure to the site's contaminants.

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Table 1
Cancers Associated with Specific Contaminants

Contaminant	Cancer Type
2,4,5-T and 2,3,7,8-TCDD	soft tissue sarcoma * non-Hodgkins lymphoma ·* Hodgkin's disease
2,4-D	non-Hodgkins lymphoma * soft tissue sarcoma
benzene	acute myelogenous leukemia * other leukemias * Hodgkin's disease * non-Hodgkins lymphoma

* less evidence

** not necessarily proven casual relationship
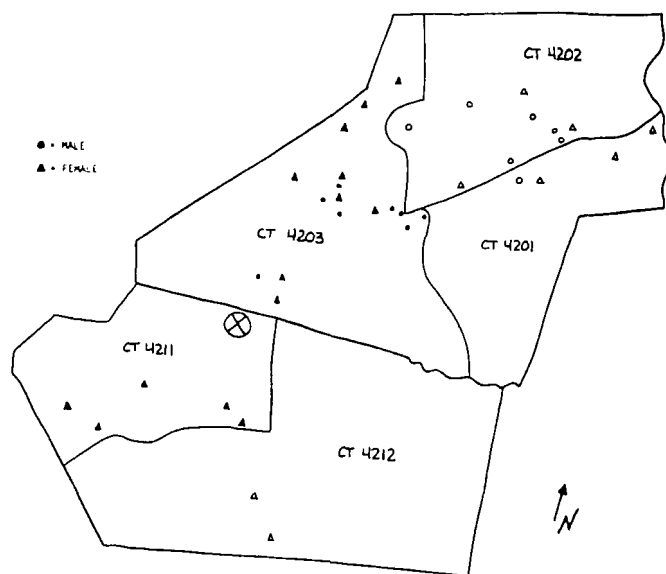
Figure 3
Non-Hodgkin's Lymphoma Incidence 1982-1986

Risk-Based Cleanup Levels For Soil

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ABSTRACT

Soils contaminated with barium, copper and lead were found as a result of a two-phased remedial investigation at a metal refinery in the southeastern United States. Contaminated soils were detected both on the site and off-site. Levels of contamination ranged from 10 - 25,000 mg/kg barium, from 10 - ~200,000 mg/kg copper and from < 10 - ~5,000 mg/kg lead. For most samples, high concentrations of both lead and barium were associated with high copper levels, although lead was detected less frequently than either of the other two metals. All three metals were found on the site primarily in their elemental, nonionic forms - relatively insoluble in water, even when acidified. EP Toxicity testing of these soils produced data containing less than 1% of the bulk concentrations of barium, copper and lead.

A background level of 100 mg/kg copper was established as an interim background goal for remediation purposes; however, cleanup to this level would have required removal of soils from the majority of the site and properties adjacent to the site and would have been extremely costly. As an alternative to cleaning up to background, a determination of a risk-based cleanup level was undertaken. This cleanup level was based on the concentration of copper that would be considered a human health problem.

A risk-based cleanup level was derived using the *Risk Assessment Guidance for Superfund*.[2] For copper, this cleanup level was found to be 1,850 mg/kg. However, since only minor amounts of this metal were considered bioavailable or absorbable (ionic), even this risk-based level was believed to be too restrictive and further refinement of the concentration was made. Using a conservative, literature-based bioavailable fraction of 0.1 (10%) for elemental copper, a risk-derived cleanup level of 18,500 mg/kg copper was developed. This level was ten times higher than the value developed using 100% bioavailability and was 200 times greater than assumed background levels, but still was considered protective of human health. With this revised risk-based cleanup level, the total volume requiring removal was reduced from 4,500 yd^3 to 1,000 yd^3 and the estimated cost of soil remediation was reduced by approximately $370,000.

Results from this study support the use of risk assessment as a mechanism for achieving a balance between the cost of remediation and the potential or actual risks present at a particular site.

INTRODUCTION

Risk assessment is a scientific tool used in many areas of environmental investigation. Risk assessment is used to characterize the probability of harm to public health, public welfare and the environment from potential or actual releases of hazardous substances. Risk assessment generally consists of four steps:

- Hazard Identification   Identification of indicator substances or chemicals
- Exposure Assessment - Identification of actual or potential routes of exposure, characterization of exposed populations including environmental populations and estimation of exposure levels or doses
- Toxicity Assessment - Determination of the nature and extent of potential effects from exposure to hazardous substances
- Risk Characterization - Determination of the probability or likelihood of adverse affects on human health, welfare and the environment

The process of completing a risk assessment involves the use of technical and scientific data applied using informed professional judgment. In many situations, a risk assessment must be completed when adequate scientific data are lacking. Appropriate, scientifically valid assumptions must then be made to evaluate a particular risk scenario. Choice of appropriate assumptions, such as the amount of soil ingested per day, weight of an individual or percent absorption of a particular substance, can lead to wide variations in the final risk ranges developed during the risk assessment.

The importance of understanding the assumptions used in risk assessment and the influence that these assumptions have on the final risk levels is supported by the following case study of a state Superfund site. The site, a metal refining facility, is located in the southeastern United States. Soils and sediments on and surrounding the site are contaminated with copper, barium and lead. Two manuals, *Superfund Exposure Assessment Guidance*[1] and *Superfund Risk Assessment Guidance for Human Health Evaluation*[2] were used to complete a risk assessment for soil primarily contaminated with copper. This risk assessment was used to develop risk-based cleanup levels which were considered site specific. These cleanup levels were then used to derive the areas of the site and calculate volumes of soil/sediment possibly requiring remediation.

METHODOLOGY

Soil Investigation

A total of 201 surface soil samples were collected at the site (Fig. 1). Additionally, 24 composite soil samples, representative of conditions 0.5 to 1.5 feet below ground surface, were collected across the site. Each soil sample was analyzed for barium, copper and lead. Two off-site locations were collected to establish background soil quality conditions. Background level for copper in the soils appeared to be approximately 100 mg/kg. Copper was used as an indicator metal because elevated barium or lead levels (above background levels) were normally associated with levels of copper which were an order of magnitude higher than either the barium or lead. Additionally, due to
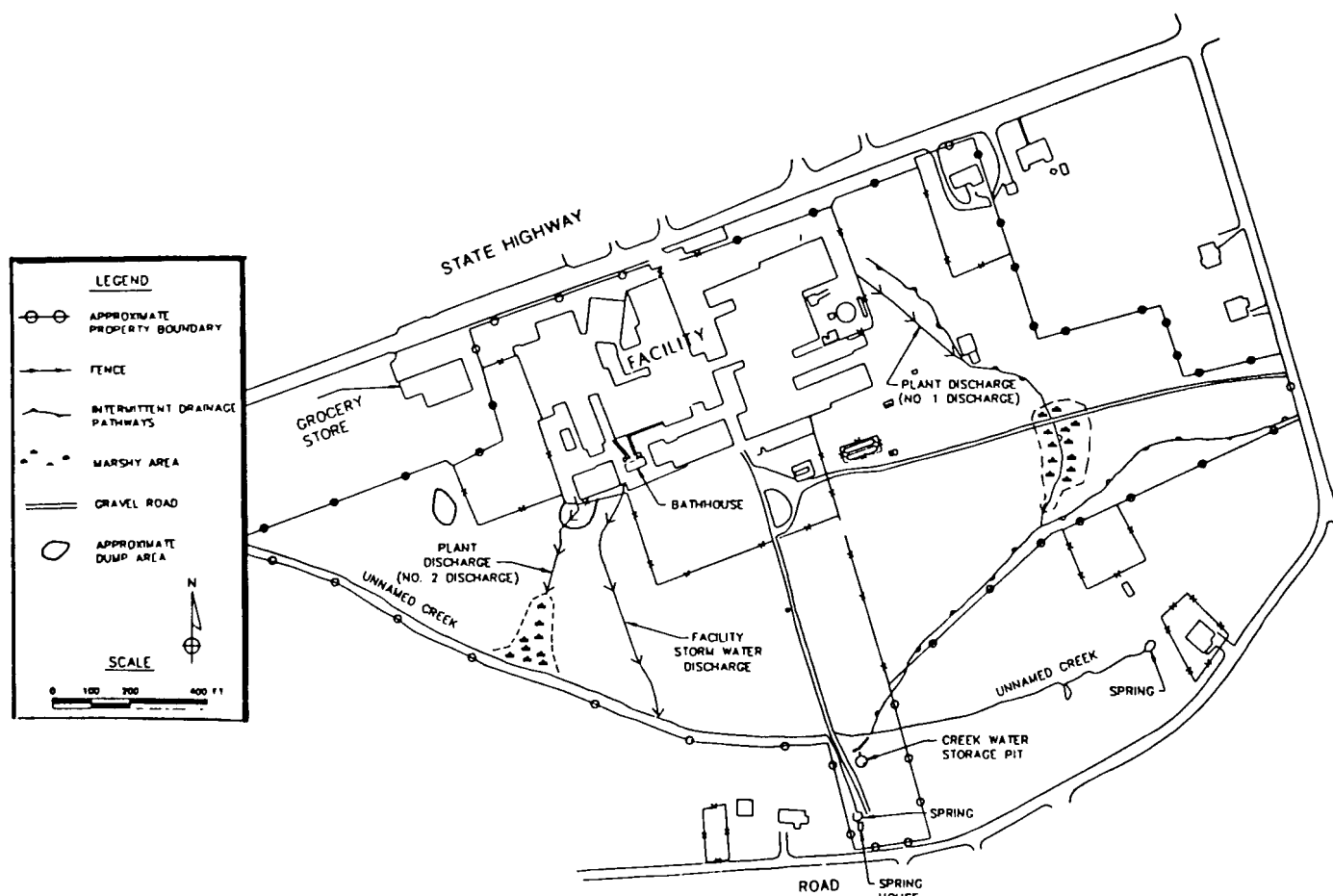
Figure 1
Site Location Map Displaying
Present Plant Discharge

its widespread presence on the site, it appeared that copper would drive the remedial effort.

An isoconcentration contour map for copper in on-site soils is shown in Figure 2 and is representative of soil conditions from 0 to 0.5 feet below ground surface. Barium and lead levels across the site were found generally at concentrations at less than 100 mg/kg, similar to background levels. At the locations where barium and lead levels exceeded background, copper levels of similar or higher magnitude also were encountered. Figure 2 reveals two areas labeled Areas A and B which are defined by the 1000 mg/kg isoconcentration contour line and two other areas labeled C and D which are defined by the 100 mg/kg isoconcentration line. Within Areas A and B, copper levels generally ranged between 2000 and 3000 mg/kg and five smaller areas within Area A display copper levels greater than 10,000 mg/kg. Only one sample within Area B exhibited a copper level greater than 10,000 mg/kg. Except for five sample locations which lie outside these areas, all other on-site areas displayed copper levels below 500 mg/kg. The background level for copper, 100 mg/kg as defined by the two background samples, was exceeded at a majority of the sample locations. Within Areas C and D, however, all copper levels were equivalent to or below background.

Although a few off-site samples displayed copper levels above background, all the levels were within 100 mg/kg of background and all were within 200 feet of the facility's southern property boundary. Off-site samples collected farther from these locations were equivalent to or below background for copper. Composite soil samples collected from across the site from soils at 0.5 to 1.5 feet below ground surface all had substantially lower copper levels than the levels found in surface soil samples. Based on the composite sample results, it appeared that the elevated copper levels were restricted to a depth of no more than

0.5 feet below ground surface.

Development of Cleanup Levels

Quality criteria, target concentrations or cleanup levels have not been established by the U.S. EPA or the state in question for copper in soils. In the absence of these criteria, we developed risk assessment-based quality criteria levels for copper. These preliminary quality criteria were based on exposure scenarios obtained from the U.S. EPA *Superfund Exposure Assessment Manual*[1] and oral reference doses (RFD$_o$) from the U.S. EPA *Superfund Public Health Evaluation Manual*[3] and the *Integrated Risk Information System*[4] Only oral ingestion was addressed directly using the following assumptions and exposure scenarios:

- Soil is 100% contaminated at the analyzed levels
- The copper is in a nonelemental, water-soluble form
- 100% absorption of the metal by the gastrointestinal tract

Target soil concentrations were calculated using three exposure scenarios with varying amounts of soil ingested and human weight corresponding to age and years. Target soil concentration for copper was calculated corresponding to an intake level equal to the oral RFD. Depending on a particular exposure scenario, the target soil concentration ranged from 1,850 to 259,000 mg/kg (Table 1). These initial assessment efforts assumed that copper was in an ionic form and that the human gastrointestinal tract (GI) will absorb 100 percent of the ingested copper. However, the copper found at the site was in its elemental form. An intensive literature review suggested that a significantly lower percentage (10 percent) of elemental copper would be absorbed by the GI tract as compared to the 100 percent assumed for ionic copper.[3]
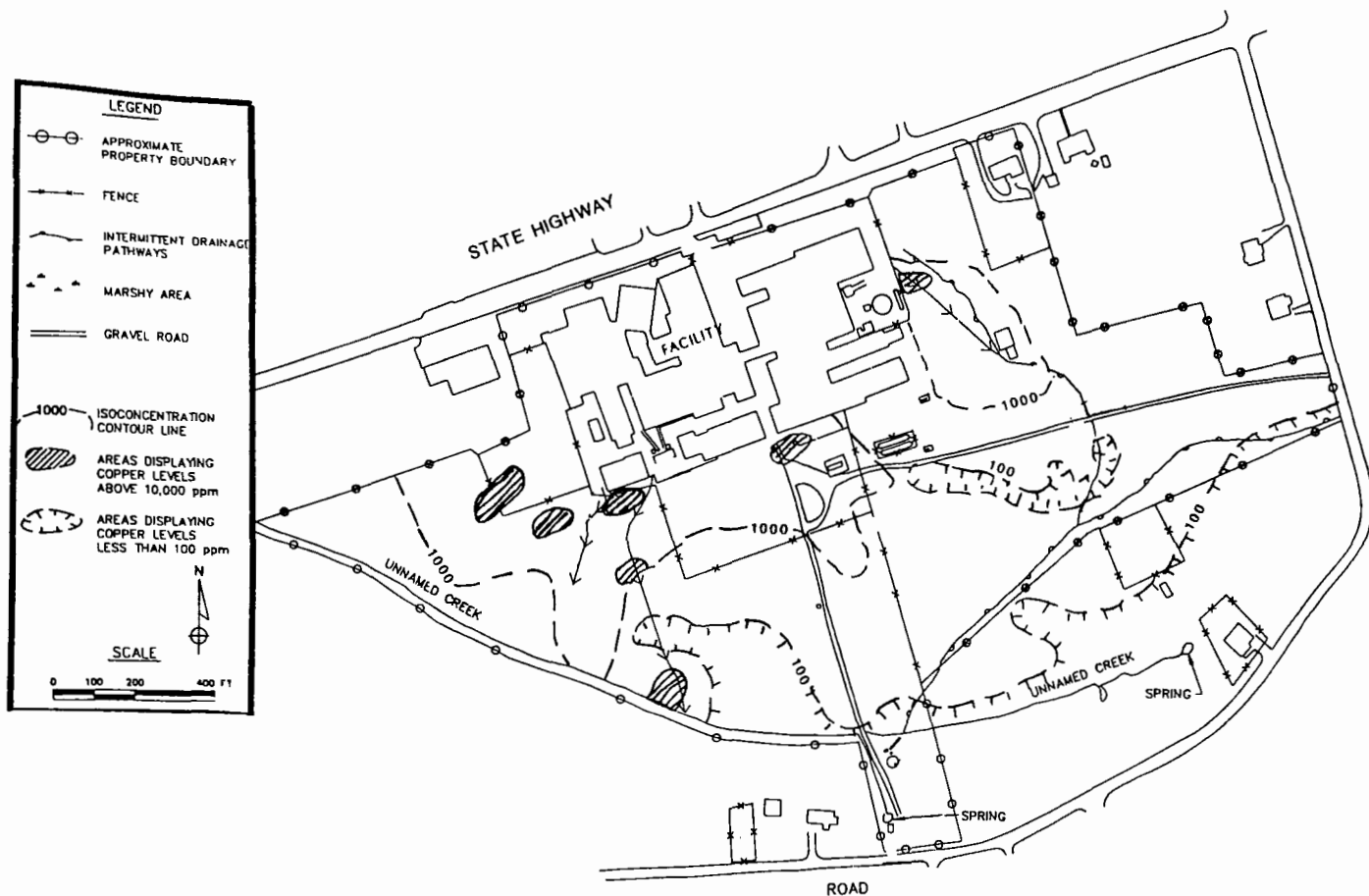
Figure 2
Isoconcentration Contour Map for
Copper in On-site Soils

Table 1
Development of Soil Cleanup Levels for Copper

Exposure Scenario	Amount Soil Ingested (mg/d)	Weight (Kg)	Age (Yr)	Absorption Factor	Maximum Daily Dose (mg/kg/d [c])	Cleanup Soil Level (mg/kg)
A	200	10	1.5-3.5	1.0	2×10^{-5} [c]	1,850
B	10	17	5	1.0	5.9×10^{-7} [c]	62,900
C	10	70	18+	1.0	1.4×10^{-7} [c]	259,000
D	200	10	1.5-3.5	0.1	2×10^{-6} [c]	18,500

Maximum daily dose is the amount of contaminated soil [c] in mg/kg that may be ingested on a daily basis without exceeding the RfD (acceptable intake for chronic exposure, AIC).

Copper as an Essential Element

Copper is considered an essential trace element in plant and animal metabolism at low levels.[5] It is involved in oxidative enzyme systems, such as ascorbate oxidase, amine oxidase, tyrosinase and cytochrome C oxidase, as an integral part of an enzyme or cofactor.[5,6] Some mollusks and arthropods use a copper-protein pigment, hemocyanin, to transport oxygen to tissues in plasma.[7] Plant chloroplasts contain a blue copper-protein, plastocyanin,[6] that functions as an integral enzyme in photophosphorylation.[8] Copper deficiencies are considered rare in plants and result in chlorosis (bleaching) and reduction in

carotenoid pigments.

The recommended daily allowance (RDA) for the adult diet ranges from 2.0 to 3.0 mg/day.[9] The RDA varies from 0.5 to 2.5 mg/day for children under the age of 11 years. Despite wide differences in dietary intake of Cu, proper Cu balance is maintained in most individuals.[10]

Copper Absorption

Bioavailability or uptake potential of metals is a function of particle size and volume, membrane solubility and complexation state.[11] Copper, as well as other mineral nutrients, usually is absorbed in the

ionic form by plants and animals.[7] The biologically active form of Cu is ionic, the Cu^{2+} valence state. Copper is commonly found in human foods; the concentration of copper in food normally reflects the copper levels of the soil or water in which the copper originated.[12] The amount of Cu absorbed from the diet is a function of body needs.[12] Cu is primarily absorbed in the stomach due to low pH and in the upper portions of the small intestine via active transport.[5,13,14]

Estimated levels of ionic Cu absorption from dietary intake range from <1 percent[5] to 36 percent.[14,15] However, based upon Underwood[12] and Vanderveen,[16] 10 percent is considered the upper boundary for the absorption of elemental Cu in the diet.

Development of Cleanup Levels for Elemental Copper

Using a maximum of 10 percent absorption of elemental copper in the human GI tract, a health-based risk level of 18,500 mg Cu/kg was developed (Table 1). This level is considered protective of human health for the conditions found at the site (i.e., presence of elemental copper). The development of this level utilized oral exposure scenarios obtained from the U.S. EPA Superfund Exposure Assessment Manual[1] and Acceptable Chronic Intake Level (AIC) of 3.7×10^{-2} mg/kg/d from the U.S. EPA.[3] This AIC corresponds closely to the U.S. Department of Agriculture (USDA) recommended daily allowance (RDA) of 2.9×10^{-2} mg/kg/d and the level of 4.3×10^{-2} mg/kg/d found in several over-the-counter dietary supplements (e.g., Parke-Davis). AIC values have been replaced in current U.S. EPA guidance[1] by RFDs. IRIS[4] currently does not list an oral RFD for copper; however, at the time this work was completed, the value found in the U.S. EPA's Superfund Public Health Evaluation Manual[3] was considered valid.

DISCUSSION

The assumption used to develop risk-based cleanup levels or target levels which ultimately will be used for remedial decisions need to be reasonable and scientifically justified. Assumption of 100% absorption of elemental copper is considered unrealistic. According to Risk Assessment Guidance for Superfund,[1] exposure levels may be adjusted for differences in media since the affects levels (RFD) are based on intake through water. The intake may be adjusted accordingly based on the bioavailability or absorption of the compound or element from the environmental matrix in question. Low bioavailability of elemental copper in soils at this site is further supported by the results of the Extraction Procedure (EP) toxicity test performed during the overall site investigation where less than 1 percent of the Cu leached from the soils tested. The extraction associated with the EP toxicity test is performed with an acid that has a similar pH to the acid found in the human stomach.

Table 2 describes the areas, volumes and cost of disposal for the soil for each of the derived target levels. Using a conservative literature-based bioavailable fraction of 10% for elemental copper, a risk-derived cleanup level of 18,500 mg/kg was developed. This level was 10 times higher than the target level developed using 100% bioavailability and was approximately 200 times greater than the assumed background levels. However, this level was still considered protective of human health based on the elemental nature of copper found on the site. Using this revised risk-based cleanup level, the total volume of contaminated soil requiring removal was reduced from 4,500 yd³ to 1,000 yd³, and the estimated cost of soil remediation was reduced by $370,000.

Table 2
Cost Analysis for Soil Remediation

Approach	To Copper Level (mg/kg)	Volume (cubic yards)	Costs ($)
Excavation and Off-Site Disposal	100 or less	15,500	2,100,000
Excavation and Off-Site Disposal	2,000 or less	4,500	475,000
Excavation and Off-Site Disposal	20,000 or less	1,000	105,000

CONCLUSIONS

Results from this study support the use of risk assessment as a mechanism for achieving a balance between the cost of remediation and the potential or actual risks present at a particular site. The utilization of realistic and scientifically valid assumptions produces realistic cleanup levels which can potentially reduce remediation costs and at the same time reduce the environmental disturbance during remediation.

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Bayesian Data Analysis Procedure for Contaminant Transport Studies

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ABSTRACT

This paper describes a Bayesian data analysis procedure for groundwater contaminant transport studies at Superfund sites. The Bayesian procedure starts with a prior probability distribution of a model parameter as determined from literature search, expert judgement or previous applications of the Bayesian procedure. Next, the procedure uses the data collected during the Remedial Investigation to boost those parts of the prior distribution that are consistent with the data and suppress those that are not. The result is a posterior probability distribution that can be used in a statistical simulation, such as the Monte Carlo method, to assess the likelihood and the magnitude of future contamination. The potential applications of the Bayesian data analysis procedure are demonstrated in four examples in this paper.

UNCERTAINTIES IN GROUNDWATER CONTAMINANT TRANSPORT STUDIES

Uncertainty permeates every aspect of groundwater contaminant transport studies for Superfund sites: (1) the transport mechanisms are poorly understood at most sites, (2) the timing, intensity and location of past spills or leakage are rarely known, (3) and a reliable inventory of the hazardous materials contained within a particular site seldom exists. Recognizing these uncertainties, the current U.S. EPA guideline for exposure assessment[1] allows the use of either site-specific measured or modelled contaminant concentration values. When using contaminant transport models, the U.S. EPA guideline encourages model calibration using monitoring well data; but there is no guideline on how close the model should be calibrated to match the data. When using measured values, the guideline further allows the risk assessor to assume that the measured concentration remains constant over the period concerned (currently 75 years for carcinogenic effects). Considering all the potential uncertainties in an exposure assessment, the methods in the U.S. EPA guideline may appear conservative, but do they always produce conservative results?

The potential discrepancy between the assessed exposure using measured data following the U.S. EPA guideline and the actual exposure may be illustrated by the two hypothetical examples shown in Figure 1. This figure shows a hypothetical site containing a series of injection wells in active use over a 15-year period from 1970 to 1985. The contaminant concentration in the groundwater was monitored by three monitoring wells adjacent to an exposure point A (Fig. 1). By assuming that the series of injection wells can be replaced by an equivalent line source and that groundwater flows in a direction perpendicular to the line defined by the injection wells, a simple two-dimensional model was adopted for the contaminant transport study.[2] The difference between the two hypothetical examples lies in the seepage velocity used in the calculation.
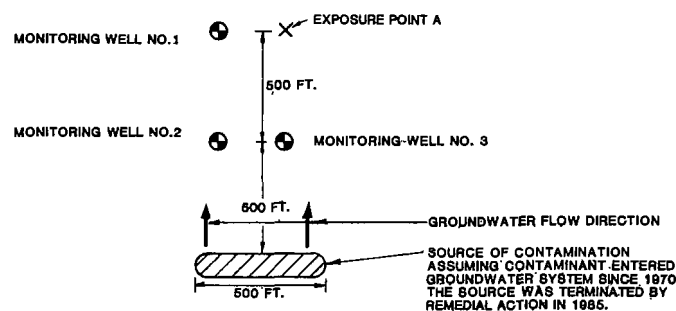
CASES	DETECTED CHEMICAL CONCENTRATION(PPB)					
	WELL No. 1		WELL No. 2		WELL No. 3	
	1985	1990	1985	1990	1985	1990
EXAMPLE 1	100	NA	68	NA	79	NA
EXAMPLE 2	27	NA	98	NA	82	NA
EXAMPLE 3	100	100	68	109	79	102

NA: NOT ANALYZED

CASES	HYDROGEOLOGICAL PARAMETERS		
	SEEPAGE VELOCITY (FT/DAY)	LONGITUDINAL DISPERSIVITY (FT)	SOURCE CONCENTRATION (PPB)
EXAMPLE 1	0.5	5	110
EXAMPLE 2	0.1	1	230
EXAMPLE 3	0.5	5	110

Figure 1
Hypothetical Site

The first example used a relatively fast seepage velocity of 0.5 ft/day. Using this velocity value, the calculated contaminant concentration at the exposure point is shown in the Case 1 curve in Figure 2. The area under this curve corresponds to the exposure concentration (defined as the total concentration available for intake at the exposure point) for a 75-year period from 1990. This is much less than the exposure concentration calculated by multiplying the measured concentration in the last sampling event over 75 years in accordance with the U.S. EPA guideline. In other words, the U.S. EPA guideline could overestimate the exposure concentration in this example.

This is not so, however, with the second example where a slow seepage velocity of 0.1 ft/day was used. As is also shown in Figure 2, the U.S. EPA guideline, when based on measurements made while the contaminant concentration at the monitoring wells is still rising, could underestimate the exposure concentration. Is there, then, a procedure that copes better with the uncertainties than those in the U.S. EPA guideline?
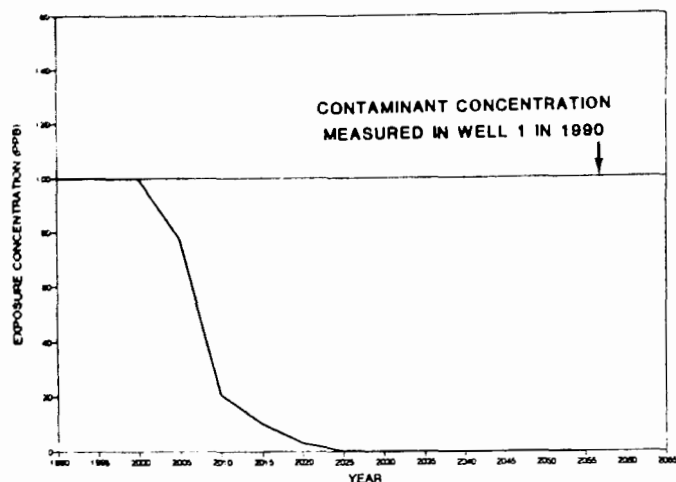
CASE 1: SEEPAGE VELOCITY 0.5 FT/DAY
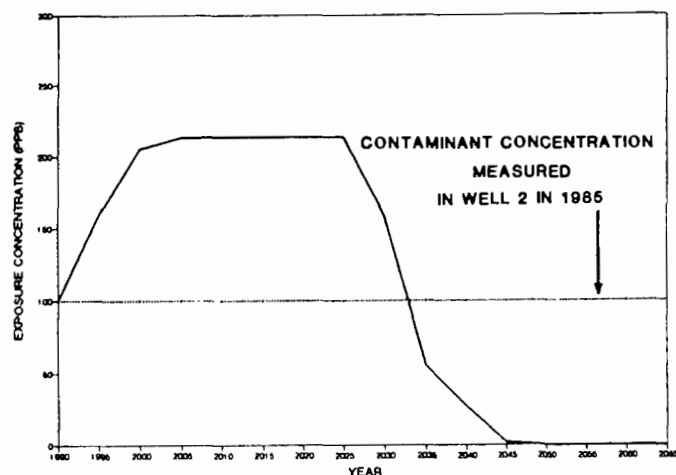
CASE 2: SEEPAGE VELOCITY 0.1 FT/DAY

Figure 2
Theoretical Exposure Concentration

QUANTIFYING UNCERTAINTY

The problem discussed above is not unique to contaminant transport studies. Many other closer-to-life problems also face uncertainty and involve risk. Some examples are the seismic risk of nuclear power plants[3] and the risk of failure of large dams.[4] Whether an elaborate model is used or not, a common need among these problems is to quantify the uncertainty of the outcome—in the present case, the exposure concentration. Contrary to the traditional attitude toward risk, which aims at the rarely attainable goal of eliminating the uncertainty, the main thrust of the modern approach in risk assessment is to first recognize the uncertainty and then make an attempt to quantify it. In the examples above, a risk assessor would be making strides in recognizing that the U.S. EPA guideline does not always produce conservative results.

A common way to quantify uncertainty is to use statistical simulation techniques such as the Monte Carlo method[5,6,7] or the discrete simulation method.[8,9] Before running a statistical simulation, however, the uncertainty in the models and parameters used in the simulation must first be quantified. Quantifying the uncertainty or-in more practical terms—assigning the probability distribution of the model parameters has traditionally been achieved using one of two approaches: using prior knowledge or taking measurements. Both approaches may be used in contaminant transport studies. For example, the likelihood of a contaminant originating from a source may be assessed using records of past operations as a clue. For another example, the seepage velocity may be determined from actual measurement of water level

and permeability. These two approaches should complement each other; the question is how. The Bayesian method, to be discussed in the following sections, may provide the answer.

BAYES' THEOREM AND ITS APPLICATIONS

While widely quoted in the literature of Bayesian Statistics,[10] there does not appear to be a single, universally-accepted form of Bayes' theorem. It appeared that the English mathematician, for whom the theorem is named, never actually wrote the theorem but instead expressed in words what is now known as Bayes' rule in conditional probability. Grandy[11] pointed out that Laplace, in 1714, appeared to be the first to formulate the equation that constitutes Bayes' theorem as it is known to the statisticians today; although the equation can be derived by generalizing Bayes' rule.

In spite of its ambiguous origin, all forms of Bayes' theorem deal with the following quantities:

- A prior probability
- A measurement whose outcome relates to, but may not reveal the parameter value of interest
- A likelihood
- A posterior probability

The likelihood is the (conditional) probability of observing the outcome of the measurement given the prior probability and the posterior probability is the probability that incorporates the outcome of the measurement in the prior probability. Given these four quantities, Bayes' theorem states, in essence, that the posterior probability is proportional to the product of the prior probability and the likelihood. In effect, the theorem boosts those values that are more likely to produce the observed outcome and suppresses those values that are not.

Bayes' theorem has been used in many scientific and engineering fields. Some examples are Radio Astronomy,[12] Geotechnical Engineering,[13,14,15] Hydrology[16] and Reservoir Engineering.[17] Diverse as these applications may appear, few of them can be applied to contaminant transport studies where the measurements (such as contaminant concentration measured in the monitoring wells) do not directly reveal the value of the unknown parameters (such as the location, timing and concentration of past releases). The method described in this paper was developed for this class of problems.

THE BAYESIAN DATA ANALYSIS PROCEDURE

The details of the Bayesian data analysis procedure have been published elsewhere.[18] Appendix A in this paper presents the calculation sequence of the data analysis procedure. For simple problems, the calculation can be conducted by hand following the sequence. For complicated problems, however, a computer will be needed to cope with the amount of computation involved. The calculation sequence depicted in Appendix A had been implemented in a computer program that can run on the IBM-PC microcomputer. This program was used to calculate the four examples presented below.

EXAMPLES IN CONTAMINANT TRANSPORT STUDIES

Four examples are used in this section to illustrate the potential application of the Bayesian data analysis procedure. First, the two examples discussed at the beginning of this paper are reanalyzed to demonstrate how the proposed data analysis procedure can improve the estimates of exposure concentration. These two examples are then followed by a third, hypothetical example that demonstrates how the procedure can be used to assist in decision-making during Remedial Investigation. The fourth example used data from a Superfund site to demonstrate the feasibility of applying the Bayesian procedure to practical problems.

All the examples presented below were calculated using a simple two-dimensional contaminant transport model with a published analytical solution.[2] The contaminant concentration in the monitoring wells in the hypothetical sites was first calculated from the analytical solution. Then, to provide a touch of reality, the calculated value was tainted with a random error of up to 20%. The contaminant concentrations so obtained are shown in the tables in Figure 1; these values were used

to calibrate the input parameters in the first three examples discussed below.

Example 1

The first example corresponds to the first case in the hypothetical site shown on Figure 1. In applying the Bayesian procedure to this case, it was assumed that the location, concentration and timing of the releases are known, as is the direction of seepage flow. The two remaining parameters required for contaminant transport modelling are the seepage velocity and the longitudinal dispersivity. The prior probability distributions of these two parameters are shown in Figure 3. The prior probability distributions and the contaminant concentrations in the monitoring wells were then combined by the Bayesian procedure to produce the posterior probability distributions shown on the same figure. The values of the seepage velocity and the longitudinal dispersivity that were used to make up this hypothetical example also are indicated in Figure 3. As this figure shows, the posterior probability distributions did indeed converge to the "correct" values.
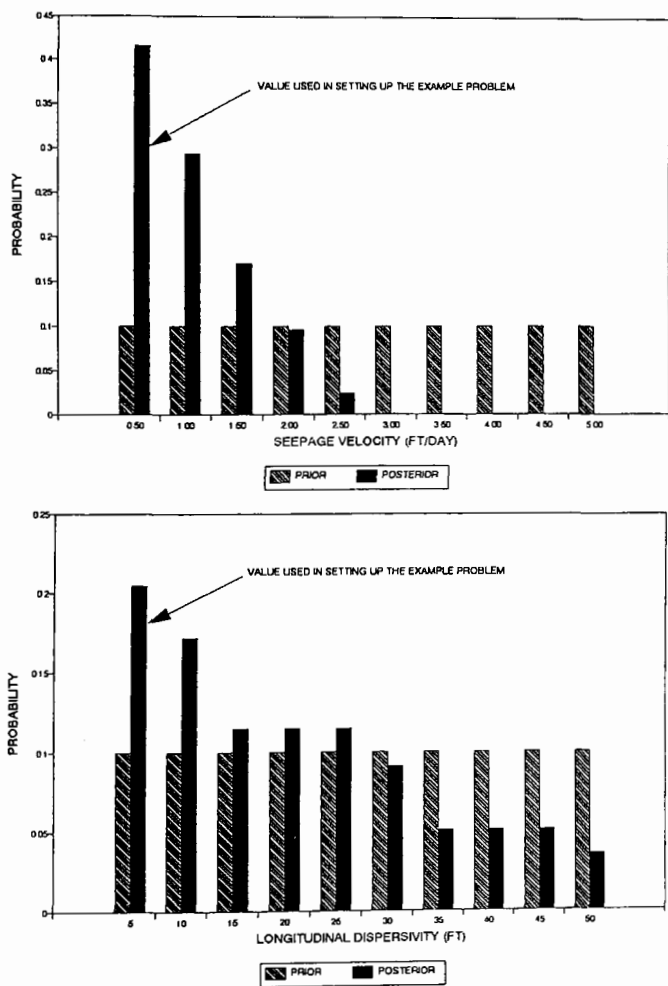
Figure 3
Prior and Posterior Probability Distributions, Example 1

Figure 4 shows the probability distribution of the exposure concentration calculated from the posterior probability distributions of the seepage velocity and the longitudinal dispersivity. For comparison, the exposure concentration calculated by the method in the U.S. EPA guideline and the theoretical concentration (given the input values) also are indicated in this figure. In this example, it is seen that while the U.S. EPA guideline grossly overestimated the exposure concentration, the most probable exposure concentration calculated by the Bayesian procedure almost coincides with the theoretical value.
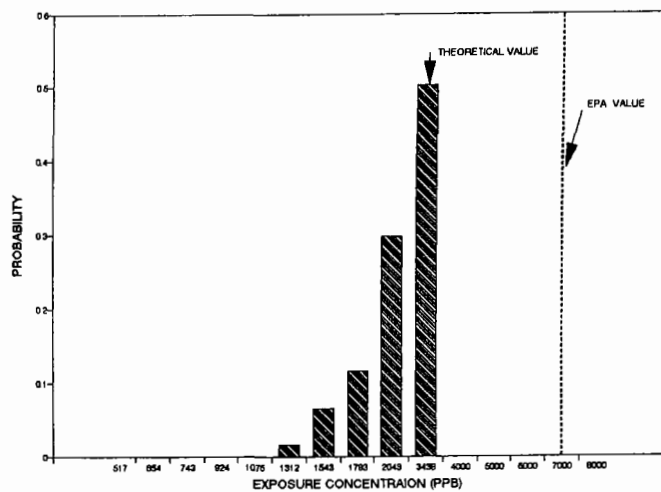
Figure 4
Probability Distribution of Exposure Concentration, Example 1

Example 2

This example corresponds to the second case in the hypothetical site shown on Figure 1. Going through the same steps as in the first example, Figure 5 shows the prior and posterior probability distributions of the seepage velocity and the longitudinal dispersivity and Figure 6 shows the probability distribution of the exposure concentration calculated from the posterior probability distributions. As in Figure 4, Figure 6 also shows the exposure concentration calculated by the method in the U.S. EPA guideline and the theoretical exposure given the input values. In this case, the Bayesian procedure has largely corrected the deficiency in the U.S. EPA guideline that resulted in underestimating the exposure concentration.

In Figures 4 and 6, it is seen that the Bayesian method would, in both cases, result in a more realistic assessment of the potential exposure than the method in the U.S. EPA guideline that uses the measured concentration. This is not the only benefit that the Bayesian procedure brings, as the ability to generate the probability distribution of the exposure concentration could lead to applications that were not possible before. One such application is to assist in decision-making in Remedial Investigation, as will be demonstrated in the example below.

Example 3

This example follows on the first example with the addition of one more round of sampling. The question to be asked is whether further rounds of sampling are warranted and, if so, how does the risk assessor or the remedial project manager decide when enough samples have been collected for the Feasibility Study?

To answer this question, the prior probability distributions of the seepage velocity and the longitudinal dispersivity are duplicated from Figure 3 to Figures 7 and 8, respectively. These figures also show the posterior probability distributions of these two parameters after incorporating the results of the first and the second rounds of sampling. If this were an actual site, then the risk assessor or the remedial project manager would examine the posterior probability distributions after each round of sampling. In examining the distributions, they would look for two possible outcomes. One, the residual uncertainty (as reflected by the spread of the distribution) has been narrowed to within acceptable limits. Two, the most recent sampling results produce little change in the posterior probability distributions, indicating that the sampling activity may be approaching the point of diminishing return. Either of these outcomes may signal the end of the current sampling activity. Alternatively, the risk assessor or the remedial project manager may examine the probability distributions of the exposure concentration (Fig. 9) and continue, terminate or modify field work as this probability distribution evolves through successive rounds of sampling.
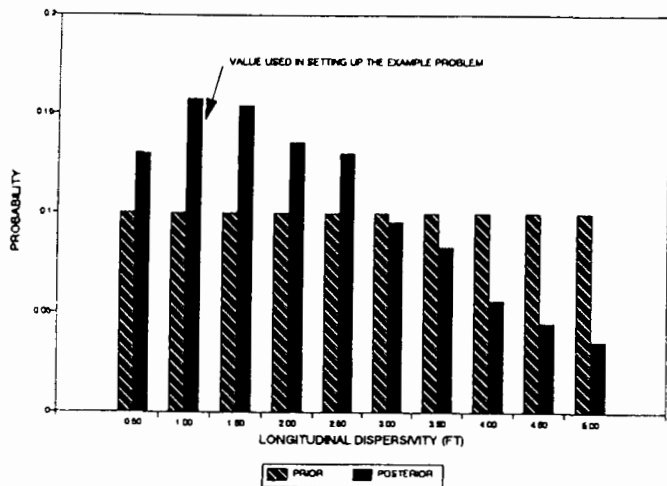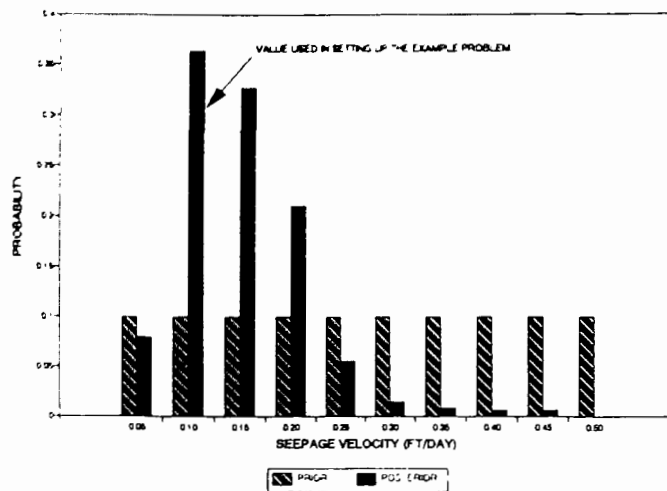
Figure 5
Prior and Posterior Probability Distributions, Example 2
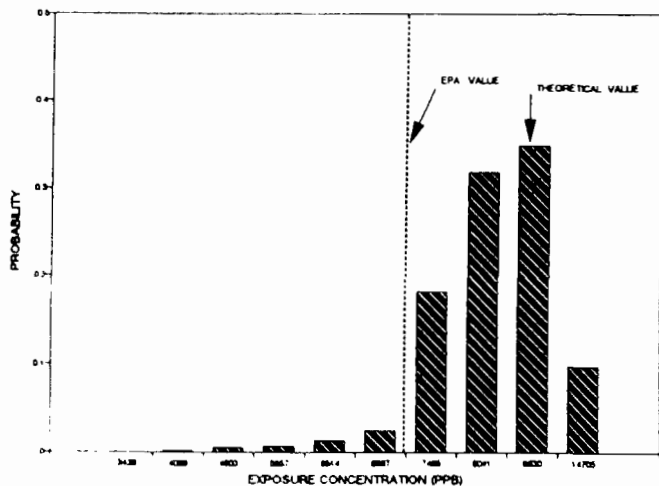
Figure 6
Probability Distribution of Exposure Concentration, Example 2

Example 4

All of the first three examples presented above have been concerned with a hypothetical, over-simplified site. In practice, real sites always contain a large number of uncertainties and the samples may not always exhibit a consistent pattern. The intention of this fourth example is to demonstrate that the Bayesian data analysis procedure applies equally as well to a real site as it does to a hypothetical site.
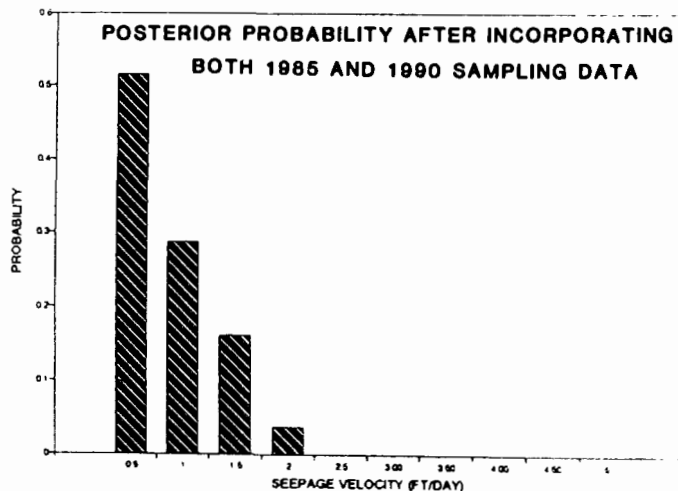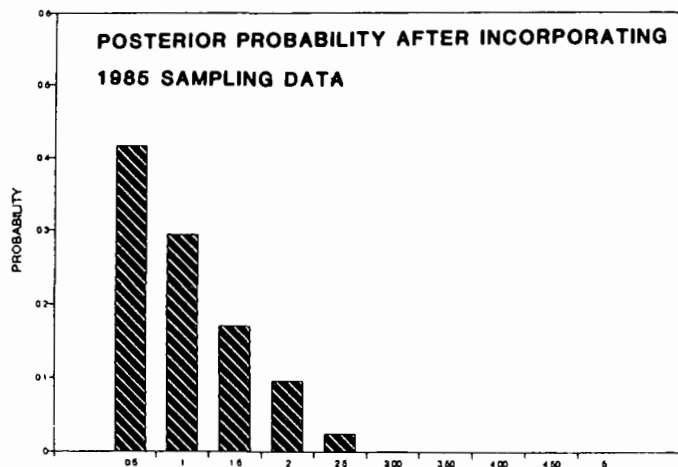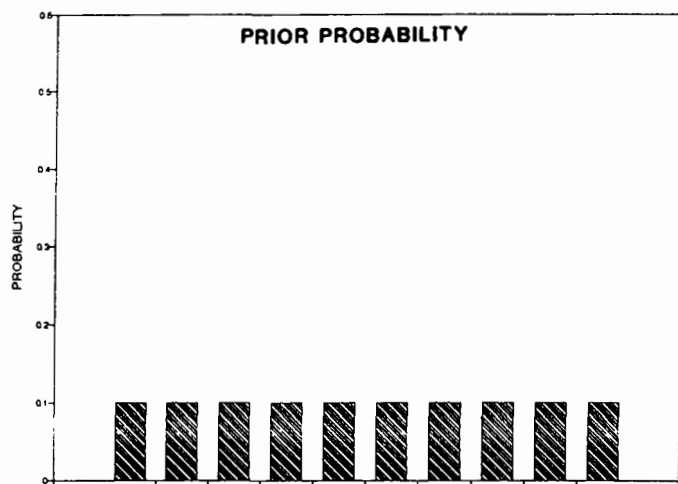
Figure 7
Prior and Posterior Probability Distributions
of Seepage Velocity, Example 3
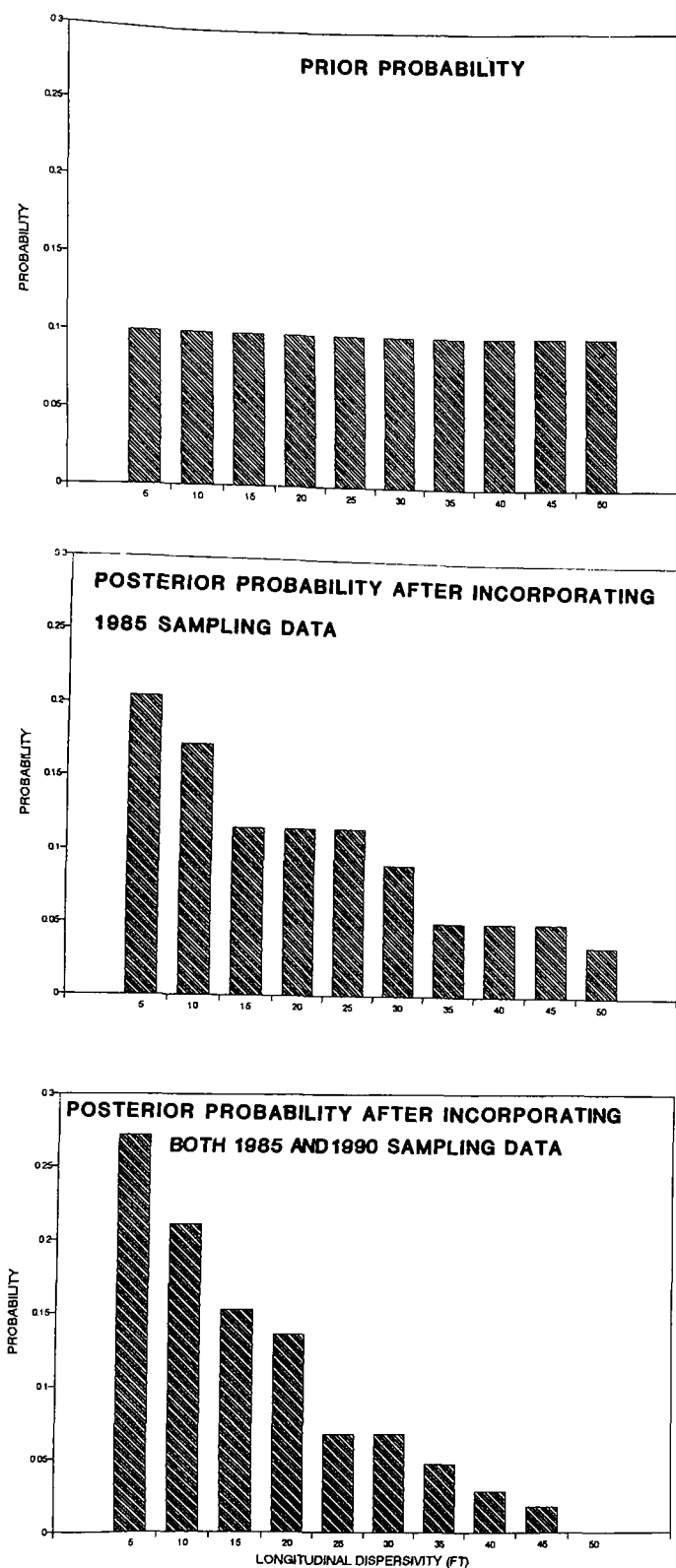
Figure 8
Prior and Posterior Probability Distributions
of Seepage Velocity, Example 3

over a period of ten years or so when the landfill was in active operation, then the major uncertain parameters required for contaminant transport study are: seepage velocity, longitudinal dispersivity and concentration at release. Note that the Bayesian procedure can also be used to evaluate the probability of the closed landfill being the source; however, such discussion is beyond the scope of the present paper and will not be further considered.
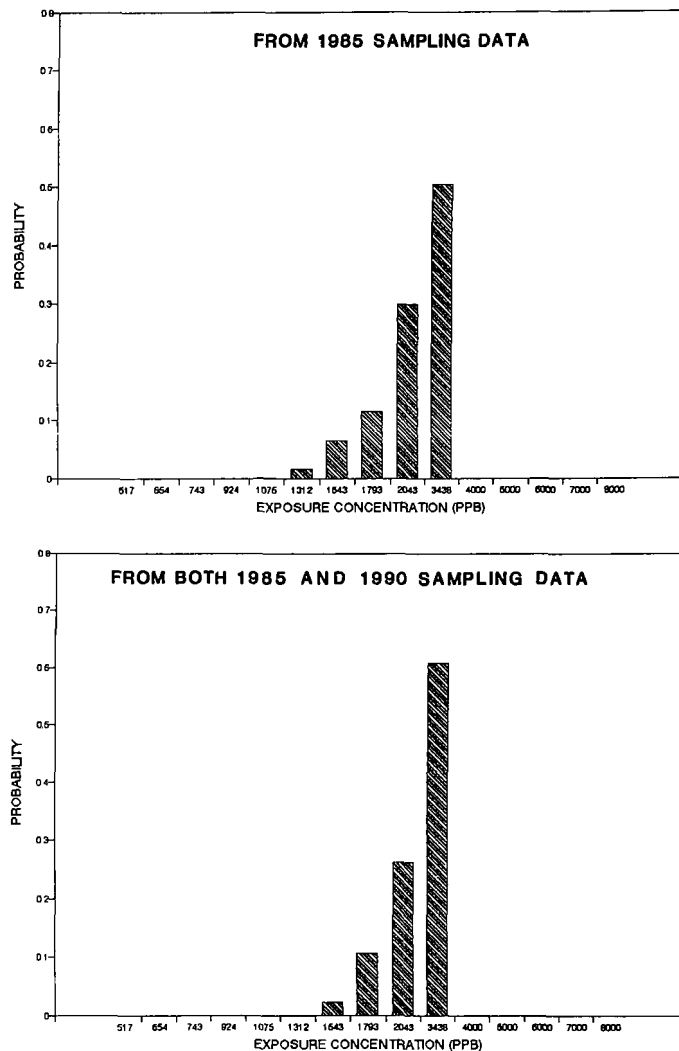
Figure 9
Probability Distributions of Exposure Concentration, Example 3

The example concerns a closed landfill (Fig. 10) that was operated in the late 1960s and early 1970s. For demonstration purposes based on a review of the site history, the site hydrogeology and a chemical fingerprinting study, it is assumed that the closed landfill contributed the barium detected in the downgradient monitoring wells. Assuming that the release of barium from the landfill, had it occurred, took place

Figure 11 shows the prior probability distributions of the release concentration, the longitudinal dispersivity and the seepage velocity. The posterior probability distributions, after incorporating the results collected in eight monitoring wells, are shown on the same figure. Figure 12 shows the probability distribution of the exposure concentration (calculated over a 75 year period from 1990 to 2065) at exposure point A (Fig. 10). For comparison, this figure also shows the exposure concentration calculated by the method in the U.S. EPA guideline based on the results of the most recent sampling event. Note that, for this real case, the application of the Bayesian procedure has produced a most probable exposure concentration that is less than one half of that estimated by the U.S. EPA guideline.

It is seen in Figure 11 that all prior probabilities were assumed to follow a uniform distribution. This assumption reflects the analyst's limited site knowledge. In practice, the risk assessor, armed with a thorough knowledge of the site, is likely to develop more realistic prior

probability distributions than the simple uniform distribution used here. This calculational process would result in more focused posterior distributions than those shown in Figure 11 and would further improve the estimate of the exposure concentration.

CONCLUSIONS

A Bayesian data analysis procedure has been developed for contaminant transport studies. This procedure offers a rational method for combining the "soft" data (personal experience, interviews and literature search) and the "hard" data (sampling and field tests). The potential applications of the Bayesian procedure are demonstrated in four examples. These examples show that the Bayesian procedure produces better estimates of exposure concentration than the existing U.S. EPA guideline. This procedure will provide probabilistic contaminant transport studies for public health assessment in Superfund sites.

ACKNOWLEDGEMENT
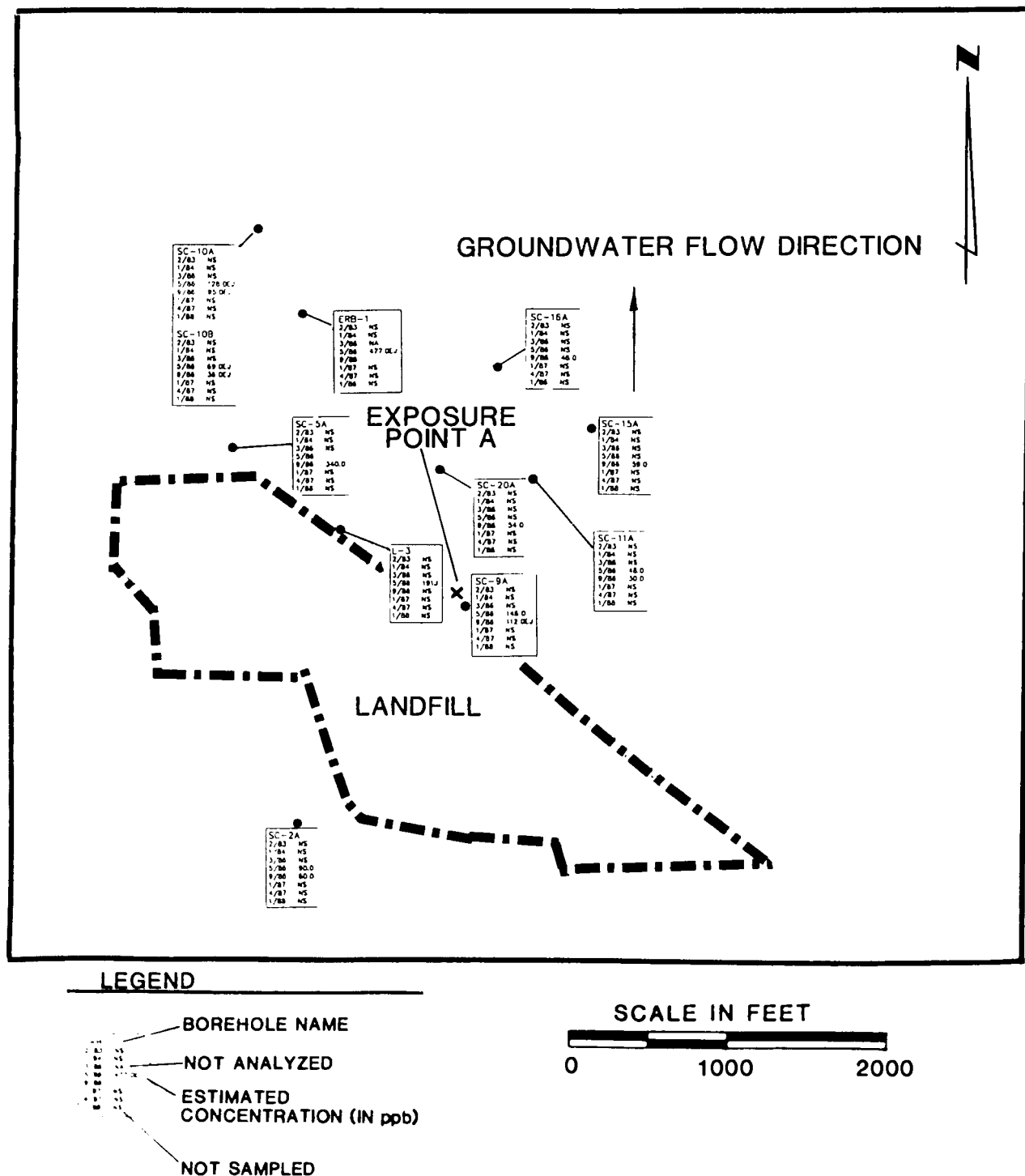
Figure 10
Site Plan, Example 4

who gave us the idea for this work and to Dr. John Read, who introduced us to some of the literature on Bayesian methods.
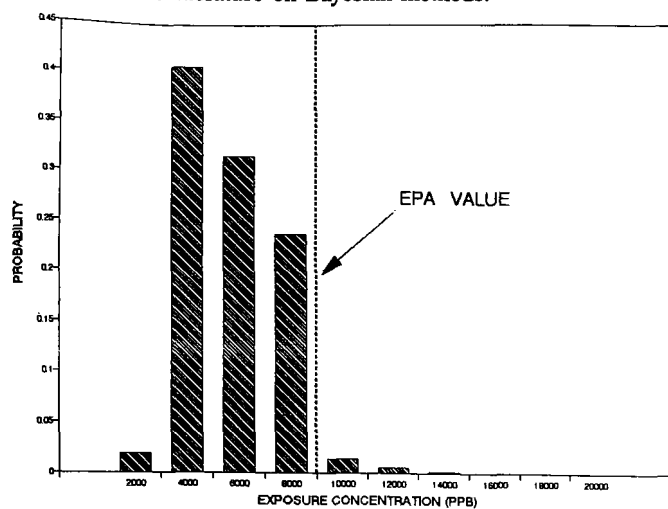
Figure 11
Prior and Posterior Probability Distributions
of Seepage Velocity, Longitudinal Dispersivity
and Source Concentration, Example 4

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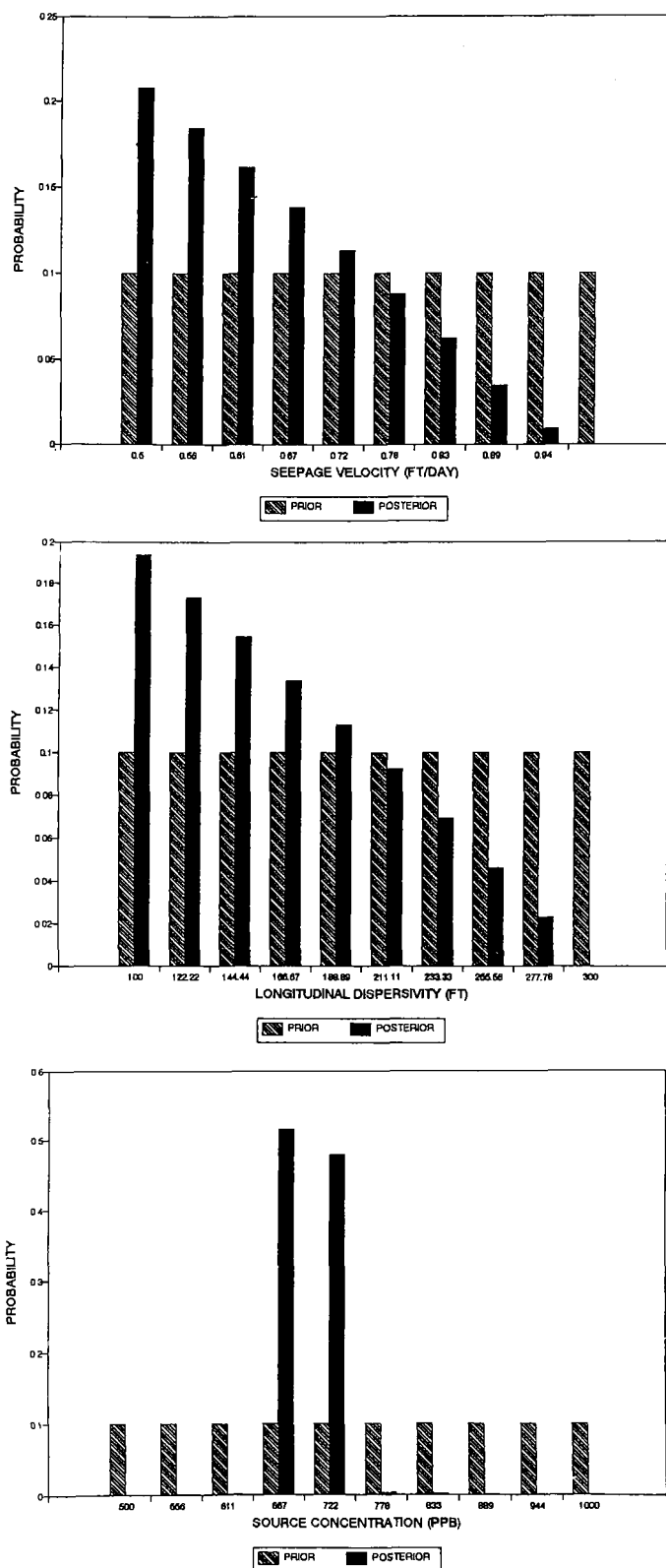
Figure 12
Probability Distribution of Exposure Concentration, Example 4

APPENDIX A

Calculation Sequence for Bayesian Procedure

Consider a problem involving M parameters and an observation z. The observation z may be a single measurement or a collection of

measurements. For the type of problem considered in this paper, $z=z(\mathbf{x})$, i.e., z depends on, but does not directly reveal the values of x^m. Furthermore, the prior probability distributions of the parameters x^m have all been specified as discrete probability distribution $(p_{i_m}{}^m, x_{i_m}{}^m)$.

The first step in assigning a discrete probability distribution to a parameter x^m is to identify all possible $x_{i_m}{}^m$ values of the parameter. For certain parameters with a limited number of choices, such as the source location, identifying all possible values is a trivial task. For certain other parameters, such as the seepage velocity, where the total number of possible values is - in theory - infinite, the choice often reflects a compromise between the accuracy required and the computing resources available.

Having identified all possible values, or having selected a few representative values that cover the range of interest, the next task is to assign a probability $p_{i_m}{}^m$ to each of the values. This is the probability that the parameter x^m will have the value $x_{i_m}{}^m$, or using standard notation in probability theory, $Pr(x^m = x_{i_m}{}^m)$. Such probability may be based on actual measurements (by the frequency of occurrence) or from past experience, interviews, and professional judgement. For each parameter, the corresponding probabilities must add up to one:

$$\sum_{i_m} p_{i_m}^m = 1 \tag{1}$$

The proposed procedure considers one parameter x^m at a time. For each x^m, the calculation proceeds by first calculating the likelihood function $p(z \mid x_{i_m}{}^m)$ for each discrete value $x_{i_m}{}^m$, i.e., the conditional probability of observing z given $x^m = x_{i_m}{}^m$. Having calculated the likelihood functions for each of the discrete values of x^m, the posterior probability $\overline{p}_{i_m}{}^m$ can then be calculated using Bayes' theorem in the following form:

$$\overline{p}_{i_m}^m = \frac{p_{i_m}^m \, p(z \mid x_{i_m}^m)}{\sum_{j=1}^{n_m} p_j^m \, p(z \mid x_j^m)} \tag{2}$$

The procedure described above may be summarized in seven calculation steps:

Step 1   Select a parameter x^m.

Step 2   Select a discrete value $x_{i_m}{}^m$ from the discrete probability distribution of this parameter.

Step 3   Calculate the discrete probability distribution $(r_{i_1 \ldots i_m}, z_{i_1 \ldots i_m})$ of the observation z given $x^m = x_{i_m}{}^m$:

$$r_{i_1 \ldots i_N} = p_{i_m}^m \prod_{n=1}^{M} p_{i_n}^n \qquad n \neq m \tag{3}$$

$$z_{i_1 \ldots i_N} = z(x_{i_1}^1, \ldots, x_{i_m}^m, \ldots, x_{i_N}^M) \tag{4}$$

where $z_{i_1 \ldots i_m}$ are the collection of discrete values of z when $x^m = x_{i_m}{}^m$ and $r_{i_1 \ldots i_m}$ are the corresponding probabilities.

Step 4   Calculate the likelihood function $p(z \mid x_{i_m}{}^m)$ by summing the probabilities $r_{i_1 \ldots i_m}$ of all outcomes $z_{i_1 \ldots i_m}$ that are equal to z.

Step 5   Repeat Steps 3 and 4 for the next discrete value of x^m until all n_m discrete values of x^m have been considered.

Step 6   Calculate the posterior probability $\overline{p}_{i_m}{}^m$ by Equation (2).

Step 7   Repeat Steps 2 through 6 for the next parameter until all M parameters have been considered.

A Performance-Based Approach to Public Health Risk Evaluation and Remedy Selection at Superfund Sites

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ABSTRACT

The escalating cost of remedial action under Superfund is encouraging researchers and practitioners to develop alternative methodologies for evaluating cost-effective health risks that protect public health. Performance-based approaches to problem solving are not new. They have been used successfully in the mining industry and in the high-level radioactive waste field to support risk-based decision-making. However, only recently have these same concepts received consideration for addressing health impacts of exposure to hazardous substances.

The current guidelines for evaluating potential public health responses at Superfund sites follow a deterministic analysis that focuses only on the magnitude of a potential health outcome. A deterministic analysis accounts for uncertainty by choosing upper bound or conservative input parameters; this process significantly increases the cost of remediation without quantifying the degree of conservatism in the outcome.

A performance-based approach attempts to quantify the uncertainties that are discarded in a deterministic analysis and carry them through all stages of the evaluation. In this way, the result of a performance analysis is not a single value of magnitude, but is a range of magnitudes and probabilities. These probabilities describe the confidence the analyst has in the estimates of magnitude and directly relate to the uncertainties in the available knowledge of the site.

This paper describes a performance-based approach that has been successfully applied to evaluating public health responses from exposure to hazardous substances at a Superfund site. The approach has been developed in keeping with 40.CFR.300. The results of the evaluation are presented in a form that can be used to demonstrate regulatory compliance, support a formal decision analysis to identify the most cost-effective remedy and ultimately protect human health and the environment.

INTRODUCTION

The current guidelines for evaluating potential public health impacts at Superfund sites acknowledge that uncertainty exists at all stages of the public health risk evaluation and remediation selection process. For example, it is acknowledged that uncertainties may exist in the baseline data and, in the case of analyses that must be extrapolated over time, there may be uncertainties in explaining past and predicting future events. To account for these uncertainties, the procedures recommended in the public health evaluation guidance documents[1] follow a deterministic logic that considers a set of likely and unlikely-but-possible exposure scenarios using expected value and worst-case input data values. The range of values calculated using this logic is considered to represent the range of magnitude of public health risk at the site. Unfortunately, such analyses do not quantify uncertainty and rarely contain sufficient plausible information for realistic decision-making. Comparisons between the calculated magnitudes and the regulatory acceptance levels and comparisons between the effectiveness of different possible remedies, become cumbersome and invariably focus on the worst possible outcome that will rarely, if ever, occur.

This paper outlines an alternative, performance-based method for quantifying uncertainty and evaluating the true risks associated with the Superfund public health risk evaluation and remedy selection process. While a deterministic analysis provides an estimate of the potential magnitude of an adverse public health response, a performance-based analysis specifically addresses magnitude and chance. The magnitude of a noncarcinogenic response is taken to be the ratio of the dose received by the individual divided by a specific reference dose. The magnitude of a carcinogenic response is the expected recurrence of an adverse public health response. Chance is a quantitative assessment of the confidence that the magnitude, as defined, will be equal to or will exceed a nominated value. Chance is related to uncertainties in predicting the response to a given dose, uncertainties in the system used to predict what the dose may be at a given point in time and uncertainties in how the dose will vary with time. Risk is a measure of the penalties incurred when an unacceptable event occurs.

OUTLINE OF CONCEPT

Mathematically, the probability that the magnitude of a particular health response will be equal to or greater than some specific value can be represented by a cumulative density function (CDF). A CDF provides the means of progressively estimating the likelihood that the occurrence of a given phenomenon will equal or exceed a given set of values.

The principle is illustrated in Figure 1. If the CDF curve is flat, as illustrated by curve A, then the level of uncertainty is high and the outcome could be one of a wide range of values. If the curve is steep, as illustrated by Curve B, then the level of uncertainty is small and the values can be predicted to lie within a small range of values. Certainty will be represented by a vertical line (Curve C).

The CDF presents two of the components of true health risk, magnitude and chance, both of which are needed to evaluate performance. Performance must then be measured against what is acceptable before any risk can be assessed. What is acceptable is generally a reflection of the third component of true risk, exposure to loss. Exposure to loss is defined by society's preparedness to comply with whatever financial, judicial, political or social penalties that may be imposed if an unacceptable event occurs. Exposure to loss will be characterized in part by the difference between a CDF representing the expected performance and a CDF representing the acceptance limits.

Although the regulations do not explicitly specify acceptance levels in terms of CDF values, the words do allude to the fact that unlikely-
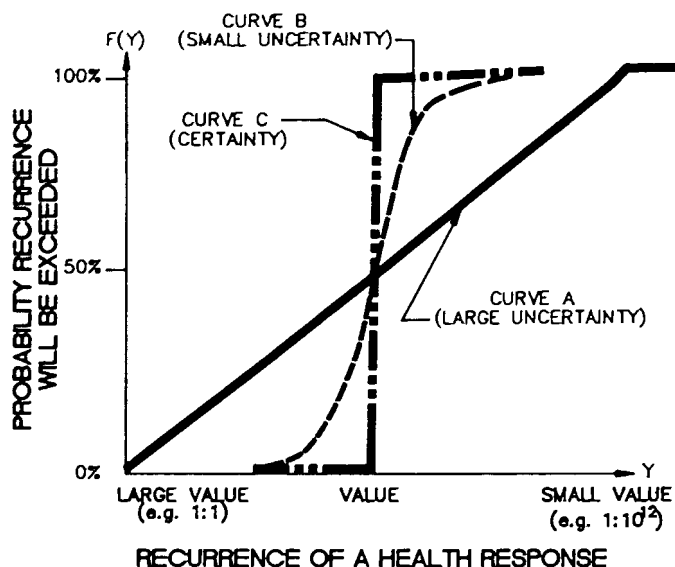
Figure 1
Illustration of Performance Curves for
Various Levels of Uncertainty

RECURRENCE OF EXCESS CANCERS

Figure 2
Base Line Performance Curve for Hypothetical Example

but-possible exposure scenarios need to be evaluated differently to most likely scenarios. The *Human Health Evaluation Manual*[1] refers to the analysis of a reasonable maximum exposure. In view of the predilection toward using 95 percentile upper bound values for calculating the reasonable maximum exposure under the promulgated guidelines, it is suggested that a calculated recurrence having a 95% chance of not being exceeded may also be acceptable for representing the reasonable maximum exposure. The regulations could, in concept therefore, be represented as a CDF.

The seriousness of a release of hazardous substances can be evaluated graphically by plotting the CDF for the expected performance of the base line case together with the CDF for risk acceptance levels. This comparison is shown for a hypothetical example in Figure 2. The bench mark scale or phenomenon is the expected frequency of an excess carcinogenic response. Curve A is the CDF representing the risk acceptance level and Curve B is the CDF representing the health impact from exposure to cigarette smoke if no effort is made to reduce the quantity of smoke in the environment. CDFs to the right of Curve A represent an acceptable chance of survival; values to the left represent an unacceptably high chance of contracting cancer. Curve B is totally to the left side of the acceptance level, indicating that the current human exposure to cigarette smoke results in an unacceptably high recurrence of fatal responses. The magnitude of the difference between the two curves reflects the seriousness of the problem.

Effectively, Figure 2 represents the end of the Remedial Investigation phase under Section 430, Subpart E - Hazard Substances Response, of the National Oil and Hazardous Substances Pollution Contingency Plan (40.CFR.300). During the Feasibility Study phase, detailed analyses of remedial alternatives that reduce the health risks should include the development of a CDF for the residual health risks after implementation using the same approach. The CDFs of different remedial alternatives can then be represented on a single graph. In this way, the effectiveness of each remedy in reducing residual health risks to acceptable levels can be directly compared with each of the other remedies with the base line case and with the acceptance levels.

Such comparisons are shown in Figure 3. Figure 3 illustrates the ultimate goal of the proposed performance-based approach to public health risk evaluation as a consequence of exposure to releases of hazardous chemicals. Presenting the results of the analysis in this way enables several important requirements of the regulations to be addresses simply and quickly in a single-sheet summary of results:

• The shape of each CDF characterizes the uncertainties in the predicted results;
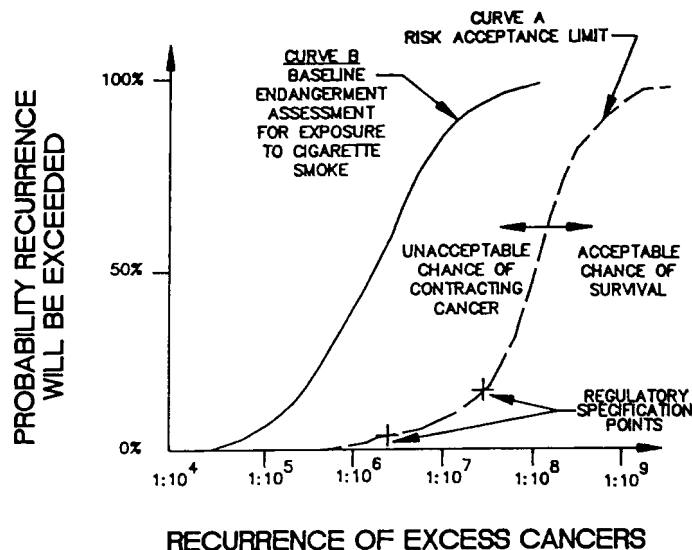
• The relative positions of the base line CDF (Curve B) and the risk acceptance limit CDF (Curve A) helps establish whether a risk exists;
• The magnitude of the difference between the base line CDF and the risk acceptance limit CDF characterizes the seriousness of the risk;
• The magnitude of the differences between the residual risk CDFs (Options 1, 2, and 3) and the base line CDF measures the effectiveness of each proposed remedy in reducing health risks; and
• The magnitude of the difference between the residual risk CDFs and the risk acceptance limit CDF measures the ability of each proposed remedy to meet regulatory requirements.

RECURRENCE OF FATAL RESPONSES
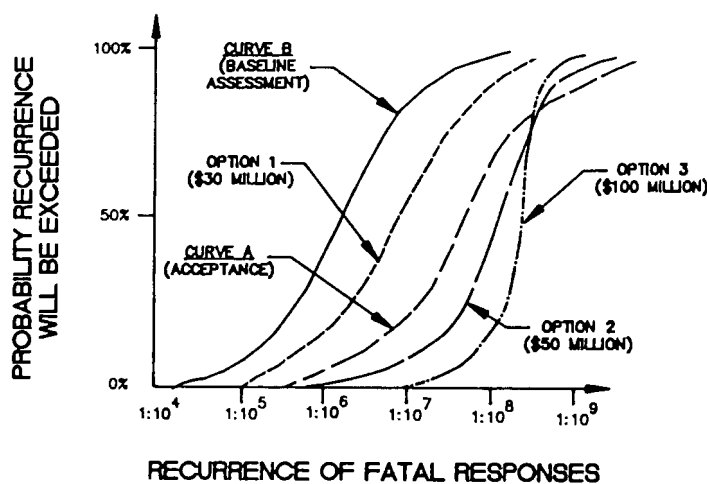
Figure 3
Comparison of Performance Curves of
Different Remedial Alternatives

In addition, coupling the residual risk CDFs for each remedy with the estimated implementation costs (Options 1, 2, and 3) provides the basic input for a formal decision analysis to select the most cost-effective remedy.

METHOD

A health risk exists only if a specific series of circumstances occurs in combination:

• There is a source of substances that are hazardous to public health
• There are release mechanisms which allow the hazardous substances

to escape to the environment
- There are physical mechanisms which are capable of transporting the hazardous substances away from the source
- There is a receptor location that intercepts the transport mechanism
- There is a human intake mechanism which allows hazardous substances that have reached the receptor location to be absorbed into the body
- Hazardous substance are absorbed into the body in sufficient quantities to cause an unacceptable health response

This combination of circumstances constitutes an exposure scenario. The performance-based approach quantifies the range of values and uncertainties associated with each of these circumstances in a set of individual probability distribution functions (PDFs) for several different and representative scenarios and then this approach combines and condenses the individual PDFs into a single CDF to estimate the likelihood of an adverse health response (Curve B, Fig. 2).

The method is illustrated in Figure 4. It comprises three main elements: a Performance Analysis (Boxes 1 to 5), a Risk Acceptance Analysis (Box 6), and a Risk Assessment (Box 7).
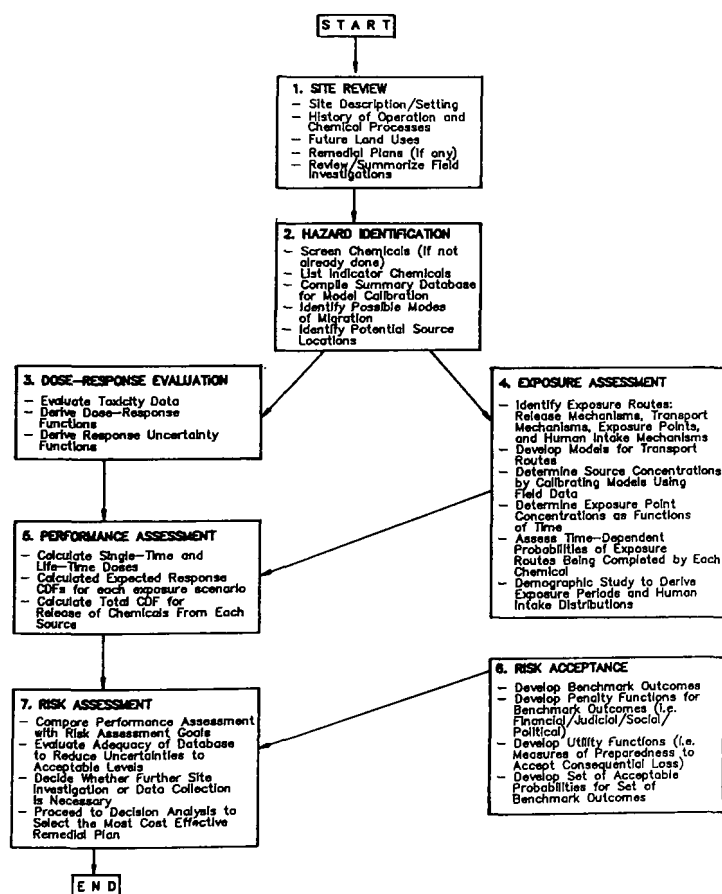
Figure 4
Schematic of Performance Analysis Method

The first stage of the Performance Analysis includes the Site Review and Hazard Identification (Boxes 1 and 2). This stage requires a review of all the information collected during the site investigations. It enables a data base to be set up containing PDFs for all the input parameter values as well as the information needed to calibrate the transport models used in the Exposure Assessment (Box 4). The methodology then splits into two parallel stages, the Dose-Response Evaluation (Box 3) and the Exposure Assessment (Box 4).

The purpose of the Dose-Response Evaluation is to characterize the health impacts resulting from exposure to a certain range of dosage. The evaluation establishes dose-response functions to estimate the

expected health responses and response uncertainty functions to describe the uncertainties in the predictions made by the dose-response functions. Historically, dose-response functions have been derived as a deterministic curve-fit to data for observed responses to high doses on laboratory animals. At high dose rates, the results are repeatable. However, the uncertainty in the predicted response increases as the dose decreases. Therefore, a response uncertainty function is required to provide a measure of the statistical spread of possible responses for each level of dose intake.

The primary goal of the Exposure Assessment is to compile the necessary data to establish PDFs for the expected single-time and lifetime intakes of hazardous substances which potentially may complete the exposure circuit from source to individual. The information collected during the Exposure Assessment is then combined with the Dose-Response information in the Performance Assessment stage of the analysis (Box 5) to generate a suite of PDFs describing the health response for all potential exposure routes, exposure points and exposed individuals. These PDFs may be aggregated into CDFs representing any specific health issue of concern, but eventually are aggregated into the single CDF representing the health outcome for the site in general (Curve B, Fig. 2).

The Public Health Risk Assessment (Box 7) is completed when the aggregated Performance Assessment CDF (Curve B, Fig. 2) is compared with the Risk Acceptance Limits (Curve A, Fig. 2) to assess whether the current performance of the site presents an acceptable level of risk. The risk assessment process can be reiterated to isolate the most sensitive factors, exposure routes and release mechanisms and thereby help identify the most cost-effective remedy.

The Risk Assessment can be only performed when both the Performance Assessment and the Risk Acceptance Analysis have been completed because, without either a Performance Assessment or a Risk Acceptance Analysis, there is no perceived risk, only a measure of likely or acceptable performance. The risk acceptance limits are generally provided by regulatory requirements, but where such regulations do not exist a formal Risk Acceptance Analysis (Box 6) is required to derive defensible acceptance limits.

The performance-based approach to public health risk assessments described in this paper is consistent with the broad framework and intent of 40.CFR.300, but is believed to have the following advantages over the public health risk assessment methods now being used:

- It provides a means of rationalizing and consolidating the data and information generated by a risk evaluation into a single-sheet format;
- It provides a means of estimating and graphically illustrating the range of values and uncertainties associated with each risk evaluation;
- It provides a means of combining the risks associated with different exposure scenarios into a single risk characterization of the site which can be used to estimate the likelihood that an adverse health impact will exceed a nominated value;
- It provides a graphical means of comparing the base line risks with the acceptance criteria and comparing them both with the predicted residual risks after a particular remedy has been implemented;
- It enables the use of formal decision analysis techniques when selecting the most cost-effective remedy; and
- It enables the use of formal decision analysis techniques when addressing other site related health-risk issues such as a Potentially Responsible Party's exposure to litigation from past exposure to individual people.

CASE STUDY

The performance-based approach to public health risk assessments described in this paper has been applied to a Superfund site which has already been investigated in accordance with the procedures outlined in 40.CFR.300. The purpose of the case study was to demonstrate the method on a real Superfund site and illustrate quantitatively the uncertainties in a typical Superfund public health risk assessment.

The 825-acre case study site is located in a floodplain area of low physiographic relief. It is occupied primarily by light industrial companies, trucking firms, petrochemical supply and production companies,
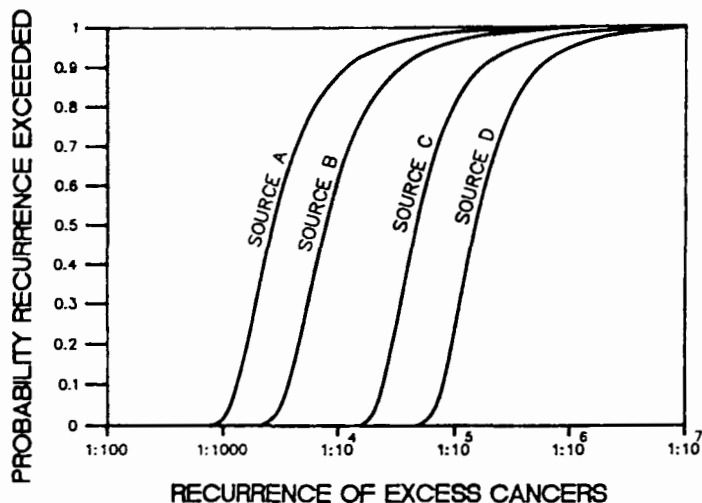
Figure 5
Performance Curves for Case Study

VARIABLE	SCENARIOS INVOLVING INTAKE BY:				
	DERMAL CONTACT	SOIL INGESTION	DRINKING SURFACE WATER	INHALATION	DRINKING GROUND WATER
Chemical Concentration	30%	16%	99%	2%	96%
Rate of Intake	17.5%	21%	<1%	24.5%	0.5%
Attendance Record	17.5%	21%	<1%	24.5%	2.5%
Mass^{-1}	17.5%	21%	<1%	24.5%	0.5%
Dose-Response Function	17.5%	21%	<1%	24.5%	0.5%
	100%	100%	100%	100%	100%

Read.[2] The results for carcinogenic health responses are illustrated in Figure 5. In this particular study, the relative contributions to the coefficients of variation of the results by different system components are compared in Table 1.

CONCLUSIONS

This first demonstration project has confirmed that a performance-based approach can be applied to evaluating public health risk at Superfund sites. It has also served to identify which areas of analysis require further refinement for improving the defensibility of the results. It is hoped to be able to advance this approach in the future in order to stay in the forefront of possible developments in public health risk assessment.

ACKNOWLEDGEMENTS

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small businesses and a few private residences. The land surrounding the site is mostly used for business and industrial purposes, although there is a residential development located approximately one mile from the site.

Industrial and waste disposal activities at four potential sources within the site have contaminated the local groundwater, surface water and soil. The potential sources of contamination were all redeveloped or closed before the site was added to the NPL, but included an oil refinery, a biocide manufacturing plant, a solid waste landfill and a mixed waste disposal area. Contaminants detected include volatile and semi-volatile organic compounds, biocides (pesticides, insecticides and herbicides) and heavy metals.

To focus the study on the demonstration of the method, the analysis was limited to using indicator chemicals, exposure routes and exposure points that had already been defined in the previous human health evaluation. A total of 25 indicator chemicals, four transport mechanisms, eight receptor categories and nine exposure points were used to characterize human health response for each potential source. Performance analyses were carried out for 637 exposure scenarios that could be completed. These were then aggregated into four performance curves, one for each source location. Further details on the health response calculation and derivation of the input PDFS for this study are described by Elliott and

Discussion of the U.S. EPA's Proposed Indemnification Guidelines and Risk Management for Superfund Program Response Action Contractors

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ABSTRACT

This paper presents a brief overview of U.S. EPA's proposed guidelines for indemnifying response action contractors (RACs) as authorized by Section 119(c) of SARA. This paper also discusses risk management options that RACs can use to assist them in developing a formal risk management program.

Subject to certain restrictions, Section 119(c) of SARA authorizes the U.S. EPA to indemnify RACs working at Superfund sites. the U.S. EPA's authority is discretionary — the U.S. EPA is not obligated to provide indemnification. Section 119 of SARA was enacted in response to the lack of pollution liability insurance in the mid-1980s. On October 31, 1989, the U.S. EPA published proposed guidance for Superfund RAC indemnification in the *Federal Register* (54 FR 46012) with a request for public comment not usually included in guidance. The key features of the proposed guidance include: (1) the "diligent efforts" requirement, (2) the indemnification limits offered, (3) the required corresponding deductibles, (4) potentially responsible party (PRP) and other key exclusions, (5) subcontractor requirements and (6) the U.S. EPA's determination of the availability of pollution liability insurance.

The U.S. EPA's proposed indemnification guidelines are one part of a formal Superfund RAC risk management program. This paper presents a general overview of the U.S. EPA's proposed guidelines for indemnification of RACs, focusing on the "diligent efforts" requirements, limits, deductibles and key exclusions. The paper goes on to discuss the U.S. EPA's determination of the current availability of adequate pollution liability insurance and reviews the risk management process and risk management techniques already in place for RACs. Finally, the paper reviews loss financing options for RACs, such as: (1) purchasing adequate limits of insurance, (2) loss retentions and insurance deductibles, (3) self-insurance programs and (4) contractual transfers.[4]

INTRODUCTION

Congress in SARA[1] Section 119 granted the U.S. EPA and other federal agencies the discretionary authority to indemnify RACs working for the U.S. EPA, other federal agencies, states and PRPs. SARA Section 119 contains the following key provisions:

- Establishes a federal negligence standard by exempting RACs from liability under all federal laws except in cases of negligence, gross negligence or intentional misconduct. This standard does not preempt state law.
- Provides the U.S. EPA and other federal agencies with discretionary authority to indemnify RACs for claims brought because of RAC negligence. However, no agency is authorized to provide indemnification for state-enforced strict liability standards.
- Requires limits and deductibles to be incorporated into all indemnity agreements.[1]

Section 119 indemnification can be provided:

- Solely to RACs working in the Superfund program.
- Only for liability related to actual releases of hazardous substances resulting from RAC response actions under the Superfund program
- As a supplement or substitute when commercial insurance is unavailable, inadequate or unreasonably priced
- Only when the RAC has made a diligent effort to obtain insurance from nonfederal sources and has found that none is available at a fair and reasonable cost.[3] The determination of diligent efforts and fair and reasonable insurance costs rests solely with the U.S. EPA.[1]

The U.S. EPA is currently responding to public comment and is in the process of promulgating the final guidance. Promulgation of the guidelines is anticipated in the near future, probably in early 1991.

KEY FEATURES OF THE U.S. EPA'S PROPOSED GUIDELINES

Diligent Efforts Requirement

SARA Section 119 provides the U.S. EPA with the discretionary authority to offer indemnification to RACs working in the Superfund program. Because of the lack of adequate and affordable pollution liability insurance in the mid-1980s, it was the intent of Congress that Section 119 indemnification provide an interim solution to the lack of insurance until commercial liability insurers are capable of and willing to provide adequate insurance for RACs.[2] Therefore, in the proposed guidance, as directed by SARA, the U.S. EPA has imposed a diligent efforts requirement on RACs: RACs must make diligent efforts to obtain insurance coverage from nonfederal sources before entering into an indemnification agreement with the U.S. EPA and before beginning work at a new Superfund site under multisite contracts. The proposed guidance describes diligent efforts as: a RAC must submit in writing:

- "The names and addresses of at least three commercial insurers or alternative risk financiers to whom the RAC has submitted applications; and"
- "A copy of each application submitted, insurance policies offered (including the declaration page) and any rejection letters received. If pollution liability insurance was offered by a commercial insurer, but not accepted by the RAC, an explanation of the reasons why such coverage was rejected must be included."[5]

Cost reimbursement RACs may satisfy the diligent efforts requirement by procuring and maintaining pollution liability insurance in the minimum amount of $1 million, or self-insure for the same.

Indemnification Limits and Deductibles

Among the most important and controversial, features of the U.S. EPA's proposed guidelines are the indemnification limits offered and

their corresponding deductibles. As shown in Table 1, the minimum limit of $1 million offered in the proposed guidelines has a corresponding deductible of $10,000. As the limits increase, so do the deductibles. The maximum limit of $50 million has a corresponding deductible of $3.5 million. (This was done to duplicate the features of limits and deductibles often found in commercial liability insurance.)

There are several important aspects of the indemnification limits and deductibles that RACs must recognize. First, the indemnification limit as proposed is a contract aggregate limit.[5] For example, if a RAC requests, is offered and accepts a $50 million limit of indemnification on a 4-year contract, the $50 million limit is for the entire 4-year period. Therefore, if this same RAC received indemnification payments of $1 million (above the corresponding $3.5 million deductible) in the first year, only $49 million of indemnification would remain for the remaining 3 years of the contract. Second, the corresponding deductible of a U.S. EPA indemnity agreement, as proposed in the guidelines, is a per occurrence deductible. Each time a RAC incurs a loss resulting solely from its negligent actions, it must pay the full amount of the deductible before U.S. EPA indemnification would pay for the loss. Therefore, that same RAC with a $50 million limit in its indemnification agreement must incur a loss greater than the $3.5 million deductible to receive an indemnification payment from the U.S. EPA. The per-occurrence deductible mirrors those found in commercial liability insurance policies.

PRP and Other Key Exclusions

The U.S. EPA's proposed indemnification guidelines contain some key exclusions. First, the U.S. EPA will not agree to indemnify a RAC under contract to a PRP.[6] Even though Section 119 gives the U.S. EPA the discretionary authority to indemnify a RAC employed by any PRP that has entered into an agreement (such as a consent decree) with the U.S. EPA, the Agency has chosen not to exercise that authority.

Other exclusions that limit the U.S. EPA's indemnification are that the indemnification will be provided only for losses resulting from a RAC's negligence. This indemnification excludes instances where strict liability, gross negligence and willful misconduct are the cause of the loss. Furthermore, indemnification is statutorily excluded for owners or operators of facilities regulated under the Solid Waste Disposal Act, as amended and any owner or operator of a facility that receives solid or hazardous waste for disposal, treatment or storage.

Subcontractors

Another feature of the proposed guidelines is the U.S. EPA's decision that it will not directly indemnify subcontractor RACs. U.S. EPA indemnification can be extended to subcontractors only as a "pass-through" from the prime contractor. (A prime contractor RAC is the contractor that has a direct contract with the U.S. EPA.) The following scenario describes how a subcontractor RAC would receive indemnification as a pass-through from the prime contractor:

Prime contractor A has a $10 million indemnification agreement with the U.S. EPA. This agreement, accordingly, has a $250,000 per occurrence deductible (refer to Table 1 above). Prime A wants to procure well drilling services from subcontractor Z. Z has a liability exposure in drilling wells and requests $2 million of indemnification from A. If A grants Z's request, A can include any deductible. Furthermore, A's indemnification limit from the U.S. EPA would be reduced $2 million, to $8 million, until Z's agreement ends.

The U.S. EPA must approve all indemnification agreements between a prime contractor and a subcontractor. Also, because subcontractors are defined as RACs, they are subject to the same diligent efforts requirements as the prime contractors. Subcontractors must demonstrate that they made diligent efforts, as described above, to obtain pollution liability insurance and agree to continue to make such efforts as required.

U.S. EPA Determination of Pollution Liability Insurance Availability

An important determining factor that the U.S. EPA will consider before it enters into an indemnification agreement with a RAC is the

Table 1
U.S. EPA's Proposed Indemnification Limits and Deductibles

Limit	Deductible	Limit	Deductible	Limit	Deductible	Limit	Deductible	Limit	Deductible
$ 1,000,000	$ 10,000	$ 2,000,000	$ 40,000	$ 6,000,000	$ 130,000	$ 11,000,000	$ 300,000	$ 26,000,000	$ 1,100,000
		3,000,000	60,000	7,000,000	160,000	12,000,000	350,000	27,000,000	1,200,000
		4,000,000	80,000	8,000,000	190,000	13,000,000	400,000	28,000,000	1,300,000
		5,000,000	100,000	9,000,000	220,000	14,000,000	450,000	29,000,000	1,400,000
				10,000,000	250,000	15,000,000	500,000	30,000,000	1,500,000
						16,000,000	550,000	31,000,000	1,600,000
						17,000,000	600,000	32,000,000	1,700,000
						18,000,000	650,000	33,000,000	1,800,000
						19,000,000	700,000	34,000,000	1,900,000
						20,000,000	750,000	35,000,000	2,000,000
						21,000,000	800,000	36,000,000	2,100,000
						22,000,000	850,000	37,000,000	2,200,000
						23,000,000	900,000	38,000,000	2,300,000
						24,000,000	950,000	39,000,000	2,400,000
						25,000,000	1,000,000	40,000,000	2,500,000
								41,000,000	2,600,000
								42,000,000	2,700,000
								43,000,000	2,800,000
								44,000,000	2,900,000
								45,000,000	3,000,000
								46,000,000	3,100,000
								47,000,000	3,200,000
								48,000,000	3,300,000
								49,000,000	3,400,000
								50,000,000	3,500,000

availability of commercial pollution liability insurance. The proposed guidance states that the U.S. EPA will determine on a case-by-case basis whether adequate insurance is available at a "fair and reasonable price" at the time the indemnification request is submitted by the RAC. Although the proposed guidance does not specify what the U.S. EPA will consider a "fair and reasonable price," it is likely that the U.S. EPA will base the determination on a percentage of the contract value. In other words, it is unlikely that the U.S. EPA will consider an insurance premium of $100,000 "fair and reasonable" for a contract that has a value, or estimated RAC revenue, of $100,000.

U.S. EPA guidelines, when promulgated, will govern the U.S. EPA's indemnification of RACs for work initiated after October 17, 1986 and will supersede OSWER Directive #9835.5, "the U.S. EPA Interim Guidance on Indemnification of Superfund Response Action Contractors Under Section 119 of SARA." The guidelines will also govern all RAC indemnification by the U.S. EPA for future response action contracts.

DISCUSSION OF RISK MANAGEMENT TECHNIQUES FOR SUPERFUND RACs

Risk Management

Risk management is traditionally defined as the practice of analyzing all noncompetitive and nonproductive exposure to risk or loss (loss by fortuitous or accidental means) and taking steps to reduce those potential or real losses to levels acceptable to the organization. To undertake this practice, RACs must develop a risk management process to control pure risk (risk that can only result in a loss). This risk management process typically includes a four-step process: (1) identifying and analyzing the loss exposures, (2) selecting the appropriate risk management technique(s) (which typically include risk retention, contractual or noninsurance transfer, loss control, risk avoidance, and insurance transfer) to handle exposures, (3) implementing the chosen technique(s) and (4) monitoring the results to verify and improve the process.[7] RACs must practice sound risk management techniques to identify and control their loss exposures. Figure 1 provides an overview of the risk management process.

Exposure Identification/Analysis

Numerous tools exist to assist RACs in identifying and analyzing losses. These tools include (1) base line risk assessments, (2) remedial investigations (RIs) and feasibility studies (FSs) and (3) records of decision (RODs). Furthermore, because NCP laws, regulations and guidance assist RACs by directing actions at remedial action sites, RACs have a distinct advantage over many other industries when it comes to risk management.

One primary liability exposure that should concern RACs and is the focus of this paper, is the liability a RAC would face if there is a release, or threatened release, of contaminants at a site during the remedial activities performed by the RAC.

One task that is done during the early stages of a Superfund site cleanup that assists RACs in risk identification is a base line risk assessment. Base line risk assessments are done to help determine what risk the site poses to human health and the environment. These risk assessments provide RACs with valuable information to help them identify the liability loss exposures they may face during remedial activities. Risk assessments will identify the surrounding population that could be affected by the contamination at the site, as well as the environmental impacts of the site. Therefore, RACs can use this information in the risk management process to help identify and analyze the liability loss exposures that may exist in the event of a release during remedial activities. This information will assist RACs in developing proper loss control programs and choosing adequate risk financing levels.

Another RAC activity that assists RACs in risk identification involves performing very detailed Ris and Fss at a site. Ris are designed to help identify where contamination exists, what contaminants are there and how the contamination is affecting the surrounding population and the environment. Fss are developed to determine what technologies can be applied to clean up the site. The RI and FS provide the U.S. EPA

and RACs with extensive information regarding the site that can be used in the risk management process to help determine what release exposure may exist when remedial actions take place at the site. For example, if a remedial action calls for the excavation and removal of buried drums at a site, the RI/FS will help the RAC determine where the drums are. This information would help to avoid, or at least control, the liability exposure that would result if the drums were accidentally pierced during excavation, causing a release of their contents.
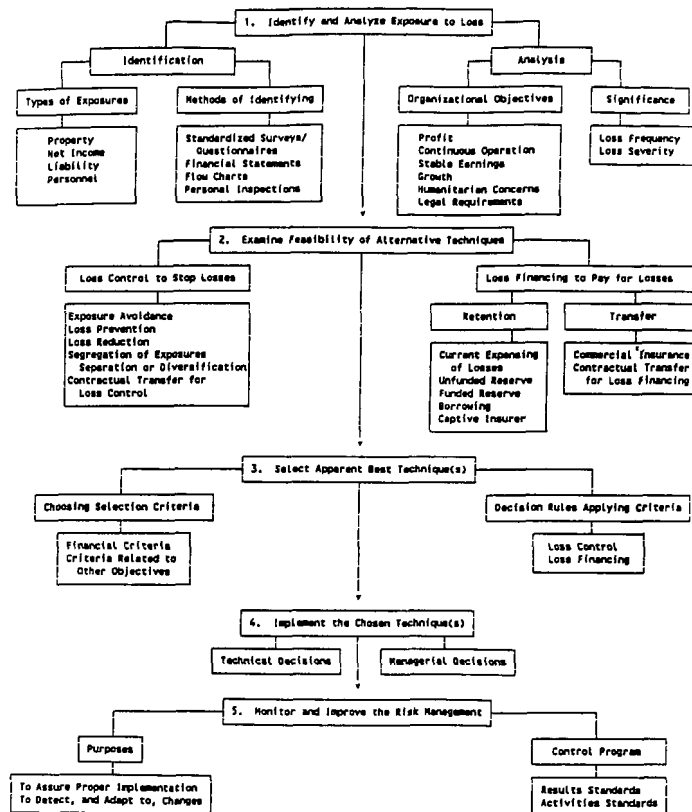
Figure 1
The Risk Management Process

Loss Control

One of the first things that Superfund RACs are required to do before going on-site is to develop a health and safety plan. These plans are a risk management tool that help RACs limit the liability exposures to their personnel and limit the exposure of the surrounding community by allowing only certified and properly equipped personnel onto the site. A properly implemented health and safety plan, along with physical barriers that are constructed to restrict access to the site (for example, fences and gates), help to manage one of the primary pathways from which RAC liability may arise: on-site exposure.

The experience of the RAC's personnel and the ability to draw on the expertise of the U.S. EPA's On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs), provide RACs with valuable risk management expertise and information. Although some RACs may be new to the industry, most have well-educated and well-trained personnel in the field who are responsible for implementing the remedial activities. Furthermore, RACs can rely on the expertise of the U.S. EPA's OSCs and RPMs to provide further guidance and direction during remediation of a Superfund site.

Should a release occur at a site during a remedial action, the RAC's own expertise should be used to help contain and control the amount of damage caused by the release, providing another loss control advantage. As part of an overall loss control program, RACs also should ensure that proper control devices and equipment are in place at the site in case of a release. Furthermore, RAC personnel should be properly trained in the implementation of containment procedures.

The U.S. EPA's Environmental Response Team (ERT) would probably be involved if a serious release were to occur during remedial activities, another asset to a RAC's risk management program. ERT brings necessary expertise to assist in the control and containment of contaminants, thereby helping to minimize the incurred losses resulting from a release.

A U.S. EPA-directed device that assists RACs in loss control is the site-specific ROD. The ROD is the product of the RI/FS. The ROD provides RACs with a very important loss control mechanism by specifying the remedial action(s) that will be implemented at the site based on the RI/FS. Since RACs do not choose the remedial action that is implemented at the site (the U.S. EPA does), this process controls a RAC's loss exposures because the RAC is only doing what it was told. RACs' professional liability may be limited because they implement remedial actions based on remedial designs approved by the U.S. EPA. Recent case law shows that this defense has not been consistently successful, however.

Another loss control method that RACs have available is the remedial design. As part of the ROD, remedial designs are based on extensive study during the RI/FS. Therefore, the extensive study that is done before a ROD is signed helps to limit the RAC's liability exposure by limiting the possibility that the RAC will implement the wrong remedial action.

RACs have many other loss control devices and actions that they can implement in their risk management programs. Briefly, these loss control steps include the following:

- Developing a formal risk management and control manual for field personnel
- Avoiding remediation work that calls for expertise not available within the RAC's organization
- Developing detailed, site-specific contingency plans
- Dedicating a full-time staff for a formal risk management program responsible for implementing all steps in the risk management process

After a RAC has identified, analyzed and controlled loss exposures, it is necessary to develop a risk financing program to pay for any resulting losses that were either unidentified or uncontrolled. The next section discusses how a RAC can develop a risk financing program.

RISK MANAGEMENT FOR SUPERFUND RACs—RISK FINANCING

RAC risk financing is part of the risk management program that anticipates losses and arranges to pay for them with a mix of loss reserves, self-insurance, contractual transfer, insurance, and U.S. EPA indemnification. The indemnification program the U.S. EPA has proposed provides RACs with an alternative risk financing mechanism when commercial pollution liability insurance is inadequate or too expensive. U.S. EPA indemnification, when offered, is one mechanism that RACs can use to help pay liability losses resulting from negligence associated with Superfund remediation work. The options RACs can use to help finance such losses and the steps that they should undertake before reaching a risk-financing decision are shown in Figure 2. Some risk identification and control techniques that RACs use were explained above. This section describes the three ways RACs can finance losses: retention, transfer and insurance (Fig. 2).

In choosing an adequate risk-financing mix, a RAC should consider the following questions:

- In the event of a loss, what financial position do we want to be in: survival, continuity of operations, profitable, stable earnings or growth?
- What loss amount can our business expect?
- What is the current availability of funds to pay for losses as they occur?
- If regulatory requirements are established for various insurance coverages and other risk-financing techniques, how does this affect our decision?
- What alternative uses of funds (opportunity costs) affect our risk-financing decision?

This section briefly explores the role the U.S. EPA indemnification can play in a RAC's overall risk financing plan.

To help define its intended financial condition should a loss occur, the RAC should identify its post-loss goal. Typically, post-loss goals range from the basic objective of survival to the ambitious and often unattainable, goal of continued growth. As described below, a RAC's post-loss goals are affected by its expected losses. Once a RAC chooses its post-loss goal, it can proceed to analyze various risk-financing mechanisms.
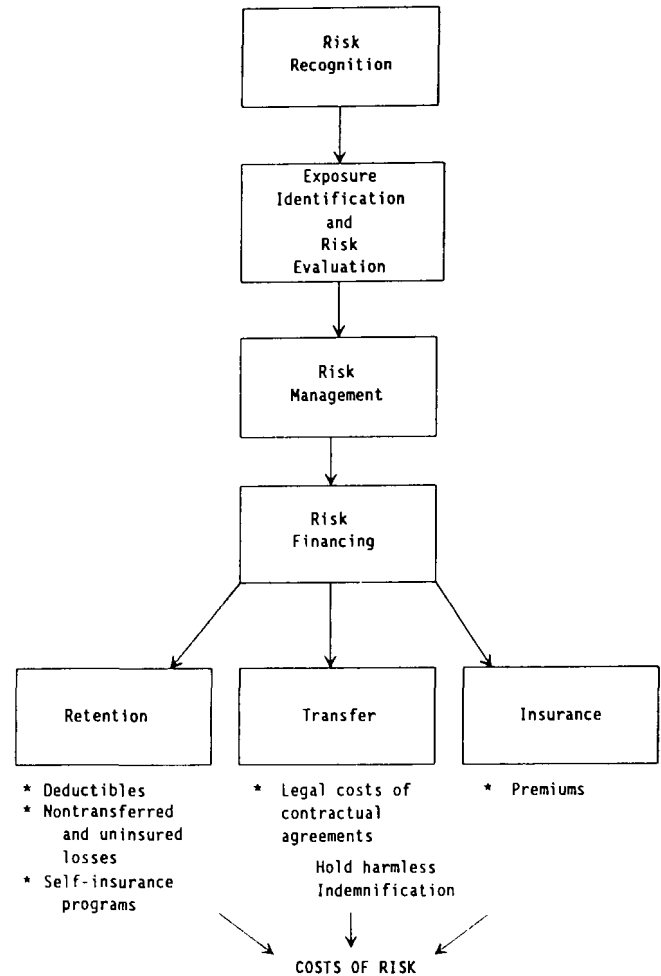
Figure 2
Steps Toward Risk Financing

After a RAC establishes its post-loss goals, the first crucial step, as described in the previous section, is the identification and analysis of loss exposures. The two factors that affect potential losses are severity and frequency. RACs are believed to be in a high-severity, low-frequency expected loss industry.

Insurance is the typical risk-financing mechanism used to limit the adverse impact of a high-severity, low-frequency loss. RACs would seek contractor's pollution liability (CPL) insurance and environmental engineer's errors and omissions pollution liability, otherwise known as professional pollution liability, insurance. Available limits of commercial insurance for project-specific CPL are $10 million per occurrence and $10 million annual aggregate. Available limits of commercial insurance for blanket CPL are $5 million per occurrence and $5 million annual aggregate. Available limits of commercial insurance for blanket and project-specific environmental engineer's errors and omissions pollution liability are $5 million per occurrence and $5 million annual aggregate. Factors that will affect a RAC's decision to insure are the availability and cost of insurance.[8]

RACs also should explore retention and transfer as risk-financing mechanisms. As Figure 2 indicates, retention consists of insurance deductibles, nontransferred and uninsured (or unreserved) losses and

self-insurance programs. Retention can be most effective when a RAC properly reserves funds to pay for future losses. Transfer typically involves contractual hold harmless and indemnification agreements that relieve the RAC from the costs of risks. Self-insurance is a viable risk financing method that the U.S. EPA recognizes as meeting the diligent effort requirement of the proposed indemnification guidelines. By working with qualified insurance brokers, a RAC can develop a self-insurance program that would help pay for losses in the event of a release of contaminants during a remedial action.

RACs must be aware that indemnification and insurance are only two ways to finance risks. A mix of retention, contractual clauses, insurance and U.S. EPA indemnification should be used to offset the potential liability costs of doing remedial work at Superfund sites.

CONCLUSION

U.S. EPA indemnification is one part of a RAC risk management program. RACs should examine all the information that they receive through base line risk assessments, RI/FS and RODs to help identify their potential liability exposures and to determine necessary risk-financing and loss control actions. A formal risk management program will help RACs to better understand and deal with the pollution liability risks that are inherent in their profession, so that if a release occurs during remedial actions, the RAC is better prepared to control the extent of the damage to human health and the environment and the financial implications to the RAC organization.

DISCLAIMER

The views expressed in this paper are the authors' alone and do not necessarily reflect the views of the U.S. Environmental Protection Agency (the U.S. EPA).

ENDNOTES

1. The Comprehensive Environmental Response, Compensation and Liability Act of 1980 (P.L. 96-510) as amended by the Superfund Amendments and Reauthorization Act of 1986 (P.L. 99-499), Section 119 (c) (1).
2. Report of the Conference Committee of the Superfund Amendments and Reauthorization Act, Oct. 3, 1986. Report 99-962, p.237.
3. *Federal Register, 54*, p. 46012, Oct. 31, 1989.
4. Head, G.L., *Essentials of Risk Financing*, Vols I and II, 1988.
5. *Federal Register, 54*, p. 46025, Oct. 31, 1988
6. 54 FR 46029.
7. Head, G.L., *Essentials of the Risk Management Process*, Volume I, p. 9 (adapted). Published by the Insurance Institute of America.
8. Obtained from Dave Dybdahl, Vice President, Corroon & Black Environmental Services, September, 1990.
9. Refereed above as Endnote 1.

Assessing Uncertainty in the RI/FS Process

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ABSTRACT

Though pervasive throughout the process, uncertainties in the CERCLA RI/FS process generally are not recognized as a priority issue. RI reports typically address uncertainty in a qualitative fashion and generally only in the risk assessment; and FSs often only address uncertainty in volumes of contaminated media and remediation costs using sensitivity analyses. These analyses can provide useful information, but do not provide a comprehensive analysis of uncertainty. Qualitative analyses of uncertainty can be assumed to hold less importance and are more difficult to incorporate into the decision-making process than quantitative results.

As more techniques are developed to evaluate uncertainties quantitatively, decision-makers may place increased reliance on quantitative descriptors of uncertainties to assist in comparing options and planning for contingencies resulting from deviations in the proposed remedial action plan. A number of methods have been and currently are being developed to evaluate uncertainty more quantitatively.

This paper identifies several factors believed to contribute to uncertainty in remedial investigations and feasibility studies and evaluates their relative importance in the interpretation of data in defining the nature and extent of contamination and in the selection of a remedy. Methods and strategies that can be used to describe and reduce uncertainties are presented.

THE IMPORTANCE OF UNCERTAINTY ANALYSIS

Few solutions to problems addressed in science and engineering are free from uncertainty, and the RI/FS process is no exception. Because uncertainties predominate over clear-cut facts in many RI/FS studies, the need for uncertainty analysis in the RI/FS process appears well-deserved. The recognition of the scientific limitations of data acquisition and methods of analysis can benefit the development of reasonable and defensible remedial action strategies. A recognition of the uncertainties can help to emphasize the need for contingencies in any remedial action plan.

To gain an understanding of the relative importance of the different factors that contribute to uncertainty, it is necessary to first consider the basic goals of the RI/FS process, and then consider what factors are critical to the decision-making process. The basic purpose of the RI/FS process is to determine: (1) if there is an unacceptable endangerment posed by the site to human health and the environment, and if so then (2) determine the nature and extent of the contamination and (3) determine a cost-effective means of achieving a suitable remedy. The following sections identify factors that are considered critical to determining if there is an unacceptable risk, determining the nature and extent of contamination and evaluating the cost of a potential remedy. This paper does not attempt to qualify all possible factors that could influence uncertainty. Instead, quantitative approaches to analyzing uncertainty for several key parameters are addressed.

UNCERTAINTIES IN DEFINING THE NATURE AND EXTENT OF CONTAMINATION

Many of the major uncertainties in the RI/FS process result from an incomplete understanding of the nature and extent of contamination. How well the nature and extent of contamination is defined (e.g., what contaminants are present, where are they now and how might they migrate to human and animal receptors) can affect the assessment of the risk posed by the site to human health and the environment and will impact the development and selection of a remedial action plan. A poor assessment of the nature and extent of contamination can result in the selection of a less cost-effective remedy or an inappropriate level of protection to the community and the environment.

The definition of nature and extent is a product of planning, field sampling, analytical work and interpretation of data. Errors that occur in any of these stages can introduce uncertainty in the conclusions of the remedial investigation. Sampling error is the improper use of the prescribed methods for sample collection and storage. Sampling bias, such as sampling only areas of suspected or observed contamination, could skew results of a risk assessment or proposed remedy if the bias is not accounted for in the interpretation of results. Although sampling error and sampling bias can significantly affect the results of an RI, they are difficult to assess and characterize. Several approaches have been developed, however, to quantitatively evaluate analytical error.

The difference between the reported concentration and the actual concentration of a contaminant in a sample is the analytical error. Analytical error can be described quantitatively via measurement of accuracy and precision. Accuracy of a test often is measured by the percent recovery of a surrogate compound from a laboratory spike. While low surrogate recoveries may indicate significant analytical error, correction for the bias is not standard practice. Surrogate recoveries as low as 25% can be used to validate reported concentrations for a host of other compounds that exhibit different recovery rates than the surrogates.

For initial investigative work, the relative impact of analytical error is likely to be less significant than error introduced in the sampling planning stage (i.e., conceptual error). Should the reported values play a major role in the decision-making process and have concentrations that approach action levels, then the

consequences of this error could be considerable. Uncertainty in reported values due to analytical error could be addressed by: (1) accounting for the uncertainty in the results and deriving "probable" range of actual values, (2) resampling or (3) selecting more sensitive methods of analysis. Defining probable ranges for a reported value can be performed when the bias associated with analytical accuracy is known and when the precision of an analytical test is known. Replicate samples are commonly used to define the precision of an analysis in terms of relative percent difference or relative standard deviation. A range of probable concentrations can then be derived by adding and subtracting percent bias and relative standard deviations (having a corresponding probability) to the reported concentration.

Some variation in reported results can contribute to differences in analytical reliability between laboratories. This variability is likely to be small relative to spatial variability of contaminants within a sample or about the site, particularly for solid matrices. If the variability in results between laboratories is a concern, this concern can be addressed by having split samples or laboratory performance audit samples (i.e., a sample spiked to known quality) analyzed by different laboratories. Uncertainty due to laboratory variability can be reduced by maintaining the same laboratory over the course of a project.

The spatial variability of contaminant concentrations and physical properties of contaminated media on-site can impart significant uncertainty on the interpretation of data. Replicate samples can provide valuable information regarding the spatial variability within the media sampled throughout the site and provide an indicator as to how well a single sample reflects "representative" conditions for a given location. Reported concentrations for replicate samples taken from soil or sediment could easily differ by as much as a factor of two (relative differences greater than 66%). Such variability could be contributed by both the variability inherent to the sample collection and analysis used and the difficulties in homogenizing the sample.

The collection of samples that are representative for an area typically requires that replicate, co-located or composite samples be taken from the area in question. Replicate and co-located samples can provide a means of estimating the variability at a given point and, therefore, may prove more useful than composites unless the areas to be remediated are well-defined and concentrations are well above detection limits. The use of screening methods and correlations can help reduce cost, but may have limited use as input data to risk assessments.

The uncertainty in values estimated for unsampled locations can be equally as important as, if not greater than, the uncertainty in sampled locations (i.e., reported values). Analysis of uncertainty in unsampled locations generally requires some consideration for spatial statistics. Spatial statistical analyses can be used to estimate probabilities of locating or classifying areas as above or below action levels and can assign probabilities to estimates of volumes of contaminated media.

Several examples of how spatial statistical methods can be used to quantify probabilities of grid sampling networks to locate "hot spots" are found in the literature. The application of these methods requires some prescription of permissible conditions, e.g., the definition of maximum allowable probability of a false positive or false negative for the maximum hot spot area to go undetected or be misclassified. The sampling grid that provides the desired level of confidence can be determined using readily available nomographs.

While interpolation can be used to estimate values at unsampled locations, simple interpolation does not provide measures of the uncertainty associated with the estimate. Kriging and probability kriging, also known as geostatistical methods, have been applied to estimate concentrations at unsampled locations and to estimate uncertainty associated with the estimates. Kriging uses a generalized least squares approach to model and predict spatial correlation of a given parameter. The model uses weighted averages of known values to estimate values for locations having undefined values. The method attempts to account for spatial dependence, i.e., that the magnitude of the difference in observations increases as the distance between sample locations increases, using a statistic similar to a covariance. The method also estimates (quantitatively) the uncertainty associated with the estimated values. This information has been used to assign confidence limits to estimated values, which has implications for estimates of average concentrations for risk assessments or volumes of contaminated media in feasibility studies.

The application of these methods, however, requires some understanding of the algorithms and their limitations, can increase the number of assumptions input to the data analysis and may not produce results more accurate than would be produced by applying best practical judgment given the available information. The utility of the method is that it can provide an approach to deriving confidence intervals for estimated values.

UNCERTAINTIES IN DEFINING THE LEVEL OF RISK

Considered by many to be the cornerstone of the RI/FS, the risk assessment must fashion a quantitative description of the risk a site poses to human health and the environment based on theoretical and empirical equations that incorporate an admittedly high level of uncertainty. Although it has undergone some recent revisions, the approach used to perform risk assessments is somewhat standardized through the direction of U.S. EPA guidance documents. The U.S. EPA guidance on preparing risk assessments has devoted a section exclusively to uncertainty analysis. While U.S. EPA guidance calls for risk assessments to discuss uncertainty in the risk assessment in some detail (e.g., the weight-of-evidence analysis), quantitative analysis is not recommended. U.S. EPA guidance, although acknowledging that the risk measures are "not fully probabilistic estimates of risk," suggests that highly quantitative statistical uncertainty analysis usually is not practical or necessary. Many of the factors used in the risk calculations, however, do have probabilities associated with them, and the approach is based upon a number of assumptions that have limited scientific supporting evidence.

Estimated risks for carcinogenic chemicals, for example, are calculated based upon an assumed dose, an estimated potency of the carcinogen and an assumed exposure period, each of which has an associated probability of occurrence. Exposure concentrations typically used are the 95% upper confidence limit on the arithmetic average (or geometric mean) of measured concentrations in the media of concern. Carcinogenic risk is a product of the concentration value and the dose, which incorporates the slope factor. The slope factor, which estimates the risk per unit dose, typically represents an upper 95th percentile confidence limit on the probability of a response per unit intake of a chemical over a lifetime. Clearly then, the risk assessment does incorporate some confidence intervals in the calculation of risk. Risk assessments, however, typically do not address this confidence analysis in a quantitative manner.

Alternative approaches to risk assessments that incorporate some quantitative methods for addressing uncertainties have recently been proposed. Burmaster[2] suggested the use of Monte Carlo techniques to develop probability distributions for risk, where the input parameters are permitted to be random independent variables. This approach clarifies the fact that a significant number of assumptions are used to derive the estimated risk and also provides an alternative means of estimation.

The technique, and other methods like it, requires that the probability distributions of each random variable, e.g., the amount of soil or water ingested per day, be defined. In all likelihood, these distributions would have to be assumed. The U.S. EPA guidance argues that, for this reason, the value of this technique is greatly diminished and review becomes too cumbersome to handle. Instead, the guidance suggests presenting quantitative

uncertainty analysis graphically for individual parameters to illustrate the relative sensitivity of each parameter.

Alternative approaches to evaluation of uncertainty would be to calculate risks from a variety of input combinations of estimated probability for individual parameters. For example, risks could be calculated for any combination of the possible exposure periods (with associated probability), exposure concentrations (with associated probability) and possible exposure weights (e.g., child vs. adult). The combinations could be assembled to illustrate the range of possible risks.

UNCERTAINTIES IN THE SELECTION OF REMEDY (THE FEASIBILITY STUDY)

The purpose of the FS is to define an appropriate remedial action, assuming one is warranted. More often than not, the selection of a remedy will be influenced most strongly by the perceived capabilities of the alternatives' technologies to achieve the remedial action goals, and the comparative cost of the alternatives. The performance of a technology can be assessed best through bench- and pilot-scale testing. Testing should be performed not only on "representative samples," but also the range of input conditions likely to be encountered by the technology. This process requires that the variability in characteristics be defined. The quantity of media considered contaminated (i.e., the volume) will greatly influence the estimated costs of the alternatives. An assessment of the uncertainty in the estimated volume of contaminated media will require not only an estimated distribution of contaminants about the site, but also an estimate of their spatial variability.

One of the simpler approaches to evaluating uncertainty in the extent or volume of a contaminated soil is to use best judgment (e.g., based on historical use patterns and physical barriers to contaminant transport) in conjunction with some linear interpolation to contour around observed values to estimate the volume of contaminated soil. While such an approach may be supported by the available information, it may incorporate some bias in the interpretation and does not generate information that can be used to estimate the confidence in the values outlined. Alternative approaches include the use of statistical methods such as kriging. The U.S. EPA has proposed the use of geostatistical methods such as kriging for the development of sampling plans.[13]

An advanced method of kriging, e.g., probability kriging, has been used to derive probability-contour maps, i.e., concentration contours having associated confidence limits.[5] This method is significantly more complex than ordinary kriging, however, and is not as readily available for application as ordinary kriging. An alternative approach is to use the estimation variance, derived in ordinary kriging, to derive volumes with associated confidence intervals. This approach assumes that the kriging variance (estimation variance) is normally distributed, and the use of this approach has been cautioned by some researchers due to the sensitivity of the calculated kriging variance.[13]

Volume typically is not as significant an issue of uncertainty in groundwater remediation as it is for soil. Groundwater remedies, by and large, can be designed to be robust, implemented in phases or modified without substantial loss in work performed to date or increase in overall capital cost. Nevertheless, the evaluation of uncertainties can become worthwhile when capture zones for wellhead protection and tradeoffs of maximizing cleanup times while minimizing capital costs are to be evaluated. A variety of work has been done to date in the evaluation of uncertainty in the effectiveness of groundwater pumping schemes. Many of the quantitative approaches to evaluating this uncertainty address aquifer parameters such as transmissivity or porosity as a random variate. The WHPA model, for example, incorporates a subroutine for quantitatively characterizing uncertainty in the effectiveness of an extraction well to contain a groundwater plume by use of Monte Carlo simulation with parameters such as transmissivity and porosity as random variables.[15] The model, however, ignores the correlations that exist between parameters and is limited to the application of a single extraction well in a homogeneous aquifer. More elaborate analyses, where the aquifer is treated as nonhomogeneous, have been investigated by a number of researchers. Because uncertainties in aquifer parameters and extraction system performance generally are resolved through pump tests, an "observational approach"[1] to investigations may prove to be more cost-effective than detailed uncertainty analyses.

CONCLUSION

Methods of quantifying uncertainty in the RI/FS process have been developed, and more methods are likely to be developed in the near future. Although they may introduce greater complexity to the decision-making process, the need to address uncertainties will become more important to devise defensible sampling strategies and remedial actions, given the scientific limitations in the data and in the methods of analysis used. Uncertainty analyses should be a principal focus of the RI/FS and should be used to develop appropriate contingency plans to the selected remedial action plan. The consequences of not addressing uncertainty will depend on the extent to which PRPs, the public and the agency overseeing the RI/FS consider uncertainties to be an issue.

ACKNOWLEDGEMENTS

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Indirect Assessment of Risk to Groundwater from Hydrocarbon Contamination in Overlying Soils

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ABSTRACT

A leak in a petroleum pipeline in California's Central Valley contaminated the adjacent soil with hydrocarbons. The initial investigation established that high levels of total petroleum hydrocarbons (TPH) contaminated the area's clayey jointed soils to a depth of 30 feet. The unsaturated zone was known to be at least 40 feet deep, but depth to groundwater was uncertain. The TPH contamination appears to follow a 90 degree joint set and has a sharp, well-defined base. Benzene, ethylbenzene, toluene and xylene (BETX) constituents also were determined to be present.

Brown and Caldwell Consultants (BCC) proposed assessing the risk to groundwater indirectly by applying, in the field, the Leaking Underground Fuel Tank Field Manual (LUFT Manual) risk assessment procedures of the California State Water Resources Control Board. The advantage in using this method was the avoidance of drilling to possibly great depths through a clean soil column. The procedures assess the risk of groundwater contamination on the basis of cumulative BETX concentrations in the soil column. If the cumulative concentrations indicated no risk, drilling would cease. If risk were indicated, drilling would continue to groundwater and a groundwater sample would be collected for analysis.

The California Regional Water Quality Control Board, Central Valley Region (Regional Board), the agency charged with protection of water quality in the Central Valley, insisted on a direct groundwater sample. BCC installed a monitoring well in May of 1990 and collected groundwater samples for analysis. BCC also later characterized BETX contamination of the soil column according to the LUFT Manual method. Application of the LUFT Manual method in the field would have resulted in drilling to 75 feet, terminating the borehole in the unsaturated zone and concluding that groundwater at a greater depth would not be contaminated. After installing a groundwater monitoring well and collecting a direct sample, BCC found that groundwater, occurring at 106 feet below ground surface under confined conditions, had not been contaminated with hydrocarbons leaching from the soil contamination.

INTRODUCTION

A leak in a pipeline carrying petroleum products contaminated approximately 33,000 yd³ of soil with hydrocarbons. The products carried in the pipeline include a gas-oil mixture, crude oil and petroleum distillate with carbon chain lengths ranging from C-6 to C-32. Figure 1 shows the site, borehole locations, the monitoring well location installed during the investigation and two cross-section lines.

The pipeline is located in the California Central valley adjacent to the California Aqueduct (Aqueduct). The pipeline leak occurred at a bend in the pipeline where the pipeline crosses the Aqueduct. The Aqueduct is a concrete-lined canal carrying water from the Sacramento-

San Joaquin Delta to southern California.

The two major concerns were that hydrocarbons might have contaminated the underlying groundwater and that hydrocarbons might enter the water carried in the adjacent Aqueduct. The leak site was approximately 8 feet below ground surface and 60 feet from the Aqueduct embankment. Approximately 50 yd² of contaminated soil are in contact with the Aqueduct embankment (at the location of Borehole 5; Fig. 1). The concern was that any bank storage water contaminated with hydrocarbons might leak into the Aqueduct. After discussions, BCC
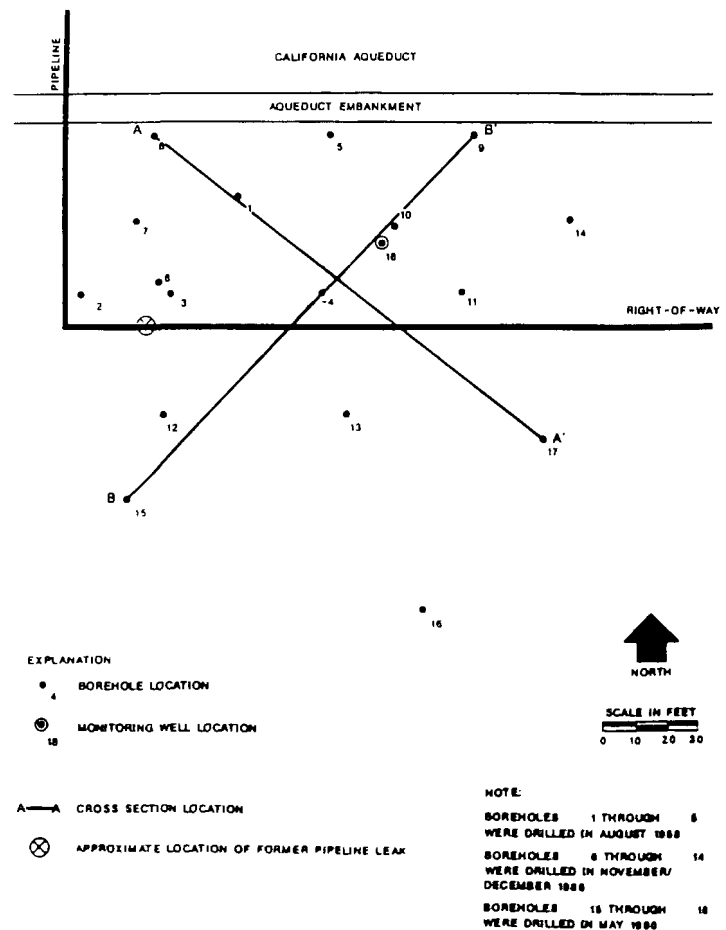
Figure 1
Site Map

and the California Department of Water Resources (DWR), which operates the Aqueduct, agreed that during normal operation of the Aqueduct, the pressure of water in the canal against the sides of the Aqueduct should prevent any significant amount of Aqueduct water in bank storage from entering the canal.

The initial investigation, which took place in the summer and fall of 1988, succeeded in defining the extent of soil contamination at the leak site. Fourteen continuously cored boreholes (Boreholes 1 through 14) were drilled to 30- to 40-foot depths. Borehole core samples were almost entirely dry clay with evidence of joints. Contour maps of the TPH analytical results of the soil samples at 5-foot intervals were used to estimate the volume of contaminated soil and to depict the occurrence of the contamination. These contour maps indicated that most of the contamination had migrated from the leak site in two directions: to the southeast and to the northeast. These apparent migration routes, along with the joints identified in the core samples, indicated the presence of two joint sets, one set parallel and one set perpendicular to the regional northwest strike. Figure 2 shows two cross sections drawn parallel and perpendicular to the regional strike, with the TPH contamination shown in profile. The bulk of the contaminated soil was found to occur between 10 and 25 feet below ground surface. The highest TPH concentration at 20 feet below ground surface was 40,500 mg/Kg. The deepest TPH contamination was found at 30 feet below ground surface. Groundwater was not encountered in any borehole.

EXPLANATION

- •⁴ BOREHOLE LOCATION AND NUMBER
- SAND: APPROX. 75% SAND, 25% FINES
- CLAYEY SAND: APPROX. 60-70% SAND, 30-40% FINES
- SILT AND SANDY CLAY: APPROX. 20-25% SAND, 75-80% FINES
- CLAY: APPROX. 5-15% SAND, 85-95% FINES
- CONTOUR INTERVAL - 10,000 mg/kg TOTAL PETROLEUM HYDROCARBONS

NORTH

HORIZONTAL AND VERTICAL SCALE IN FEET

0   10   20   30
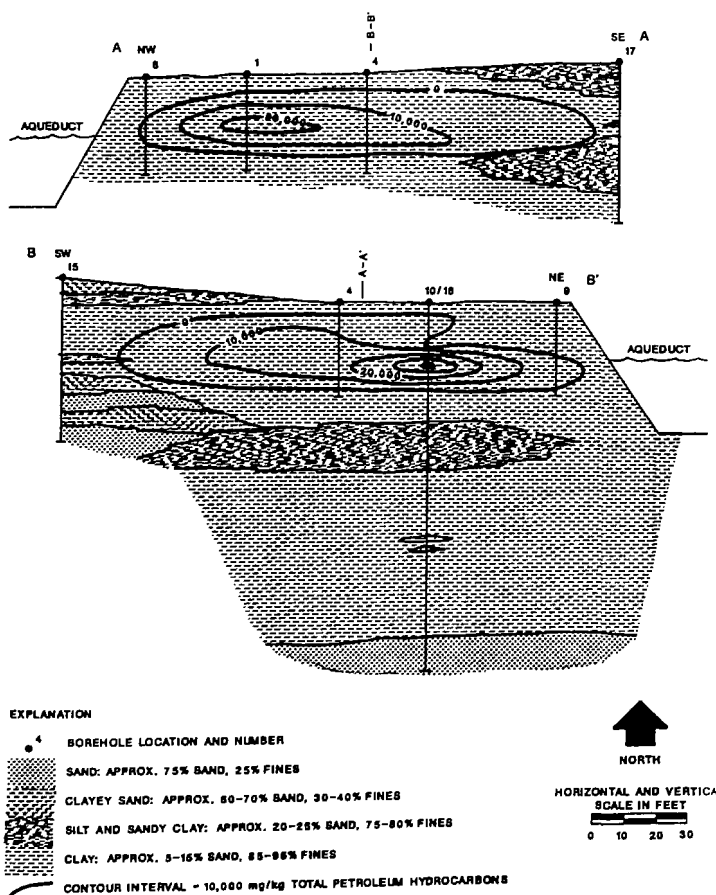
Figure 2
Cross Sections: Total Petroleum Hydrocarbon
Concentrations in Soils

ASSESSING THE RISK TO GROUNDWATER

The Regional Board was concerned that the hydrocarbons in the soil, particularly the more mobile BETX constituents, might have migrated downward and contaminated groundwater beneath the site. The Regional Board requested that groundwater monitoring wells be installed and groundwater samples be collected.

Little information was available on depth to groundwater beneath the leak site. The site lies at the western edge of the Great Valley Geomorphic Province of California. It is south of the San Francisco Bay area near the boundary between the Central Valley and the Coast Ranges. Unconsolidated and semi-consolidated sedimentary deposits of Tertiary- and Quaternary-age (including the Plio-Pleistocene-age Tulare Formation) overlie the Coast Range rocks. The Coast Range in this area is a folded and faulted sequence of metasedimentary rocks of marine origin and basement rocks of Jurassic-, Cretaceous- and Tertiary-age. The Tulare Formation, which crops out at the site, is a regionally extensive unit made up of beds, lenses and tongues of clay, sand and gravel. Thick layers of clays accumulated in intermittent shallow lakes during deposition of the Tulare Formation. This formation is the major fresh water-bearing formation in this part of the Central Valley and contains water under a variety of pressure conditions, including unconfined, semiconfined and confined.

A record search of existing well logs yielded little useful information on depth to groundwater. A field survey was conducted of wells at the nearest residences and businesses. On the basis of these data, static water level was estimated to be approximately 70 feet below ground surface at the project site. However, no direct measurements or well logs were available from the field survey. In addition, the information gathered was from wells on both sides of the Coast Range-Central Valley boundary. Uncertainty over whether the information obtained from the field survey was accurate and applied to the same aquifer made a reliable estimate of depth to groundwater difficult.

BCC was concerned about avoiding drilling through a thick column of uncontaminated soil to collect a groundwater sample. BCC and the Regional Board discussed what criteria to use in making field decisions about how far to drill before deciding that a direct sample was not necessary and they could conclude that groundwater had not been contaminated. BCC proposed applying the *Leaking Underground Fuel Tank Field Manual's* risk assessment procedures to make field decisions. The *LUFT Manual* risk assessment procedures include a method for determining if a column of soil with known BETX concentrations represent a risk to underlying groundwater. The method is intended to aid in establishing soil cleanup levels at a site where depth to groundwater is known. BETX concentrations from soil samples collected from the borehole column at 5-foot intervals are individually summed. The resulting cumulative concentrations are compared with distance to groundwater and mean annual precipitation to arrive at acceptable levels of soil contamination protective of groundwater quality. The acceptable levels have been determined from modeling of environmental fate and chemical data for BETX. The suitability of this risk assessment procedure for a particular site is determined by a check list that includes geomorphology; surface recharge; extent of soil contamination; maximum BETX concentrations; subsurface conduits; the presence of structures such as fractures, joints or faults; a minimum distance between soil contamination and groundwater; and the presence of sand or gravel layers. This particular site met all check list requirements, with the exceptions of the extent of soil contamination and the presence of joints in the soil.

To use this method as a field tool, BCC proposed having soil samples collected at 5-foot intervals with analysis on 24-hour turnaround for BETX. When the cumulative concentrations were known and acceptable depth to groundwater for those concentrations determined, BCC would drill to that depth. If the soil column beneath a cumulative concentration level was free of contamination and groundwater was not encountered, BCC would not install a monitoring well, but rather would grout the borehole back to ground surface. If groundwater was encountered, a monitoring well would be installed. If additional contamination was encountered, the cumulative concentrations would be redetermined and the process would continue until either the required column of clean soil was encountered or groundwater was encountered.

Because the Regional Board knew of several cases where little or no TPH or BETX were found in the soil column yet groundwater was contaminated and because of the volume of contaminated soil at this site, the Regional Board did not allow this use of the *LUFT Manual*

method. Instead, it required the installation of a monitoring well and the collection of a groundwater sample.

INSTALLATION OF THE GROUNDWATER MONITORING WELL

In May 1990, a 115-foot deep monitoring well was installed at the site in Borehole 18. Three additional boreholes (Boreholes 15, 16 and 17) also were drilled at this time to confirm the earlier estimate of soil contamination. During drilling of Borehole 18, a continuous core was collected for lithology and samples were collected for analysis for BETX and TPH at 5-foot intervals. Dry, fractured clay extended to 40 feet below ground surface. A 15-foot-thick clayey silt was encountered beneath the near-surface clay. Massive, unfractured clay was found beneath the clayey silt to a depth of 106 feet below ground surface, at which depth groundwater was encountered under confined conditions in a silty sand. Groundwater rose in the borehole to 47.5 feet below ground surface.

During initial installation of the monitoring well, the bentonite seal placed on top of the well sand pack could not withstand the 58.5 feet of pressure head in the annular space. The bentonite collapsed when grout was added. Groundwater rose to the surface in both the annular space and the well casing. The grout entered the sand-packed annular space, the screened interval of the well and possibly the aquifer. The casing string was pulled out of the borehole and cleaned. The borehole was reamed and the well was successfully reinstalled with a much thicker bentonite seal. The lithology of Borehole 18 and the construction of
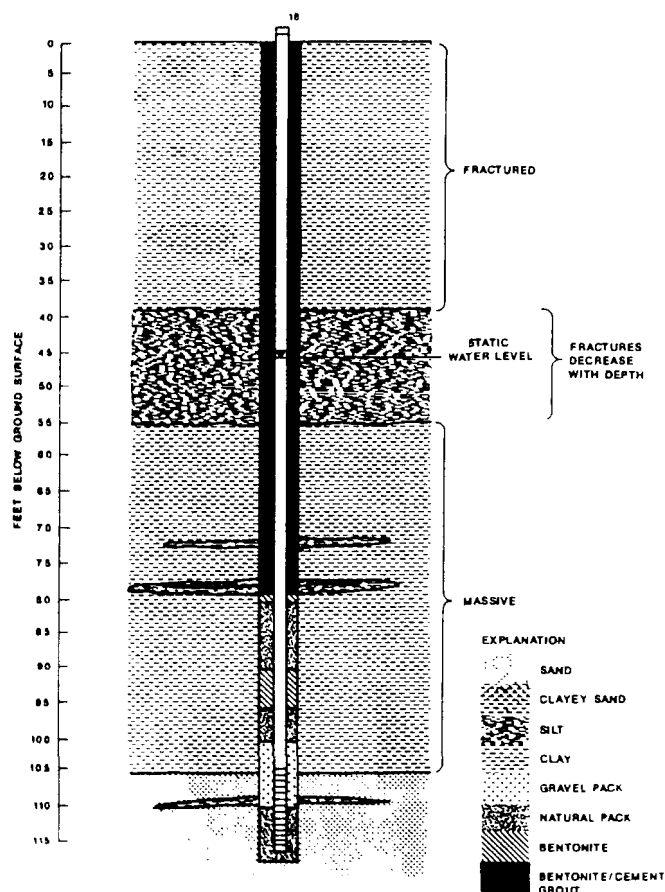
Figure 3
Geology of Borehole 18

the well are shown on Figure 3.

Trace BETX concentrations extended 15 feet below any detectable TPH. There were approximately 15 feet of clayey silt underlain by approximately 50 feet of massive clay between the BETX in the soil

and the groundwater. TPH and BETX concentrations in the soil column are shown in Figure 4.

Total Petroleum Hydrocarbons, mg/kg	Borehole 18 depth, feet	Concentrations, ug/kg			
		Benzene	Ethylbenzene	Toluene	Xylene
N.D.	5	570	670	2,060	3,860
	10	5,870	11,800	31,400	68,000
	15	7,620	15,300	32,800	85,700
40,500	20	15,900	16,800	55,500	94,700
	25	6,470	10,400	25,700	60,800
N D	30	56	15	84	60
N.D	35	29	7	130	50
N.D.	40	N.D.	N.D.	N.D.	N.D
	45				
	50				
	55				
	60				
	65				
	70				
	75				
	80				
	85				
	90				
	95				
	100				
	105				
Confined Aquifer	110				
	115				

N.D = Not detected

Figure 4
Total Petroleum Hydrocarbon and Benzene, Ethylbenzene, Toluene and Xylene Concentrations in Soils, Borehole 18

Table 1
BETX Concentrations in Groundwater Samples

Constituent	5/25/90	5/31/90	7/3/90
Benzene, µg/l	3.8	1.4	<0.5
Ethylbenzene, µg/l	9.5	3.8	<0.5
Toluene, µg/l	20.1	7.3	1.0
Xylene, µg/l	35.0	13.3	2.2
pH[a]	10.7	9.3	8.3
Cumulative gallons purged	440	770	1,520

[a]Field measurement.

A total of 1,520 gallons of water was purged from the well over the course of three sample collection events. Electrical conductivity and pH were monitored during all purging events. The BETX concentrations in the three groundwater samples collected are shown in Table 1. The field-measured pH and cumulative total gallons purged at the time of the sample's collection are also shown. A definite correlation between declining BETX concentrations and pH with increasing volumes of groundwater purged from the well can be seen. The high pH is attributed to the effects of grout entering the groundwater during the initial construction of the well. The initial BETX concentrations in groundwater samples are attributed to contact with the near-surface soils during the time the borehole was drilled and remained open during the construction of the well. The borehole was completely filled with a groundwater, grout and sand mixture during initial construction of the well.

The occurrence of TPH only in the jointed clays suggests that vertical contaminant transport, like the lateral transport along suspected joint sets, is joint controlled. BETX constituents have migrated slightly deeper
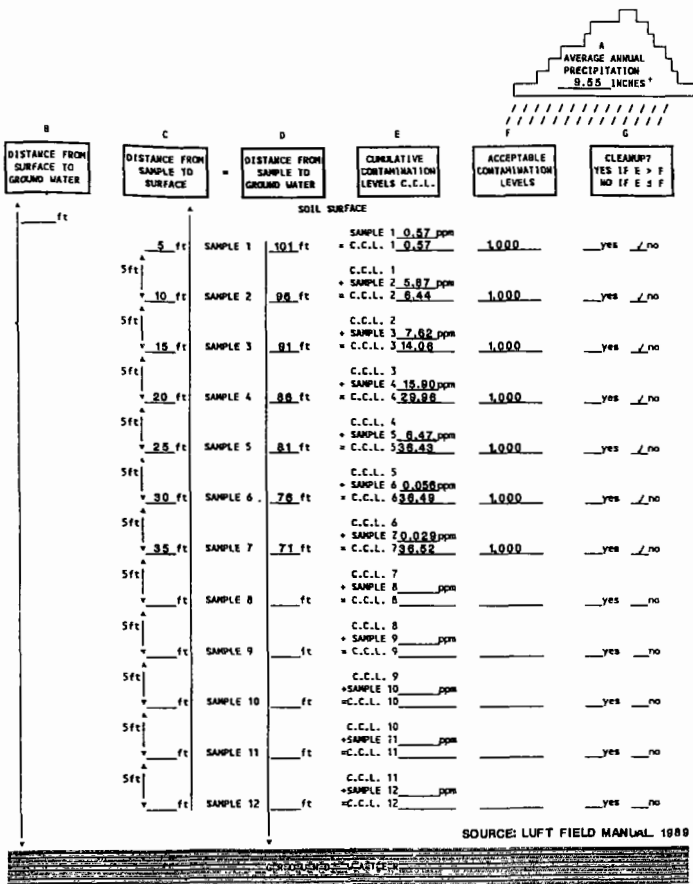
than detectable TPH. The massive clay layer beneath the deepest BETX occurrence appears to have effectively retarded any further vertical migration.

Considerable purging of the well has almost removed the contamination introduced in the immediate vicinity of the well during drilling/installation. BCC believes the aquifer has not been contaminated by leaching processes. The pressure head exhibited by groundwater in the confined aquifer indicates the massive clay aquitard is probably laterally extensive and can be expected to continue to act as an effective barrier to downward contaminant migration.

APPLICATION OF THE *LUFT MANUAL* RISK ASSESSMENT PROCEDURES

The *LUFT Manual*'s risk assessment procedures were applied to the BETX concentration results in the soil column of the 115-foot-deep monitoring well following the completion of the fieldwork. This was done by BCC at their expense to satisfy curiosity about whether, in hindsight, the field application of the *LUFT Manual* method at this site would have been a good procedure.

Of the four BETX constituents, the benzene cumulative concentrations were found to be the driving force in how deep the borehole would have been drilled if the method had been used in the field as BCC proposed. The environmental fate worksheet for benzene at this site and the table for acceptable cumulative soil contamination levels for benzene are shown in Figures 5 and 6, respectively.

The benzene cumulative concentrations would have indicated that groundwater at a depth of 75 feet below ground surface would not have been at risk of benzene contamination. Upon drilling to 75 feet below ground surface and finding no detectable benzene between 35 feet and 75 feet, BCC would have terminated the borehole at that depth and grouted. It would then have been presumed that groundwater beneath the site (deeper than 75 feet below ground surface, although the actual depth would remain unknown) was not contaminated with hydrocarbons.

CONCLUSIONS

The application of the *LUFT Manual* risk assessment procedures as a field decision tool at this site would have resulted in terminating the borehole at 75 feet below ground surface. It would have been established

Figure 5
Environmental Fate Worksheet

Stop: Do not use this table unless the site in question has been screened using the applicability checklist (Table 2-2) for general risk appraisal to protect ground water

MEAN ANNUAL INCHES PRECIPITATION

		0 to 5	5.1 to 6	6.1 to 7	7.1 to 8	8.1 to 9	9.1 to 10	10.1 to 11	11.1 to 12	12.1 to 14	14.1 to 16	16.1 to 18	18.1 to 20	20.1 to 22	22.1 to 24	24.1 to 26	26.1 to 28	28.1 to 30	30.1 to 32	32.1 to 34	34.1 to 36	36.1 to 38	38.1 to 40
	5-9.9	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	10-14.9	5	3	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	15-19.9	10	10	6	3	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	20-24.9	60	40	20	10	5	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	25-29.9	200	100	60	30	10	7	3	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	30-34.9	800	400	200	100	40	20	10	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0
DISTANCE	35-39.9	1000	1000	700	300	100	60	20	10	3	1	0	0	0	0	0	0	0	0	0	0	0	0
	40-44.9	1000	1000	1000	1000	400	100	80	30	9	2	0	0	0	0	0	0	0	0	0	0	0	0
TO	45-49.9	1000	1000	1000	1000	1000	500	200	100	20	4	1	1	0	0	0	0	0	0	0	0	0	0
	50-54.9	1000	1000	1000	1000	1000	1000	600	200	50	9	2	2	1	1	0	0	0	0	0	0	0	0
HIGHEST	55-59.9	1000	1000	1000	1000	1000	1000	1000	700	100	20	5	3	2	1	1	0	0	0	0	0	0	0
	60-64.9	1000	1000	1000	1000	1000	1000	1000	1000	300	40	9	6	4	3	2	1	1	0	0	0	0	0
GROUND	65-69.9	1000	1000	1000	1000	1000	1000	1000	1000	700	80	10	10	8	5	3	2	1	1	0	0	0	0
	70-74.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	100	30	20	10	9	6	4	2	1	1	0	0	0
WATER	75-79.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	300	60	40	20	10	10	7	4	2	1	1	0	0
	80-84.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	700	100	70	40	30	10	10	7	4	2	1	1	0
FROM	85-89.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	200	100	80	50	30	10	10	7	4	2	1	1
	90-94.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	400	200	100	90	50	30	10	10	6	3	2	1
SOIL	95-99.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	700	400	200	100	90	50	30	10	10	5	3	1
	100-104.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	800	400	200	100	90	50	20	10	8	4	2
SAMPLE	105-109.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	800	400	200	100	80	40	20	10	7	3
	110-114.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	700	400	200	100	70	30	10	10	5
IN	115-119.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	600	300	100	90	40	20	10	7
	120-124.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	500	200	100	60	30	10	10
FEET	125-129.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	900	400	200	100	40	20	20
	130-134.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	700	300	100	60	30	30
	135-139.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	500	200	100	40	40
	140-144.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	700	300	100	60
	145-149.9	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	500	200	90
	150+	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	500	200	90

Note: Individual concentrations for any soil sample cannot exceed 100 ppm. The numbers in this table do not represent soil concentrations; they reflect the accumulation of pollutant mass in contaminated soil. These numbers can be derived from the LUFT manual worksheet (Table 2-3).

SOURCE: LUFT FIELD MANUAL, 1989

Figure 6
Acceptable Cumulative Benzene Contamination Levels

that 45 feet of massive, low permeability, uncontaminated clay existed between the contaminated soil and a depth of 75 feet. The decision to terminate the borehole at 75 feet would have been reasonable.

This case history application of the indirect *LUFT Manual* method of assessing the risk of groundwater contamination from hydrocarbon contamination in the overlying soil, supported by direct evidence collected at this site, suggests that the *LUFT Manual* method could be used in lieu of direct groundwater samples at similar sites. It points out the need to move away from adhering rigidly to the idea that direct samples are always necessary. More flexibility in designing fieldwork (and changing fieldwork in progress as additional geologic information is collected) should be allowed.

Monte Carlo Techniques for Quantitative Uncertainty Analysis in Public Health Risk Assessments

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ABSTRACT

Most public health risk assessments combine a series of average, conservative and worst-case assumptions to derive a conservative point estimate of risk. However, this procedure has major limitations. This paper demonstrates a methodology for extended uncertainty analyses in public health risk assessments using Monte Carlo techniques. The extended method begins as some conventional methods—with the preparation of a spreadsheet to estimate exposure and risk. This method, however, continues by modeling key inputs as random variables described by probability density functions. Overall, the technique provides a quantitative way to estimate the probability distributions for exposure and health risks within the validity of the models used. As an example, this paper presents a simplified case study for children playing in soils contaminated with benzene and benzo(a)pyrene.

INTRODUCTION

Following guidance published by the U.S. Environmental Protection Agency (EPA), most public health risk assessments combine a series of average, conservative and worst-case assumptions to derive a point estimate of risk that is conservative, i.e., protective of public health.[1,2] The *Interim Final Human Health Evaluation Manual*,[3] the most recent guidance document from the EPA headquarters, states:

"...Each intake variable in the equation has a range of values. *For Superfund exposure assessments, intake variable values for a given pathway should be selected so that the combination of all intake variables results in an estimate of the reasonable maximum exposure for that pathway.* As defined previously, the reasonable maximum exposure (RME) is the maximum exposure that is reasonably expected to occur at a site. Under this approach, some intake variables may not be at their individual maximum values but when in combination with other variables will result in estimates of RME..." (page 6-19, emphasis in the original).

Unfortunately, the Agency offers no further definition—either qualitative or quantitative—for the key concept of reasonable maximum exposure. The guidance does not address the amount of conservatism which should be used in risk assessment.

Current risk assessment procedures have three major limitations. First, by selecting a combination of average, conservative and worst-case assumptions, risk assessors and risk managers have no way of knowing the degree of conservatism in an assessment. Second, by setting the bias high enough to swamp the uncertainty for each of many variables—but not necessarily all the variables—the risk assessment considers scenarios that will rarely, if ever, happen. Third, it is fundamentally meaningless to run traditional sensitivity analyses (e.g., to make calculations at $\pm$ 10 or $\pm$ 25 percent from each input value) to determine the uncertainties in the final point estimates because many of the

input variables are at or near their maxima. Thus, the current procedures offer comfort if the estimated risk falls below a de minimis value, but they offer no interpretation if the estimated risk exceeds a de minimis value.

Developed long ago, Monte Carlo simulation addresses the weaknesses of the current risk assessment methods identified above.[4] In extending the regular methods for public health risk assessments, Monte Carlo techniques add several steps to estimate both point values and full distributions for the exposures and risks.

First, the analyst determines (continuous or discrete) probability density functions to describe each of the variables to be included in the uncertainty analysis. In this step, the analyst must also determine if any correlations exist among the input variables and take appropriate actions if they do.

Second, the analyst uses suitable software to make a large number of realizations of the random variables in the model. For each realization, the computer draws one random value from the appropriate distribution for each of the random variables in the model and computes and stores a single result. This computation is repeated a large number of times.

Third, with computer assistance, the analyst retrieves the results and establishes: (1) the shapes of the distributions for intermediate and final results and (2) various statistical summaries of the results. In this framework, a complete risk distribution is derived from distributions for the antecedent variables.[5-7] These extended techniques make the analyses more informative to risk managers and members of the public.[8]

In Monte Carlo simulation, each of many input variables can become a random variable (rv) with known or estimated PDF. [Equivalently, an input variable can be specified by a cumulative distribution function (CDF)]. Within this framework, a variable takes on a range of values with a known probability.

The PDFs for the final estimates are often highly non-Gaussian in shape for two reasons. First, some or all of the input variables may not have normal or even symmetric distributions. Second, the input variables enter the formulae by multiplication and division (and subsequent summation), so that even if all inputs have Gaussian distributions, the results will not.

To illustrate the application of Monte Carlo simulation to human health risk assessment, we consider a simplified case for a hypothetical site. We estimate the PDFs and summary statistics for the Incremental Lifetime Cancer Risk (ILCR) for one scenario involving exposures to two chemicals (benzene and benzo(a)pyrene) found in soil for two exposure pathways: (1) inadvertent ingestion of soils and (2) dermal contact with soils. We choose PDFs for the key input variables. By assumption, each of these distributions is statistically independent of

the others. (This assumption of independence limits the analysis as discussed below.) Each of these assumptions is reasonable (or not unreasonable) in view of the current knowledge and belief. The resulting simplified risk assessment illustrates the strengths and weaknesses of the Monte Carlo method.

While the Monte Carlo approach has many strengths and while it provides quantitative estimates of the distributions of the exposures and risks to people in certain situations, the results from this simplified analysis (and any simulation) are limited by many explicit and implicit assumptions. We present this simplified analysis to explore and demonstrate the approach as an extension to methods currently recommended by the U.S. EPA, not to claim that it represents an exhaustive treatment of the technique. We seek to illustrate the Monte Carlo method as applied to a simplified public health risk assessment and we seek to extend probabilistic analyses and interpretations in such assessments.

HYPOTHETICAL SITE AND EXPOSED POPULATION

For this report, we create a hypothetical site and an exposed population for analysis. Acme, a private company, owns the 500-ft by 600-ft site which is located at the edge of Central City. Beginning its operations in the early 1850s, Acme used and maintained 27 coke ovens and 2 gas holders and produced blue gas at the site until 1945 when the buildings and equipment were demolished. From 1952 to 1988, Baker Company leased the southern third of the property from Acme for use as a fuel storage and tank truck depot.

Central City created a 20-acre City Park to the north of the site in 1933. In 1989, Central City asked Acme to donate or sell the whole property to them to enlarge the City Park. At first, thinking that they might develop the site, Acme cleared the site and removed the visually stained surface soils. However, in further talks with the city last year, Acme agreed in principle to sell the property for inclusion in the park. Depending on the outcome of a site risk assessment for the surface soils on the site, Acme retains the right to limit the use of the site to activities with little or no soil contact, e.g., a parking lot with concession stands or a swimming pool with large concrete pavilions.

Since our purpose is to illustrate the use of Monte Carlo simulation, we consider only one of the many scenarios which could be considered for this site. The scenario considers children who play in the park extension contemplated for the old Acme/Baker property. We assume that the children will spend 3 hours per day playing at the park on the site and that they visit the park one day per week, 20 weeks per year for 10 years (from ages 8 to 18 years). We make the conservative and simplifying assumption that the children contact the soil enough with their hands and lower arms to have a rate of soil deposition on their skin of ~1 mg/cm² per day and they ingest ~50 mg per day of soil from the site.

Given the uncertainties inherent in an exposure assessment, this scenario is constructed in accordance with current U.S. EPA guidelines and using conservative (or health-protective) assumptions in the spirit of analyzing the RME case, not the absolutely worst case.

EXPOSURE MODELS

To estimate health effects for compounds with carcinogenic potencies, we first estimate the average daily dose that a person receives in units of milligram of bioavailable chemical per kilogram of body weight per day [(mg/(kg-day)], averaged over a 70-year life [abbreviated as the ADD(life)]. The scenario requires two exposure models: (1) incidental ingestion of soil and (2) dermal contact with soil.

Ingestion of Soil

In this simplified case, we consider exposures from the incidental and inadvertent ingestion of contaminated soil (i.e., we include only children who do not exhibit pica). We use the equation shown in Figure 1a to estimate the ADD(life), the average daily dose (bioavailable daily dose, averaged over a life in which exposure occurs), for inadvertent ingestion of contaminated soil.

Dermal Contact with Soils

Risk assessments often evaluate exposures from dermal contact with

contaminated soils. McKone (TM) recently completed a new model which estimates the uptake of chemicals from a soil matrix deposited onto the skin surface.[9] In the model, the stratum corneum is the barrier to uptake and the amount of chemical which passes through the stratum corneum represents the bioavailable dose. The model depends on scenario specific inputs, soil properties, skin properties and chemical properties of the soil contaminants. Although both continuous and one-time deposition versions of the model are available, we use the one-time or unit-deposition model in this simplified analysis.

$$ADD(life) = \frac{(Cs \cdot SIngR \cdot RBA \cdot DpW \cdot WpY \cdot YpL \cdot CF)}{(BW \cdot DinY \cdot YinL)}$$

where:

ADD(life)		average daily (bioavailable) dose, averaged over a lifetime (mg/(kg·d)),
Cs		soil exposure concentration (mg/kg),
SIngR		soil ingestion per day on a day of exposure (mg/d),
RBA		relative bioavailability (frac),
DpW	=	exposure days per week (d/wk),
WpY		exposure weeks per year (wk/yr),
YpL	=	exposure years per lifetime (yr/life),
BW	=	average body weight of the person (kg),
CF	=	conversion factor of 1 / 1,000,000 (kg/mg),
DinY	=	total number of days per year 7 (d/wk) · 52 (wk/yr), and
YinL	=	total number of years per lifetime (70 yr/life).

Figure 1a
Exposure Model for Soil Ingestion

McKone derives a Personal Exposure Factor (PEF) which, when multiplied by the concentration of the chemical in the soil, estimates the average daily dose on a day of exposure. This PEF is averaged over a day of exposure and is a function of 17 variables: average body weight, time the soil stays on the skin, average body surface area, skin area exposed, skin soil loading, soil bulk density, soil porosity, soil water content, organic carbon fraction of the soil, skin thickness, skin fat content, skin water content, boundary layer size, octanol-water partition coefficient of the chemical, Henry's Law coefficient of the chemical, diffusion coefficient for the chemical in air and diffusion coefficient for the chemical in water. To estimate the ADD(life) for dermal exposures, we use the PEF in the equation shown in Figure 1b.

$$ADD(life) = \frac{(Cs \cdot PEF \cdot DpW \cdot WpY \cdot YpL)}{(DinY \cdot YinL)}$$

where:

ADD(life)	=	average daily (bioavailable) dose, averaged over a lifetime (mg/(kg·d)),
Cs	=	soil exposure concentration (mg/kg),
PEF	=	personal exposure factor, averaged over a day of exposure (kg/(kg·d))
DpW	=	exposure days per week (d/wk),
WpY	=	exposure weeks per year (wk/yr),
YpL	=	exposure years per lifetime (yr/life),
DinY	=	total number of days per year 7 (d/wk) · 52 (wk/yr), and
YinL	=	total number of years per lifetime (70 yr/life)

Figure 1b
Exposure Model for Dermal Contact with Soils

Since McKone's model requires 17 inputs (and creating or finding 17 different parameterized distributions is an arduous task), we per-

formed a standard sensitivity analysis to identify the most sensitive inputs. By varying each input variable ± 10 percent from its nominal value while holding all the other inputs constant, we found those variables which have the greatest effect on the output when changed.

After defining our exposure models, we need to: (1) identify point estimates for all of the model inputs, (2) find in the literature or formulate distributions for the inputs we want to vary and (3) put all of the information into an appropriate simulation program. For use in both exposure models, we formulate distributions for the concentrations (mass fractions) of benzene and benzo(a)pyrene (BaP) in the site soils and the cancer potency factors (CPFs). Considering the results of the sensitivity analysis, we formulate distributions for 6 of the 17 input variables of McKone's model: body weight, the time soil stays on skin, skin area exposed, soil loading, bulk density of soil and skin water content. In addition, for the soil ingestion model, we formulate distributions for soil ingestion rates and body weight of the children. This gives a total of 11 parameterized distributions.

POINT ESTIMATES AND PARAMETERIZED DISTRIBUTIONS

In this paper, we use three well-known distributions to describe the key model inputs: the normal or Gaussian distribution, the lognormal distribution and the uniform distribution. We assume the reader is familiar with each of these distributions.

We denote random variable X with a normal distribution as X ~ Normal (μ, σ), where μ and σ represent the arithmetic mean and standard deviation, respectively. Similarly, the lognormal distribution is denoted as X ~ Lognormal (m, s) where m and s represent the arithmetic mean and standard deviation of the underlying normal distribution, respectively. (The underlying normal distribution is generated by taking the logarithms of the values in the distribution). Finally, we use the notation X ~ Uniform (x1, x2) to show that the random variable X is distributed uniformly between fixed minimum (x1) and maximum (x2) values.

Chemical Concentrations in the Soils

For this hypothetical site, we synthesize a data set consistent with the site history. We estimate the exposure point concentration for each chemical in the soils as the 95th percentile of the arithmetic mean of the soil data, i.e., 3.39 mg/kg for benzene and 29.49 mg/kg for BaP. Next, following the Monte Carlo framework, we fit lognormal distributions to the synthetic data for each chemical to estimate PDFs for the exposure point concentrations (where Cs represents the concentration of the chemical in the soils on the site in mg/kg): $Cs_{benzene}$ ~ Lognormal (0.84, 0.77) and Cs_{BaP} ~ Lognormal (2.81, 0.68).

Cancer Potency Factors

Because of the assumptions made and the methodology used in their derivation, CPF values estimated from human or animal data are inherently uncertain values. Extending the ideas in earlier publications,[15-17] Crouch evaluated the U.S. EPA CPFs for benzene and BaP and estimated the degree to which the U.S. EPA values are overly conservative. Based on this information, we parameterize the CPFs for benzene and BaP, for use in quantitative uncertainty analyses, as lognormal distributions conditional on certain modeling assumptions. The CPFs for benzene and BaP have these distributions and each in units of (mg/(kg-day))$^{-1}$]: $CPF_{benzene}$ ~ Lognormal (−4.33, 0.67) and CPF_{BaP} ~ Lognormal (−0.79, 2.39).

We choose the published U.S. EPA CPFs as the point estimates of the CPFs for benzene and BaP, 2.9E-02 and 11.5 (mg/(kg-day))$^{-1}$), respectively.[18-20] These values occur at approximately the 88th and 91st percentiles of their respective distributions.

Point Estimates and Distributions for the Variables in the Exposure Models

Table 1 shows the 27 variables and constants in the two exposure models and the two CPFs. The first two columns of the Table show the name, symbol and units of the variable or constant. The third column indicates whether the parameter applies to the dermal contact model, the soil ingestion model or both. The fourth column gives the

point estimates for the inputs and the fifth column shows the parameterized distribution we used for those inputs we chose to vary. The sixth column specifies the sources of each of the point estimates and distributions and the seventh column gives the location of the point estimate in the distribution. All of the point values are reasonable in the sense that the U.S. EPA has endorsed or could readily endorse the values for a particular site.

RISK ASSESSMENT

In keeping with the methods recommended by the U.S. EPA,[3,11] we use the equation shown in Figure 1c for estimating Incremental Lifetime Cancer Risk from low-dose exposure to carcinogens by compound and by pathway. In the absence of specific information on possible synergisms or antagonisms among carcinogenic compounds, the total ILCR is estimated by summing the values for each compound over all pathways.

$$\text{ILCR} = \text{ADD(life)} \cdot \text{CPF}$$

where:

ILCR	Incremental Lifetime Cancer Risk, the additional probability that a person will develop cancer during lifetime (dimensionless probability)
ADD(life)	Average Daily Dose of a compound, averaged over life during which exposure occurs, (mg/(kg·d))
CPF	Cancer Potency Factor for a compound, using ingestion ((mg/(kg·d))$^{-1}$)

Figure 1c
Equation to Estimate Incremental
Lifetime Cancer Risk

Computation of the Point Estimates of Risks

We have now described all of the components of the spreadsheet. For steady conditions, the algebra in the spreadsheet describe the governing equations for source strength, transport of the contaminants, exposures and toxicities. We calculate the point estimate of risk in the usual fashion by combining the point estimates for the inputs. These point estimates of risk represent the stopping point for most risk assessments.

Computation of the Distributions of Risks

We now estimate distributions of health risks using the spreadsheet and Crystal Ball^{TM}(Market Engineering Corporation, Denver, CO). In the last column of Table 1, the random variables are grouped according to their anticipated effects on the output. The Group I variables have symmetric distributions and the point estimates fall at the average or median value. The Group II variables also have symmetric distributions, but the point estimates fall between the 75th and 95th percentiles. The Group III variables have nonsymmetric distributions and the point estimates fall near or above the mean. The Group IV variables are the CPFs. Each of these different groups has a different qualitative effect on the distribution for exposure dose.

When only point estimates are used in the simulation, the histograms for the results appear as lines because there is no variability in the outputs and the point estimates for the outputs match those estimated in the spreadsheet. In this example, most of the total risk comes from the dermal contact with BaP. Figures 2(a-g) and 3(a-g) show the histograms for the ILCRs from dermal contact with BaP in soils and from soil ingestion of benzene, respectively, using: (1) the point estimates, (2) the Group I random variables, (3) the Group II random variables, (4) the Group III random variables, (5) the combination of Groups I, II and III random variables, (6) the Group IV random variables and (7) the combination of the Group I, II, III and IV random variables. The right-hand black triangle under the risk axis shows the location of the

point estimate, and the gray area of the distribution represents the portion of the distribution which exceeds the point estimate.

The Group I random variables (body weight, surface area, soil loading, soil bulk density and skin water content) have symmetric (normal or uniform) distributions and the point estimates fall at the center of the distributions. Consequently, we expect the Group I variables to cause lightly-skewed spread around the point estimate for the outputs, with little or no lateral shift. As expected, the Group I variables acting jointly cause almost symmetric variation about the point estimates for the outputs (Figs. 2b and 3b).

Table 1
Variables and Constants in Exposure Models

Name, Symbol	Units	Model	Point Estimate	Distribution *	Source	Point Estimate Location	Group
Scenario Specific Data:							
average body weight, BW	kg	both	47	Normal (47,8.3)	10 (11)	mean	I
time soil stays on skin, T	hr	dermal	8	Normal (6,1)	10	95th percentile	III
average body surface area, SA	m2	dermal	1.4	Normal (1.4,0.17)	10 (11)	mean	I
fraction of skin area exposed, BF	frac	dermal	0.2	Lognormal (-2.15,0.5)	10 (11)	85th percentile	III
skin soil loading, SL	mg/cm2	dermal	1	Uniform (0.75,1.25)	10	mean	I
soil ingestion rate, SIngR	mg/d	ingestion	50	Lognormal (3.44,0.80)	10 (12,13)	75th percentile	III
exposure days per week, DpW	d/wk	both	1		10		
exposure weeks per year, WpY	wk/yr	both	20		10		
exposure years per life, YpL	yr/ life	both	10		10		
days in year, DinY	d/yr	both	364				
years in lifetime, YinL	yr/ life	both	70				
Soil Properties:							
soil bulk density, Rho(b)	kg/m3	dermal	1600	Normal (1600,80)	10	mean	I
soil porosity, Phi	m3/m3	dermal	0.5		9		
soil water content, Theta	m3/m3	dermal	0.3		9		
organic carbon fraction, foc	frac	dermal	0.02		9		
Human Skin Properties:							
skin thickness, Delta(skin)	m	dermal	1.5E-05		9		
skin fat content, f(fat)	kg/kg	dermal	0.1		9		
skin water content, Gamma	m3/m3	dermal	0.5	Normal (0.30,0.05)	10	mean	I
boundary layer size, Delta(a)	m	dermal	0.0045		9		
Chemical Properties:							
Kow, benzene	frac	dermal	135		9		
Kh, benzene	frac	dermal	0.224		9		
Kow, BaP	frac	dermal	1.55E+06		14		
Kh, BaP	frac	dermal	2.04E-05		14		
D(air)	m2/s	dermal	5E-06		9		
D(water)	m2/s	dermal	5E-10		9		
Soil Concentration:							
Cs, benzene	mg/kg	both	3.39	Lognormal (0.84,0.77)	10	95th % C.I. of mean	II
Cs, BaP	mg/kg	both	29.49	Lognormal (2.81,0.68)	10	95th % C.I. of mean	II
Relative BioAvailability:							
RBA, benzene	frac	ingestion	1		2		
RBA, BaP	frac	ingestion	0.3		2		
Cancer Potency Factors:							
CPF, benzene	(kg·d)/mg	both	2.9E-02	Lognormal (-4.33,0.67)	10(18-20)	88th percentile	IV
CPF, BaP	(kg·d)/mg	both	11.5	Lognormal (-0.79,2.39)	10(18-20)	91st percentile	IV

Note:

* For a normal, the mean and standard deviation are used to describe the distribution.

For a lognormal, the mean and standard deviation of the underlying normal are used to describe the distribution.

For a uniform, the low and high are used to describe the distribution
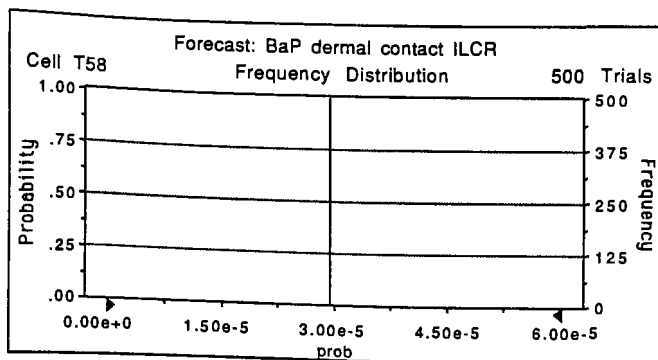
Figure 2a
Histogram of ILCR from dermal contact with
BaP in soils using the point estimates

Figure 2b
Histogram of ILCR from dermal contact with
BaP in soils using Group I random variables

Figure 2c
Histogram of ILCR from dermal contact with
BaP in soils using Group II random variables

Figure 2d
Histogram of ILCR from dermal contact with
BaP in soils using Group III random variables
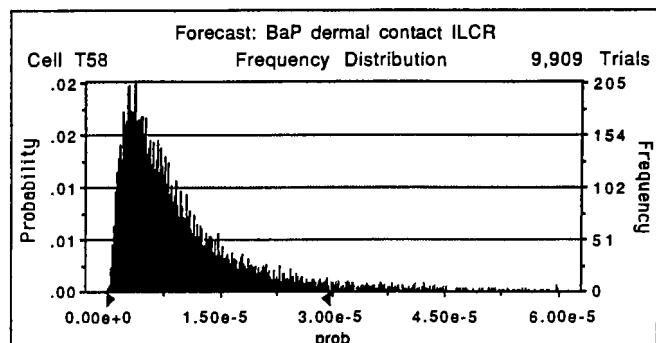
Figure 2e
Histogram of ILCR from dermal contact with BaP
in soils using Groups I, II and III random variables
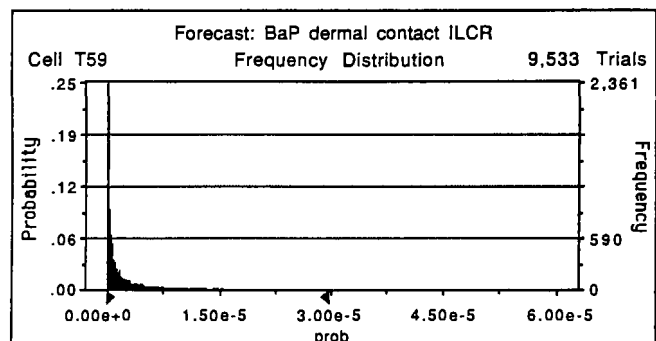
Figure 2f
Histogram of ILCR from dermal contact with
BaP in soils using Group IV random variables
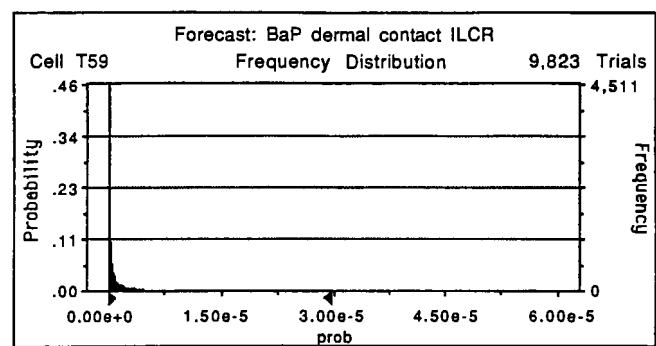
Figure 2g
Histogram of ILCR from dermal contact with BaP in
soils using Groups I, II, III and IV random variables
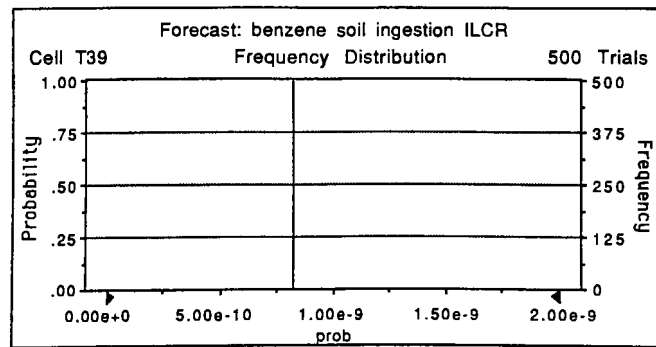
Figure 3a
Histogram of ILCR from dermal contact with
BaP in soils using the point estimates
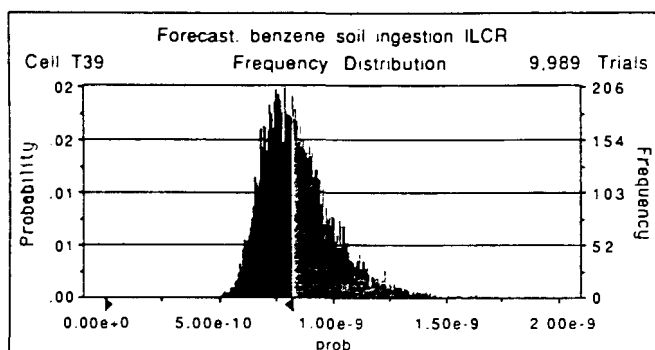
Figure 3b
Histogram of ILCR form dermal contact with
BaP in soils using Group I random variables
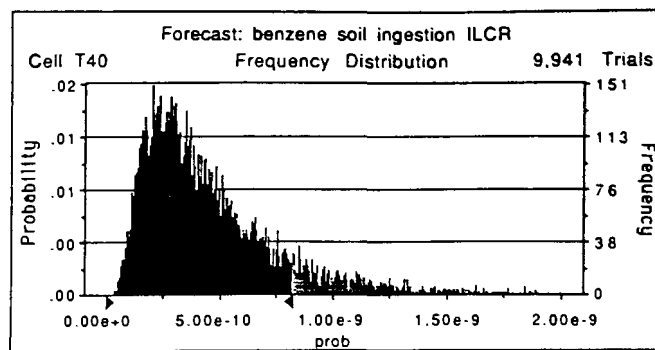
Figure 3e
Histogram of ILCR from dermal contact with BaP
in soils using Groups I, II and III random variables
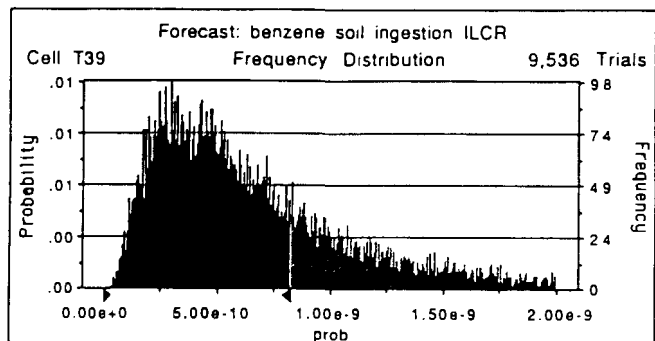
Figure 3c
Histogram of ILCR from dermal contact with
BaP in soils using Group II random variables
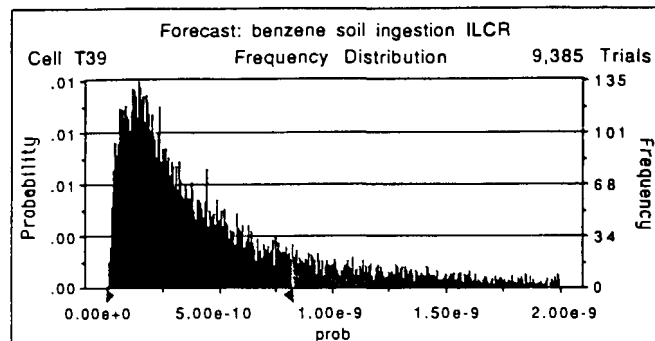
Figure 3f
Histogram of ILCR from dermal contact with
BaP in soils using Group IV random variables
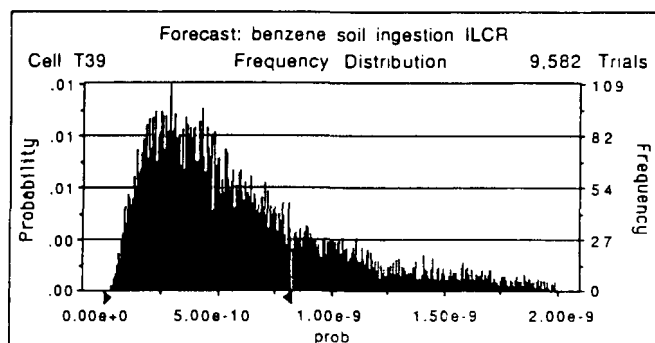
Figure 3d
Histogram of ILCR from dermal contact with
BaP in soils using Group III random variables
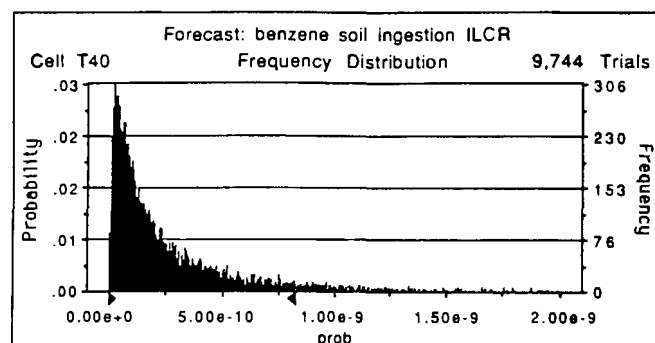
Figure 3g
Histogram of ILCR from dermal contact with BaP in
soils using Groups I, II, III and IV random variables

The Group II random variables include the concentrations of benzene and BaP in soils. Because the concentrations are modeled as lognormal distributions with the arithmetic means close to the point estimates, we expect these distributions will cause the results to have lognormally-shaped distributions. As expected, the distributions for the Group II random inputs cause moderately-skewed spread in the output distributions, with a general shift of the measures of central tendency for the output distributions to the left of the point estimates (Figs. 2c and 3c).

The Group III random variables include the soil ingestion rate, the time the soil stays on the skin and the fraction of the body exposed. For these random variables, the point estimates exceed the 70th percentile of the respective distributions, and we expect to see shifts in the distributions. As expected, the distributions in Figures 2d and 3d show dramatic shifts in the distributions toward values lower than the point estimates.

Figures 2e and 3e show the distributions with all Group I, II and III random variables in the simulation. As expected, these output

distributions have long right tails, high variance and average values much lower than the point estimates.

The CPFs for benzene and BaP with the distributions given earlier are the Group IV random variables. Figures 2f and 3f show the distributions for the five measures of risk. As expected, we see dramatic shifts in the distributions toward values lower than the point estimates. For each of the two pathways, the point estimates fall at the 88th percentile for benzene and the 91st percentile for BaP.

Finally, Figures 2g and 3g show the distributions with all Group I, II, III and IV random variables in the simulation. As expected, the output distributions in these figures have long right tails, high variances and average values much lower than the point estimates. The point estimates of risk fall between the 90th and 96th percentiles of the respective distributions. Comparing the results in the last three distributions of these figures, we see how combinations of conservative assumptions in the exposure scenarios (Figs. 2e and 3e) and in the Dose-Response Assessment (Figs. 2f and 3f) can shift the modes, medians and even

the 95th percentiles of the risk distributions far below the point estimates (Figs. 2g and 3g).

Simulation Tools, Run Times and Convergence

A variety of companies now sell software for running Monte Carlo simulations on microcomputers.[21-23] We prefer Crystal Ball^{TM}, which runs in conjunction with Excel^{TM} on Apple Macintosh^{TM} computers.

Crystal Ball^{TM} v2 running on a 25-MHz Apple Macintosh^{TM} IIci computer performed all the simulations in this report. A simulation with 10,000 iterations takes ~16 minutes. We compare the results from independent simulations as a way to test the convergence and stability of the results for the highly skewed distributions shown in Figures 5e and 6e. First, for two independent runs of 10,000 iterations each, the estimated means, standard deviations, variances and the 90th and 95th percentiles agree within one percent. Second, for two independent runs of 10,000 and 20,000 iterations, all of the summary statistics—except the sensitive 95th percentile and maximum—agreed within one percent. From this, we conclude that 10,000 iterations are sufficient to ensure convergence and stability of the output distributions. In a comprehensive Monte Carlo simulation, the analyst may spend a significant portion of time determining an appropriate number of iterations to support the final statements (unless the software does so automatically).

DISCUSSION

Advanced spreadsheets running on powerful personal computers now provide an easy and fast way to estimate full probability distributions for human health risks in assessments conducted for sites with chemical contamination. While the methods are straightforward and can easily be extended to linked spreadsheets and while the arrival of new software such as Crystal Ball^{TM} speeds the computations, more research is needed to determine and justify the specification of input distributions for exposure-related variables, and new methods are needed to quantify the distributions appropriate for Cancer Potency Factors.

As mentioned previously, the conclusions reached in this report rest on many assumptions which simplify the analysis but which also limit the results. While it is not possible to list all the simplifications — hence limitations — it is important to discuss some of the main types and to give illustrations. First and foremost, the report uses greatly simplified equations to estimate exposure to chemicals. While in the spirit of current federal guidance for public health risk assessments, these equations are dramatic simplifications of reality. This example demonstrates the point: the equation used to estimate children's exposure to soil ignores changes in body weight and in behavior as a function of age. The equation rests on the further assumption that all children are identical in size and behavior—surely an oversimplification.

Second, the report ignores obvious correlations among variables. As a prominent example, body weight and skin area are certainly correlated and the joint distribution of these variables is again a function of the age and sex of the child. As a less visible example, the thickness of the skin and the water content of it are surely correlated, if not related directly.

Third, even in the Monte Carlo simulations, the report treats many variables known to be stochastic as deterministic. For example, the simulations consider that children visit the site: (1) on a fixed number of days per week, (2) for a fixed number of weeks per year and (3) for a fixed number of years in their lives. Surely these simplifying assumptions limit the interpretation and application of the results. While it is relatively easy to overcome the third class of oversimplifications and limitations within current knowledge and computational resources, much more research is needed to address and resolve the serious limitations imposed by the first two classes of simplifying assumptions.

ACKNOWLEDGMENTS

TRADE MARKS

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A Classification System for Hazardous Chemical Wastes

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INTRODUCTION

Man has always lived with some degree of exposure to toxic materials in both the forms of natural toxins and natural background radiation. With the industrialization of society, the amount and type of toxic materials entering the environment has changed dramatically. Many of these compounds are manmade and their effects are, as yet, uncertain. The growth of industry and the country's population have increased the potential for exposure to the public and concern over the effects have risen.

Recent estimates are that industry in the United States alone generates approximately 2,500 pounds of hazardous wastes per capita each year.[1] As waste products are an inevitable consequence of production and consumption in today's society, the elimination of vast and increasing quantities of waste is an important issue facing us in the future. Despite the land ban provisions of RCRA and its amendments,[7] the ultimate fate of many hazardous waste materials is through land disposal. Landfills are simultaneously objectionable, undesirable and necessary.[2] They remain a requirement to assist in the protection of public health and safety through the prevention of uncontrolled disposal.

Presently all hazardous chemical wastes are subject to the same land disposal requirements, although many chemicals behave quite differently in the natural environment. The fate of hazardous chemical wastes in the environment is dependent upon both the characteristics of the site and the physical and chemical properties of the waste. Although characteristics of the site are quite variable from location to location, many of the physical and chemical properties of the wastes remain relatively constant. Since properties of chemical compounds will remain relatively constant at different sites, it may be possible to develop a ranking system based on these properties.

A simple, quick method of ranking hazardous substances can be used to assist managing the disposal of these materials. The use of chemical and physical parameter values, without applying weighted numbers, allows the ranking to be done objectively. As part of the decision-making process, the disposal method may be incorporated as a function of the potential hazard of the substance. One possibility is to consider those compounds with low potential hazards as candidates for municipal or sanitary landfills, while the higher potential hazard compounds should be immobilized, incinerated or placed in hazardous waste landfills with different degrees of retention.

The three chemical properties used to rank hazardous compounds are: toxicity, degradation potential and adsorption potential. The toxicity of a substance essentially describes the degree to which adverse effects may result from that substance. The more toxic a substance, the less of the substance is required to cause adverse effects. Degradation is the breakdown or change of a chemical in the environment. Many compounds are known to decay to less toxic substances quite readily, others

may remain in their original form for extended periods of time, and some hazardous compounds degrade to compounds of equal or greater toxicity. Adsorption is the ability of chemical substances to attach or bind to solid surfaces such as soil or aquifer materials. Many chemicals have a strong adsorption potential and may become relatively immobile in the environment.

RANKING ALGORITHM

Several ranking and classifications of hazardous substances have been promulgated. Many chemicals are classified into groups such as the persistent pesticide classification of Rao and Davidson:[3] pesticides are grouped as either nonpersistent, moderately persistent, or persistent. Others[4-6] have used the classification of degradable and nondegradable for other groups of compounds such as solvents and aromatic hydrocarbons.

Under RCRA,[7] hazardous wastes are classified as hazardous by their ignitability, corrosiveness, reactivity and toxicity. This method, however, gives no indication as to their potential environmental hazards once placed in a landfill. A bench mark ranking comparison was conducted by Conway[8] for pesticides. This comparison used the contaminants' physical constants to determine a leaching index, volatilization index and an exposure index. It ranks pesticides in the near surface application area.

Often ranking models rely on establishing a set of criteria such as chemical constants, hydrogeologic conditions, site designs and various other factors. Each criterion is then given a weighted index value which is then used to determine the environmental risk. The weighted values is often determined quite subjectively and may incorporate political and sociological factors that have little scientific basis.

The three characteristic parameters used in ranking substances are the chemical's toxicity, its adsorption potential and its potential for degradation. Adsorption and degradation are used because they are the two most important chemical characteristics that determine the ultimate fate of hazardous substances in the environment. The toxicity of a hazardous substance determines what concentration of the substance is necessary to have an adverse affect upon humans and/or the environment.

The toxicity level and the adsorption potential are used to determine a Hazard Potential Number (HPN) which can be defined by the equation:

$$HPN = 10^6/(K \text{ Tox}) \qquad (1)$$

where
HPN = Hazard Potential Number (unitless)
Tox = maximum concentration level (mg/L)
K = adsorption or distribution coefficient (mL/g)

and 10^6 is the constant used to convert units.

The HPN is inversely proportional to the toxic concentration of the compound. When comparing hazardous substances, the smaller the concentration required to create adverse conditions (10^{-6} cancer risk, death, etc.), the greater risk or potential for risk exists. The HPN is also inversely proportional to adsorption. Adsorption can be defined by a chemical's adsorption or partitioning constant. Again, a substance with a small adsorption constant indicates that it will not be readily adsorbed to soil and aquifer particles. Compounds that are not strongly adsorbed will tend to leach and migrate from their original source location and become a greater risk of possible contamination.

After determining the HPN for each chemical, the degradation process is considered. The degradation process for hazardous substances is often modeled using a first order reaction. The hazard potential can be viewed as reducing with time by the same first order reaction, so the equation will appear as:

$$HPN = HPN_o \exp[(k_b + k_H)t] \qquad (2)$$

where:

HPN = Hazard Potential Number (dimensionless)
HPN_o = Hazard Potential Number at time, t_o (dimensionless)
k_b = biological degradation rate constant $(time)^{-1}$
k_H = hydrolysis degradation rate constant $(time)^{-1}$
t = time

Since the amount of a chemical at a site will degrade and reduce exponentially with time, the HPN can be viewed as decreasing with time in a similar manner.

The hazard potential of a substance, with respect to time, can be characterized graphically, as in Figure 1, and several hazardous substances can be compared simultaneously.
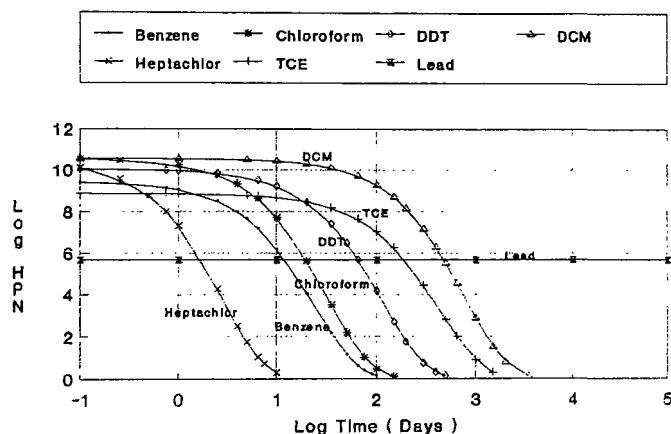
Figure 1
HPN vs. Time
Organics and Lead—Aerobic/Hydrolysis

The Hazard Potential Ranking depends upon several assumptions. The first assumption is that adsorption can be described by a linear isotherm and that an infinite number of adsorption sites exist, i.e., adsorption of the compound will always occur. The second assumption is that conditions exist for degradation to occur at the described rate. This essentially means that microorganisms are present for degradation, the necessary aerobic or anaerobic conditions are present and environmental conditions such as pH and temperature are met. Additionally, it is assumed that the products of degradation are less hazardous than the original substance or they are not hazardous. This means that their adsorption will not decrease and that they are either not toxic or less toxic. The final assumption is that equal amounts or concentrations of each hazardous substance exist. For any individual site, a weighted average hazard potential ranking could easily be calculated. However, at that time, all the site characteristics should be taken into account to determine the true hazard rather than the hazard potential.

TOXICITY

The toxicity of a hazardous substance is the concentration level at which adverse affects will occur to humans and/or their environment. The effects may be either acute or chronic. Exposure concentrations are established by government agencies such as the U.S. EPA or OSHA. To establish concentration levels, both exposure and health outcome data must be analyzed. Generally, extrapolations must be made from animal and/or human studies at high dose rates. This extrapolation is performed using either the threshold model for noncarcinogens or the linear no-threshold model for carcinogens (Figure 2). The threshold theory (Curve A) states that there exists a dose, at low levels, where no adverse effects might occur. The most common extrapolation for carcinogens is the linear no-threshold model, (curve B), which assumes that no dose level exists at which no biological effect occurs and that the degree of effect is directly proportional to the dose.[9] The no-threshold model is considered to be a conservative model that does not account for any type of biologic repair mechanisms.
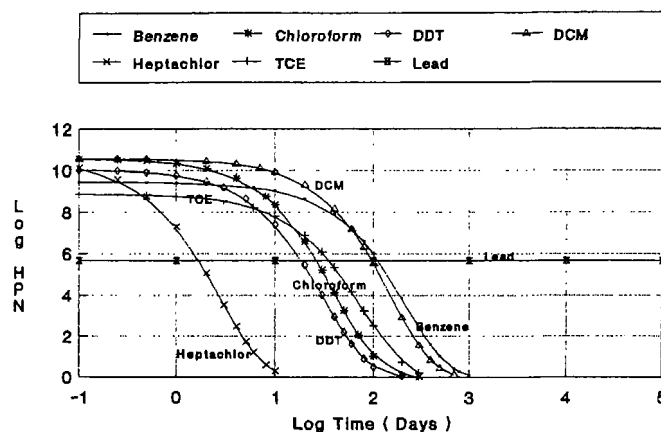
Figure 2
HPN vs. Time

Organics and Lead—Anaerobic/Hydrolysis

Correlation of chronic exposure is typically done on a population basis. Rates of illness in exposed populations are compared with reference populations. This effect is expressed as an exposure level that will cause a 10^{-5}, 10^{-6} and 10^{-7} increase in the effect. A maximum lifetime risk of 10^{-6} is considered to be an acceptable individual risk standard for exposure to carcinogens.[10] The U.S. EPA has established, in a series of publications,[11-18] the ambient water quality drinking levels at which effects may occur for many hazardous substances. The toxicity values used in this ranking model were all obtained from these publications and used the 10^{-6} risk values.

ADSORPTION

The adsorption process is the second key parameter in determining the HPN of each chemical. Adsorption is the accumulation or concentration of chemical contaminants on the soil or sediment surfaces.[18] The fate of a chemical in the environment is highly dependent upon its adsorptive behavior. Adsorption of chemicals onto soils and aquifer materials causes a reduction or retardation in the rate of movement of a contaminant through the soil or aquifer. Extremely strong adsorption may render a contaminant essentially immobile, although eventually all the adsorption sites could be occupied and breakthrough would occur. It is believed to assist directly and indirectly in the pollutant degradation process.[4]

Adsorption is generally described by the Langmuir and the Freundlich adsorption isotherms. The Freundlich isotherm can be further simplified to a linear isotherm. When adsorption can be defined as a linear relationship, the slope to the line is defined as the distribution or adsorption coefficient, Kd. The distribution or partitioning coefficient, Kd,

can vary widely between chemicals as some are more readily adsorbed than others. Additionally, for the same chemical, the degree to which it is adsorbed has been found to vary widely from soil to soil. Many researchers[19,20] have found that the adsorption of many organic compounds is dependent upon the organic content of the soil or aquifer particles. Karichoff[19] has shown a linear relationship between adsorption and organic carbon content which can be written as:

$$Kd = K_oc \times oc \qquad (3)$$

where

Kd = distribution of partitioning coefficient
K_oc = organic carbon partitioning coefficient
oc = fraction organic carbon.

Adsorption of organic compounds with respect to organic carbon, (K_{oc}), remains relatively constant for a given chemical and is nearly independent of soil type. The organic carbon partition coefficient generally assumes a linear isotherm exists for the determination of the distribution coefficient (Kd). The organic carbon partition coefficient does begin to lose consistency as soil organic carbon becomes extremely low or extremely high. Organic carbon partition coefficients are listed in several publications and also may be obtained from equations relating octanol-water partition coefficients with organic carbon coefficients.[36] The organic carbon partition coefficient was used for ranking organic chemicals.

DEGRADATION

The degradation or transformation process is the final parameter used in ranking the hazard potential of chemicals. Degradation of contaminants is a major process that determines the fate of many organic chemicals in the environment. Degradation can be described as the breakdown or transformation of a chemical substance into another substance. A fast degradation rate means the chemical may reach a safer concentration level quickly. As organic chemicals degrade, they may be transformed into less complex, more degradable and possibly less toxic substances. Degradation of chemical substances can occur by chemical and biological routes.

The rate of degradation by biological and chemical methods of many organic chemicals is dependent upon many conditions. The rate constant is often viewed as a pseudo-first order constant. Under actual environmental conditions, the rate constants for various chemicals can range over 14 orders of magnitude with corresponding half-lives of a few seconds to more than 100,000 years. Rate constants determined under laboratory conditions must be used with caution when applied to actual environmental conditions. Factors such as pH, temperature, catalysts and soil/sediment conditions may effect the rate constants.

Hydrolysis is a chemical transformation process in which an organic compound reacts with water forming a new carbon oxygen bond and cleaving an original carbon bond in the original organic molecule. A simple reaction can be defined by:

$$R-X \rightarrow R-OH + X^- + H^+ D \qquad (4)$$

The resulting product can then be more readily degraded or metabolized and may be less toxic than the initial substance.

Biological degradation is the transformation of chemical compounds by living organisms, generally bacteria and other microflora. Microorganisms can play a major role in the fate of organic chemicals because of their abundance, diversity, high metabolic activity and adaptability to varying environmental conditions. Microorganisms within the subsurface environment that breakdown or transform naturally occurring organic compounds have always existed and it has been shown that many of these same microorganisms are able to degrade synthetic or man-made organic chemicals.

The biodegradation process can occur under both aerobic and anaerobic conditions. Generally, the structure of the compound will determine under what condition and at what rate it will degrade. Some substances may degrade in both environments, possibly at different rates, while other substances may readily degrade only in the aerobic or

anaerobic environment. The biodegradation of many aromatic compounds requires molecular oxygen and therefore aerobic conditions. Many chlorinated hydrocarbons, such as pesticides, have been shown to degrade more readily under anaerobic conditions.[4]

Biological degradation is difficult to study in the natural environment, therefore laboratory studies such as microcosm studies are conducted. In general, a soil or aquifer sample is collected and the desired chemical substance is added to the sample. Under controlled conditions the loss of substances is measured at specific time intervals.

Mathematical modeling of both degradation processes can be described using first order kinetics. The use of first order kinetics also allows the easier application of the analytical transport model for evaluation. The first order model means that the rate of degradation is dependent upon the amount of substance and can be expressed by the equation:

$$d[C]/dt = -kx [C] D \qquad (5)$$

where

C = concentration of contaminant
t = time
k = first order rate constant

This can be integrated over time to obtain the equation:

$$C = C_o \exp[-k \times t] \qquad (6)$$

where

C_o = concentration at t_o

CHEMICAL INFORMATION

Seven different chemical compounds were used in this ranking model. The chemicals ranged from an elemental heavy metal to aromatic hydrocarbons to chlorinated hydrocarbons. The parameter values were obtained from various literature sources and are listed in Table 1. Degradation rate constants are reported in aerobic, anaerobic and field conditions when possible. Additionally, hydrolysis rate constants are reported for some compounds when available.

Table 1
Parameter Values

Chemical Compound	Toxicity (day-1)	Log Koc (ml/gm)	Aerobic Biodegradation (day-1)	Anaerobic Biodegradation (day-1)	Hydrolysis (day-1)	Field Degradation (day-1)	Ref
Benzene	4 6 E-04	2 03	0.042	0.004	---	--	11,19,21-24
Chloroform	1 Y E-04	1.53	0 03	0 022	0.0015	--	12,21,25-28
DDT	2 4 E-08	5 95	0 0001	0.022	0.0005 pH 5 / 0 00017 pH 11	0 00025	13,29,8,4,3 / 10-13
DCM	1 9 E-04	1 44	---	0 043	0.0015	---	14,21,27,28
Heptachlor	2 8 E-07	4 39	0 012	0.014	0.35	0 0006	15,8,11,34 / 1,29,32,35
Lead	0 05	--	0 0	0 0	0.0	0 0	14
TCE	2 7 E-03	2.0	0.0003	0.0003	0.0072	---	17,36,29,24 / 27,39

DDT = Dichloro-diphenyl-trichloroethane
DCM = Dichloromethane
TCE = Trichloroethylene

DISCUSSION

Comparison of Organic Chemicals

Despite a thorough computer search of the relevant literature and discussions with experts in the field, it quickly became obvious that there were insufficient data of adequate quality to develop a ranking system with enough compounds to make it generally applicable. Therefore, only six compounds for which sufficient information was available have been analyzed. These six chemical compounds were compared with respect to each other under three environmental degradation processes: anaerobic biodegradation, aerobic biodegradation and hydrolysis. The six hazardous compounds used are benzene, chloroform, DDT, dichloromethane, heptachlor and trichloroethylene. These were the six compounds with the best available degradation rate constants under all three conditions. Of the six compounds, four (DDT,

chloroform, DCM and heptachlor) have essentially equivalent initial HPNs followed by benzene with trichloroethylene having the lowest value. (Table 2)

Table 2
Hazard Potential Numbers (HPN) for Lead and Organics

Chemical Compound	Log HPI Koc (dimensionless)	Kaolinite		Montmorillinite	
		Log Kd (ml/gm)	Log HPN (dimensionless)	Log Kd (ml/gm)	Log HPN (dimensionless)
Benzene	7.15	-0.26	9.44	-0.006	9.19
Chloroform	8.19	-0.76	10.56	-0.51	10.29
DDT	8.27	3.06	10.05	3.31	10.31
DCM	8.28	-0.85	10.57	-0.60	10.32
Heptachlor	8.17	2.09	10.46	2.94	10.28
Lead @ pH 5.5	---	1.63	5.67	1.85	5.43
TCE	6.57	-0.29	8.86	-0.04	8.60

Comparison of Heavy Metal Lead & Organic Compounds

Metal ion adsorption cannot be directly correlated to the fraction organic carbon or to the organic carbon partition coefficient as with many organic compounds. To make a comparison between organic compounds and the heavy metal lead, the distribution coefficient, Kd, must be determined for the desired organic compound. For the two clay soils, kaolinite and montmorillinite, used in the lead adsorption analysis (USEPA 1978),[36] the percent organic carbon was 0.51% for kaolinite and 0.92% for montmorillinite. The Hazard Potential Number of lead (Figures 1 and 2) was compared with the organic chemicals benzene, dichlorobenzene, heptachlor and trichloroethylene at pH 5.5 for both soil types.

The Hazard Potential Number is a changing value. With time, the potential hazard of compounds can begin to decrease often at different rates. This process allows some substances with initially higher potential hazards to become less hazardous. This is the case with heptachlor and TCE under aerobic conditions. Initially, heptachlor is a much higher potential hazard than TCE, but it degrades more rapidly and its potential hazard drops below TCE. Comparing the changing HPN values under anaerobic and aerobic conditions shows how important the environmental conditions become in evaluating hazardous substances. Not only are the majority of the evaluated compounds degraded more readily under anaerobic conditions, but their relative risks are also changed after sufficient time has passed. DCM, which is less toxic than DDT, has essentially the same initial potential hazard because of its mobility in the subsurface. Degradation changes their relative potential hazard depending upon the environmental conditions. Because DCM has not been shown to degrade under aerobic conditions, its risk of exposure will depend upon a low hydrolysis rate constant while DDT is biodegradable at a faster rate and its overall hazard potential will decrease more significantly with time. Under anaerobic conditions, however, DCM's potential risk will decrease much more rapidly and become less than that of DDT's, given sufficient time.

When evaluated as a function of time, the respective ranking orders change in both aerobic and anaerobic environments. The initial ranking at time zero under both environments is DCM > DDT > chloroform > Heptachlor > benzene > TCE. Under anaerobic conditions (Figure 1) TCE degrades more slowly than the other evaluated compounds. After 100 days, its relative position has moved up dramatically to just below dichloromethane, which is essentially nonbiodegradable under anaerobic conditions. The new order becomes DCM > TCE > DDT > chloroform > benzene > heptachlor. The time for the HPN to decrease under anaerobic conditions is much less for several of the compounds as shown in Figure 2. Again, the ranking order changes significantly after 100 days to benzene > TCE > chloroform > DDT > DCM > heptachlor. This is essentially a complete reversal in the ranking order.

CONCLUSIONS

Most classification systems result in an invariant system. Sometimes this is based on conditions at a generic site with a specified transport time to the point of ingestion. Neither of these methodologies is satisfactory since degradation reduces the amount of a substance and decreases its potential exposure risk. Degradation has the ability to alter any ranking order with time. When degradation is incorporated into a ranking scheme as shown, hazardous substances can be compared at different time periods after disposal. This system shows how the properties of hazardous substances can be used in an objective ranking method and that the rankings can change with time.

Probabilistic Risk Assessment Applications to the Safety Evaluation of Technological Systems

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ABSTRACT

Risk assessment techniques provide a structured and systematic framework for evaluating the safety of technological systems. Information developed in the assessment aids in making decisions about the allocation of resources for safety improvements and hazard prevention by directing attention and efforts to the features and scenarios that dominate the risks.

Concepts and techniques for the application of risk assessment in relation to decisions on the safety evaluation of technological systems are provided. In particular, the basic concepts involved in the development and analysis of event trees, as applied to strategizing safety assessment tasks, are presented. The approach will provide an effective way to build the comprehensive and technically defensible information base necessary for tackling potential societal hazards. The emphasis is on identifying a systematic approach for assessing risk costs and other safety parameters associated with the failure of technological systems operating under several variable scenarios. By using the proposed methodology, those sequences of potential causative events and exposure scenarios contributing most significantly to risks can be identified and addressed.

INTRODUCTION

There is always some element of risk in every technological development/system. Faced with the bewildering array of risks in modern society, man is motivated more than ever before to develop systematic tools that will help bring the unpleasant but inevitable situation under control less expensively. This challenge is destined to remain alive. Systematic tools can be used to assess potential risks and courses of action to minimize the consequences attributed to such risks.

In recent years, great interest has evolved in the use of risk assessment tools for the evaluation of engineered facilities and other potentially hazardous activities. Risk assessment techniques provide a structured, systematic framework for evaluating the safety of such systems. In this manner, the risk associated with a decision alternative can be delineated and, if desired or necessary, measures can be taken to control or minimize the corresponding potential consequences.

Risk assessment generally embodies the heuristic approach of empirical learning, with large uncertainties in event probabilities and public consequences. Nonetheless, the central values of the final estimates do provide a "best knowledge" estimate of the relative importance of a risk. Through probabilistic modeling and analysis, uncertainties can be modeled and assessed properly, and their effects on a given decision can be accounted for systematically.

The process of quantifying risk does, by its very nature, deepen our understanding of the strengths and weaknesses of the system being examined. It shows where a given effort can do the most good in modifying a system to improve safety and efficiency. To arrive at more meaningful management decisions, however, results from the risk evaluation must also be supplemented, or complemented, with information relating to a number of external events.

PROBABILISTIC RISK ASSESSMENT (PRA) CONCEPTS

In a generic sense, risk assessment may be considered as a systematic tool for making estimates of all the significant risk factors that may prevail over an entire range of failure modes and/or exposure scenarios. The overall purpose of risk assessment is to provide a complete information set to risk managers, so that the best possible decision can be made concerning a potentially hazardous problem. A major goal in a risk assessment process is to identify failure modes and scenarios that will help work out methods to reduce the probability of failure and the attending human, economic and environmental losses of a failure event. Some major attributes of risk assessment include the following:

- It explicitly considers all failure modes and/or exposure scenarios
- It quantifies risks associated with the full range of loading conditions, system responses and exposure scenarios, not just extreme events
- It identifies factors and exposure routes contributing most to total risk of failure and/or exposure
- It facilitates determination of cost-effective risk reduction through remedial alternatives and/or risk management and prevention programs.

Tasks performed during a risk evaluation are intended to help answer the question "How safe is safe enough?" The type and degree of detail of a risk assessment performed will depend on the intended use of the process. Its purpose will shape the data needs, the protocol, the rigor and related efforts. Current regulatory requirements at the federal, state, and local levels are particularly important considerations in establishing acceptable safety levels.

Probabilistic Risk Assessment (PRA) is a method used to quantify the frequency of occurrence, the degree of system response and the magnitude of consequences of accident events or system failures at industrial facilities and other technological systems. Though its most extensive use has been in the nuclear industry, PRA has also been successfully used to estimate safety for a number of industrial facilities as well as for such undertakings such as the transport of hazardous materials. A PRA may use fault tree or event tree analysis. With the PRA method, risk is defined in terms of frequency and magnitude of consequences, or the failure probability. Subsequently, the product of frequency and magnitude, or the failure probability are summed over all incident sequences (Figure 1).

The concept of probability of failure required in the risk evaluation usually is defined by using the likelihood of structural breach and/or
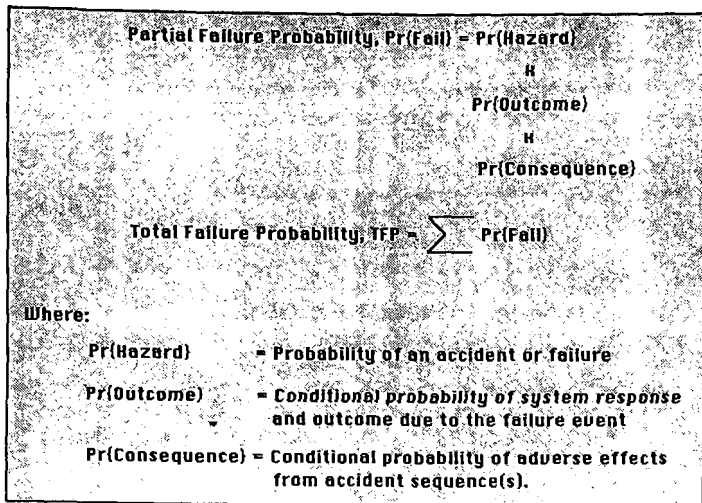
Figure 1
Risk Definition in a Probabilistic Assessment

an accident event. Estimation of the applicable probability values is achieved by the use of reliability theory and/or expert judgments or by the use of stochastic simulations and historical information. A Bayesian approach may always be employed to update estimates on the basis of additional information acquired in time.

Through probabilistic modeling and analyses, uncertainties can be assessed properly and their effects on a given decision accounted for systematically. In this manner, the risk associated with given decision alternatives can be delineated and then appropriate corrective measures can be taken accordingly.

EVENT TREE MODELING AS A TECHNIQUE IN THE APPLICATION OF PRA TO TECHNOLOGICAL SYSTEMS

Two types of decision trees can be used to identify sets of events leading to system failure—event trees and fault trees. Event and fault trees are useful techniques for identification and quantification of accidents and failures of technological systems. In this paper, the author discusses event tree concepts only. The event tree model displays, in a rather explicit way, paths of the events that relate to the safety or potential for failure of a technological system and also the anticipated consequences for the various pathways. In many situations, fault tree analysis is used to supplement event tree modeling by using the former to establish the appropriate probabilities of the event tree branches.

The event tree is a diagram that illustrates the chronological ordering of event scenarios in a problem calling for decision analytical protocol. Each event is shown by a branch of the event tree. Event trees provide tools that can be used to analyze conditions that could potentially lead to adverse consequences. An event tree uses deductive logic, starting with an initiating event and then uses forward logic to enumerate all possible sequences of subsequent events that will help determine all possible outcomes and consequences. The event tree structure requires that each event level be defined by its probability, which is conditional on preceding events in the tree structure.

Events identified as part of a failure scenario can be displayed in a tree structure that represents a sequence of events in progression, displaying branching points where several possibilities can be anticipated that can lead to an event at the top. This technique basically is an algorithm in which it is possible to assign probabilities to each of the events. Then, by simply multiplying or adding probabilities, the overall chance of failure can be calculated for a given period of time. This technique can indeed help designers anticipate risk in order to correct problems at the design stage rather than through retrofit technologies.

The methodology presented models risk as a chain of interconnected events through the use of event tree analysis. The approach allows for a systematic consideration of all potential loading conditions that may be brought to bear on a system, the potential exposure scenarios fol-

lowing system breach and the consequences of all potential exposures to any population/receptors at risk. In general, the potential risk is modeled as a chain of interconnected events according to the following pathway concept:

HAZARD -> SYSTEM RESPONSE -> OUTCOME -> EXPOSURE -> CONSEQUENCE

This is systematically developed using an event tree.

A typical event tree scenario for an accident event can be developed according to the hypothetical illustration in Figure 2, displaying the logic used in constructing the event tree. This structure provides a systematic approach for decisions on potential hazards. It also provides a mechanism for tackling hazardous problems in a logical and comprehensive manner.

Some Basic Concepts in Probability Theory

A summary of the notations and theorems pertaining to some probability definitions and concepts used in this elaboration are given below. A more detailed review may be found in several standard textbooks of statistics and probability theory.

- *Conditional Probability*, $Pr\{A/B\}$ => the probability of occurrence of event A, given that event B has already occurred. This is the proportion/fraction of items resulting in event A amongst the total set of items that give rise to event B.
- *Unconditional Probability*, $Pr\{A\}$ => is the fraction of items resulting in event A, among the complete set of all items.
- *Joint Probability*, $Pr\{A \& B\}$ => the fraction of items giving rise to the simultaneous occurrence of events A and B, among the complete set of all items. Thus, $Pr\{A \cap B\} = Pr\{B\} \times Pr\{A/B\}$.
- *Independence* => Event A is said to be independent of event B if, and only if $Pr\{A/B\} = Pr\{A\}$. This means, the probability of event A is unaffected by the occurrence of event B and vice versa, so that, $Pr\{A \cap B\} = Pr\{A \cap B\} = Pr\{A\} \times Pr\{B\}$.

The Pathway Probability Concept

Where appropriate, in a probabilistic risk evaluation, the probability of a consequence due to the occurrence of a hazardous situation is defined by a so-called pathway probability (PWP), which is the product of an initiating probability value and the conditional probabilities of subsequent events. The consequence probability, defined by the PWP, is given by the following relationship:

$$
\begin{aligned}
PWP &= Pr\{H \cap R \cap 0 \cap E \cap C\} = Pr\{H \cdot R \cdot 0 \cdot E \cdot C\} \\
&= Pr\{H\} \times Pr\{R/H\} \times Pr\{0/H \cap R\} \times Pr\{E/H \cap R \cap 0\} \\
&\quad \times Pr\{C/H \cap R \cap 0 \cap E\}
\end{aligned} \tag{1}
$$

where:

$Pr\{H\}$ is the probability of a specific Hazard (H) of an initiating event occurring;

$Pr\{R/H\}$ is the conditional probability of System Response (R), given H;

$Pr\{0/H \cap R\}$ is the conditional probability of an Outcome (0), given H and R;

$Pr\{E/H \cap R \cap 0\}$ is the conditional probability of Exposure (E), given H, R and 0;

$Pr\{C/H \cap R \cap 0 \cap E\}$ is the conditional probability of specific Consequence (C), given H, R, 0 and E.

Risk Cost (RC) Computations

The cost associated with the probability of failure (i.e., risk cost) is based on anticipated consequences. This parameter may be computed according to the following relationship:

$$
\text{Partial RC, } Ci = PWP_i \times \text{Consequences, for i-th pathway} \tag{2}
$$

$$
\text{Total RC, } C = \Sigma C_i, \text{ for all existing N pathways} \tag{3}
$$

Level 1	Level 2	Level 3	Level 4	Level 5
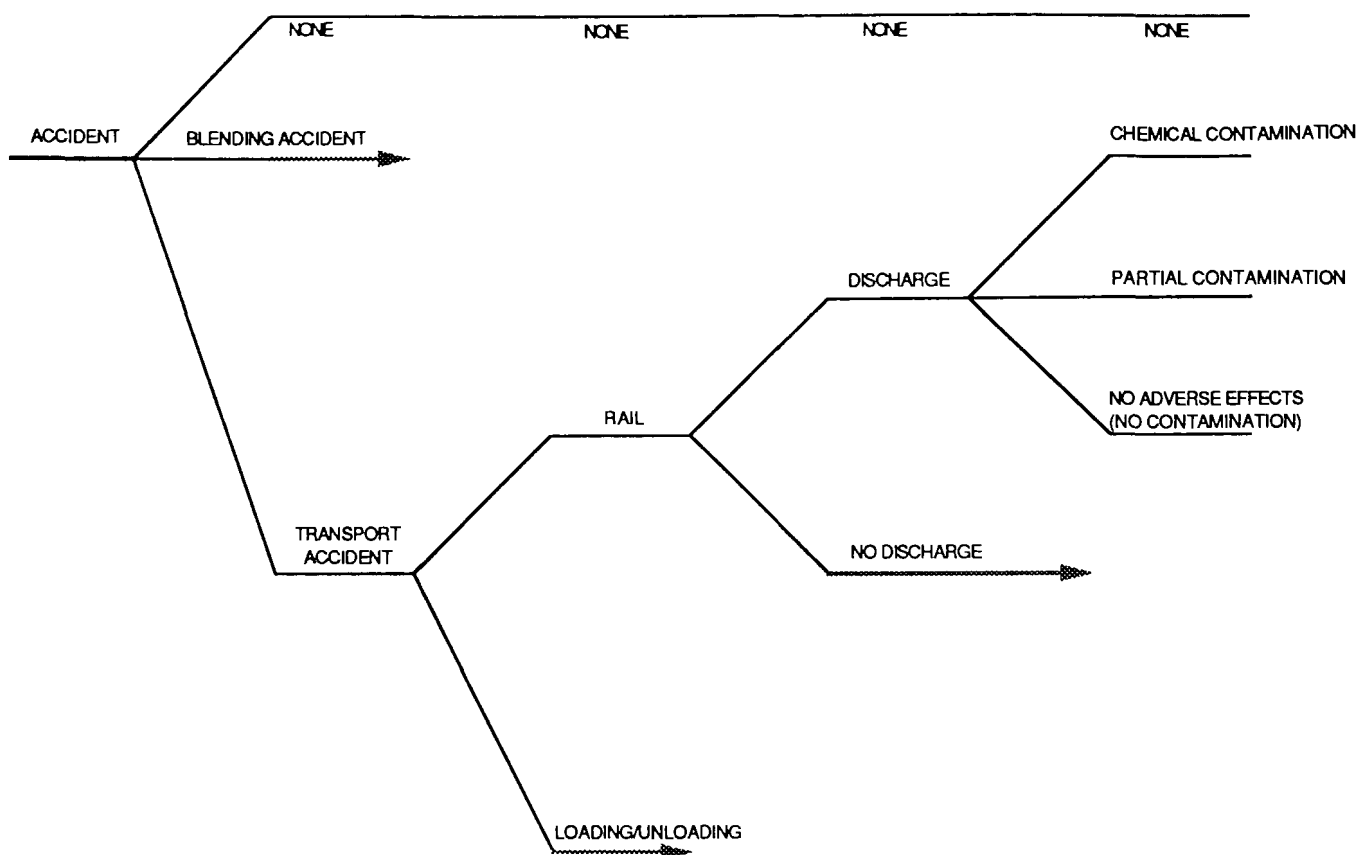
Figure 2
Using the Event Tree Concept in the Probabilistic
Risk Evaluation Process

Assessment of Potential Life Loss, LL

The potential life loss depends on the exposed population (i.e., population at risk, PAR), and is computed as follows:

$$\text{Life Loss/Event} = \text{PAR}_i \times \text{Exposure Probability (EPi)} \tag{4}$$

$$\text{LL}_i = \text{PAR}_i \times \text{EP}_i \times \text{PWP}_i \tag{5}$$

$$\text{Total LL, LL} = \Sigma \, \text{LL}_i \tag{6}$$

Results from the event tree model can be put into a spreadsheet format for better comprehension. Such a formulation also allows for easy comparison of alternative remedial actions. The effect of each remedial alternative in reducing the risks associated with corrective actions for the technological system can be evaluated and compared.

POTENTIAL APPLICATIONS OF PRA IN THE SAFETY EVALUATION OF TECHNOLOGICAL SYSTEMS

The potential for failures of technological systems, the potential for human errors and the inherent uncertainties associated with technological systems, all pose some degree of hazard. Safety and/or risk analyses are techniques used to identify possible hazards and potential consequences. Such analyses will allow for a better design and/or operation that minimizes risks and/or that improves safety. In general, the safety analysis of technological systems incorporates several steps (Figure 3). The event tree concept aids in the identification and evaluation of possible failure cases which fully represent the spectrum of possible failure paths.

The event tree concept offers an efficient way to perform a probabilistic risk evaluation when necessary. This evaluation will aid in the development of a structured risk assessment framework that will facilitate systematic decision-making associated with failure of technological systems. Failures may range from design flaws and deficiencies or faults, to operational and traffic accidents, to natural and man-made disasters. The PRA method aids in estimating the probabilities of events with adverse consequences or the potential to cause adverse consequences. The technique presented may find several applications amongst those uses discussed below.

Hazardous Materials Storage Facility Design

Safety aspects of the design of a hazardous waste facility or a hazardous materials storage facility can be evaluated using the PRA methods. In this case, the risk evaluation will address the consequences associated with the probability of failure. Incremental risks due to failure, as a result of modifications in design criteria, also can be assessed. For instance, the probability of failure using only one liner versus the probability of failure using multiple liners in a hazardous waste facility design can be evaluated and compared using PRA techniques.

Hazardous Materials Containment and Facility Failure

Risks associated with the failure of hazardous materials containments and other facilities can be evaluated using probabilistic risk assessment concepts. Failure is the result of containment breach followed by migration of the released contaminants through the environment. The risks associated with the failure of a hazardous materials facility can be evalu-
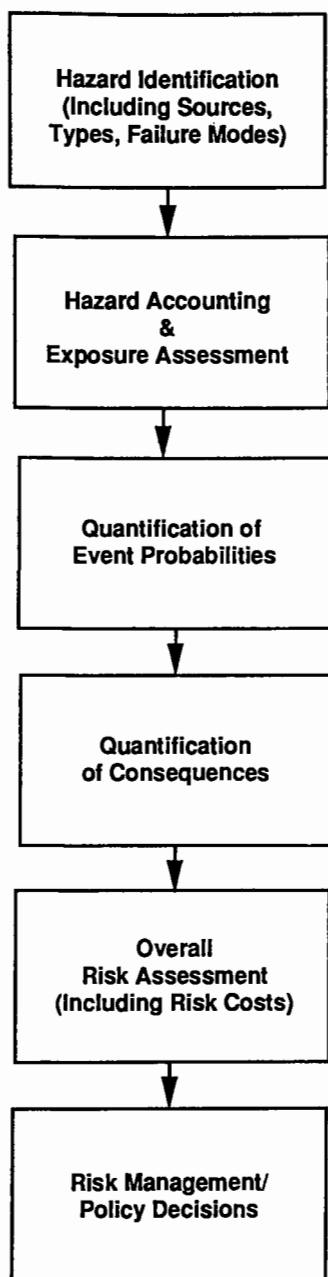
Figure 3
Steps in the Safety Evaluation of Technological Systems

ated using the event tree model. Probabilities of failure and conditional probabilities of system responses, outcomes and consequences are estimated and used for assessing potential economic losses as well as health impacts from a failure or an accident event involving hazardous materials containments.

Transportation Risks

Transportation risks can be analyzed for a system by examining several variables, including the road network, loading/unloading accidents and traffic density. In the transport of hazardous materials, an accident during transport will not necessarily cause a release. Therefore, transportation risks would be estimated as the product of the probability of an accident and the conditional probability of release from a given accident. The approach presented may find great use in assessing risks from transportation of hazardous materials.

Safety Evaluation of Engineering Structures

PRA techniques utilizing the event tree model can be used in the safety evaluation of dams and other engineered structures that will allow for evaluation of appropriate remedial alternatives by comparing potential life losses and economic damages that could result from breach of the structural integrity.

General Risk Management and Risk Prevention Programs

Risk management and prevention programs (RMPPs) are instituted to ensure reasonable safety of industrial equipment and facilities. Equipment failures will occur if and only if one or a combination of several initiating events occur that will lead to system responses that create adverse consequences. The event tree model, used in the context of PRA, facilitates the development of good RMPPs. Individual component failure rates for a given system can be used to estimate the potential for adverse situations for a given technological system.

CONCLUSIONS

The main objectives of this presentation have been to:

- Present concepts and techniques in risk assessment that may be applied to the safety evaluation of technological systems
- Provide a guidance framework for the formulation of risk assessment tasks for technological systems
- Define steps for carrying out specific safety and/or risk assessment tasks in the safety evaluation of technological systems

Major attributes of the methodology discussed here include the following inherent capabilities and features:

- It will explicitly consider all failure modes and/or exposure scenarios
- It will quantify risks associated with the full range of loading conditions, system responses and exposure scenarios, not just extreme events
- It will identify exposure factors and exposure routes contributing most to total risk of failure and/or exposure
- It will facilitate the determination of cost, effective risk reduction policies, or risk management and prevention programs

It is apparent that risk communication may dictate public perception and, therefore, public acceptance of risk mitigation alternatives. Thus, it may be important to give as much consideration to risk communication as is given to risk quantification. A systematic evaluation using structured decision methods, such as the event tree approach elaborated here, can greatly help in this direction. The event tree model can aid risk communicators in improving the quality and effectiveness of their performance.

Estimated Versus Final Costs on Hazardous and Toxic Waste Remediation Projects

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ABSTRACT

An accurate cost estimate is an essential element for both budget planning and contract administration on hazardous and toxic waste Remedial Action projects. Typically, these estimates are prepared at the Record of Decision (ROD) stage by consultants responsible for the Remedial Investigation/Feasibility Study (RI/FS). This estimate is used primarily for budgeting purposes. At the Final Remedial Design (RD) stage, the estimate is more likely to be prepared by professional cost estimating engineers. This estimate is used as a confirmation of the budget and as a tool for evaluating contractors' bids prior to a contract award. A proper estimate is essential at both levels. However, our short history in remedial action projects indicates the potential inaccuracy of these estimates.

This paper presents a comparison of estimated versus actual remedial action cost. Factors affecting cost growth are identified and discussed with recommendations for an improved process.

INTRODUCTION

This paper reviews the factors affecting potential cost growth on remedial action projects. Cost growth is defined as estimates to the final Remedial Action cost, including all change orders and modifications. This potential cost growth represents a risk to agencies or other parties paying for the site cleanup. Thus, the potential cost growth also is referred to as a cost risk.

This paper first reviews the overall remedial action cost estimating process to provide a basis for additional discussion. A limited data base of Superfund remedial action projects is provided and discussed. Finally, key conclusions and recommendations for improvement in the process are presented.

CURRENT STATUS OF THE COST ESTIMATING PROCESS

Typically, cost estimates for a remediation project are undertaken during two distinct phases of the project's evolution. The first estimate generally is done during the remedial investigation/feasibility study phase. At this point, once the nature and extent of the contamination and the appropriated remediation technology have been identified, a cost estimate is prepared. It should be recognized that this estimate at best is of a conceptual nature. The RI/FS engineer prepares the cost estimate based on the feasibility study, relying on his or her general knowledge of the remediation process to develop a likely assessment of the cost. As no definitive design has been addressed yet, the cost is developed using unit prices for major work items typical for that type of technology and that type of project. Because of the very preliminary nature of the information available, a significant contingency normally is applied. The cost developed during this phase becomes a part of the ROD and becomes part of the initial project budget.

During the following phase, the Remedial Design/Remedial Action (RD/RA) phase, cost estimates often are undertaken at the 30%, 60% and final design submittals as they are typically done on conventional construction projects. The purpose of these estimates is to track the cost of the design with respect to the budget as the design evolves. Once in the actual design phase, it is possible for the estimator to begin to generate line item detail in the labor, material, equipment, overhead and profit classifications. As the design becomes more complete in the later submittals, the confidence level in the costing increases allowing a corresponding reduction in the design contingency. The final estimate provides a basis for the government's independent estimate of cost. Selected quantities contained in the estimate can be used to provide the basis for the government's tabulation of quantities for unit price items.

SUPERFUND PROJECT EXAMPLES

Table 1 shows a list of 44 Superfund projects which have been totally or almost completed. Thirty of the projects were taken from the General Accounting Office (GAO) Report "Superfund, Cost Growth on Remedial Construction Projects."[8] The remainder of the projects were the result of direct research by the authors, primarily telephone discussions with either EPA Remedial Project Managers or Corps of Engineers Project Managers. The majority of the projects are Superfund-led projects.

Following the example of the GAO report, the projects shown in Table 1 are divided into Routine and Nonroutine categories. Routine projects typically involve containment or provision of an alternate water supply. Nonroutine projects typically involve excavation of contaminated soil or of drums and barrels. The GAO report indicated an average cost growth (original to total construction) on routine projects of 5%, while nonroutine projects averaged 19% cost growth. Both were considered to be within the industry range for routine projects (2 to 12%) and nonroutine projects (up to 25%).

All of the additional projects researched by the authors were placed in the nonroutine construction category. As may be seen, there was significant cost growth associated with several Table 1 projects: Metamora Landfill (147.1%), ChemDyne (61.1%) and Highland Acid Pits (156.7%). Seven of the projects retained from the GAO report also experienced significant cost growth above the 25% industry standard. These ranged from the Bridgeport project (27.6%) to the Jibboom Junkyard (98.9%). The inclusion of the additional projects increased the average cost growth to 39.4%.

Figure 1 graphically indicates cost growth by remedial action type. Most of the projects which experienced large cost growth involved the excavation of soil or drums and barrels, with transport to off-site landfills or burial in on-site landfills. In all cases, the project managers reported that the cost growth resulted because the excavation revealed more contamination than was reported in the Remedial Investigation report.

Table 1
Cost Growth on Superfund Remedial Action Projects
(Dollars in Thousands)

NA = Not available

Routine Construction Activities

EPA region	Activity name	State	Description of activity	ROD Estimated Cost	Original construction price	Total construction cost	Cost growth from ROD Estimate (percent)	Cost growth from orig. construction price (percent)	Reference
I	Sylvester	N.H.	Construct slurry wall/cap	NA	$ 2,222	$ 2,431	--	9.4	GAO, 1988
I	Sylvester	N.H.	Construct treatment plant	NA	5,375	5,550	--	3.3	GAO, 1988
II	Lipari Landfill	N.J.	Construct slurry wall/cap	1769	2,144	2,204	24.6	2.8	GAO, 1988
II	Price Landfill	N.J.	Relocate well field	5070	3,159	3,257	-35.8	3.1	GAO, 1988
II	Pollution Abatement	N.Y.	Construct slurry wall/cap	NA	2,963	3,475	--	17.3	GAO, 1988
III	Matthews	Va.	Construct water lines	662	1,466	1,359	105.3	-7.3	GAO, 1988
III	Drake Chemical	Pa.	Replaced water line	NA	1,197	1,291	--	7.8	USACE, 1990
V	New Lyme	Oh.	Cap, pump and treat	10,798	14,000	15,400	42.6	10.0	GAO, 1988
V	Charlevoix Municipal	Mich.	Construct intake system	1954	2,877	2,996	53.3	4.2	GAO, 1988
V	Verona Well Field	Mich.	Construct air stripper	1660	1,724	1,697	2.2	-1.6	GAO, 1988
IX	Stringfellow	CA.	Construct treatment plant	NA	4,189	4,449	--	6.2	GAO, 1988
TOTAL					$41,316	$44,109	22.8	6.8	

Nonroutine Construction Activities

EPA region	Activity name	State	Description of activity	ROD Estimated Cost	Original construction price	Total construction cost	Cost growth from ROD Estimate (percent)	Cost growth from orig. construction price (percent)	Reference
I	Re-solve Incorporated	Mass.	Excavate soil	3050	$ 4,561	$ 5,093	67.0	11.7	GAO, 1988
I	Keefe Environmental Services	N.H.	Excavate barrels	500	795	1,156	131.2	45.4	GAO, 1988
II	Syncon Resins	N.J.	Excavate barrels	NA	1,573	1,938	--	23.2	GAO, 1988
II	Love Canal	N.Y.	Excavate/containment cap	NA	3,900	5,188	--	33.0	GAO, 1988
II	Bridgeport	N.J.	Lower lagoon level	NA	1,122	1,446	--	27.6	GAO, 1988
II	Burnt Fly Bog	N.J.	Excavate main lagoon	2200	2,183	3,200	45.5	46.6	GAO, 1988
II	Pollution Abatement	N.Y.	Excavate barrels	NA	1,492	1,497	--	0.3	GAO, 1988
II	Krysowaty Farm	N.J.	Excavated soil	2164	3,367	3,891	79.8	15.6	GAO, 1988
II	Lang Property	N.J.	Excavate soil	2322	3,606	3,775	62.6	4.7	USACE, 1990
II	Metaltec/Acrosystems	N.J.	Excavate soil	NA	3,377	3,300	--	2.3	USACE, 1990
III	Lehigh Electric-Phase II	Pa.	Excavate soil	NA	2,551	2,641	--	3.5	GAO, 1988
III	Bruin Lagoon	Pa.	Excavate lagoon	1456	2,167	2,841	95.1	31.1	GAO, 1988
III	Enterprise Avenue	Pa.	Excavate soil	NA	3,017	2,948	--	-2.3	GAO, 1988
III	Leigh Electric-Phase I	Pa.	Excavate transformers	NA	1,052	1,006	--	-4.4	GAO, 1988
III	Lansdowne	Pa.	Remove radioactive hose, garage, sewer sediment	4500	4,985	9,038	100.8	81.3	GAO, 1988
IV	PCB Spills	N.C.	Excavate soil	NA	2,544	2,364	--	-7.1	GAO, 1988
IV	Miami Drum	Fla.	Excavate soil	1568	1,100	1,626	3.7	47.8	GAO, 1988
V	Metamora Landfill	Mich.	Excavate drums	41,500	17,000	42,000	1.2	147.1	EPA, 1990
V	Old Mill	Oh.	Pump and treat	3917	4,500	5,100	30.2	13.3	USACE, 1990
V	ChemDyne	Oh.	Drum removal	NA	1,800	2,900	--	61.1	USACE, 1990
VI	Bio-Ecology	TX.	Excavate soil	2709	5,815	5,319	96.3	-8.5	EPA, 1990
VI	Mid-South	Ark.	Stabilize, cap, pump and treat	3500	$ 2,385	$ 2,840	18.9	19.1	EPA, 1990
VI	Highland Acid Pits	TX.	Excavate soil	NA	2,111	5,419	--	156.7	EPA, 1990
VI	Geneva Industries	TX.	Excavate soil	NA	16,136	21,100	--	30.8	EPA, 1990
VII	Aidex	Iowa	Excavate soil	NA	6,939	7,421	--	6.9	GAO, 1988
IX	Mountain View Globe	Ariz.	Excavate asbestos site	NA	1,871	1,871	--	0.0	GAO, 1988
IX	Jibboom Junkyard	Calif.	Excavate soil	1460	1,985	3,949	170.5	98.9	GAO, 1988
IX	Celtor	Calif.	Excavate soil	3065	6,470	4,711	53.7	-27.2	USACE, 1990
IX	Del Norte Pesticide	Calif.	Pump and treat	1240	1,337	132	-89.4	-90.1	USACE, 1990
TOTAL					$111,741	$155,710	26.0	39.4	

Other Construction Activities

EPA region	Activity name	State	Description of activity	ROD Estimated Cost	Original construction price	Total construction cost	Cost growth from ROD Estimate (percent)	Cost growth from orig. construction price (percent)	Reference
II	Love Canal	N.Y.	Hydraulic clean out	NA	$ 3,343	$ 2,925	--	-12.50	GAO, 1989
VI	Tar Creek	Okla.	Clear/plug wells	NA	2,648	2,383	--	-10.01	GAO, 1989
VI	Tar Creek	Okla.	Divert Tar Creek	NA	1,694	1,524	--	-10.04	GAO, 1989
IX	McColl	Calif.	Air monitoring/site prep	NA	7,974	10,062	--	26.19	GAO, 1989
TOTAL					$15,659	$16,894		7.89	
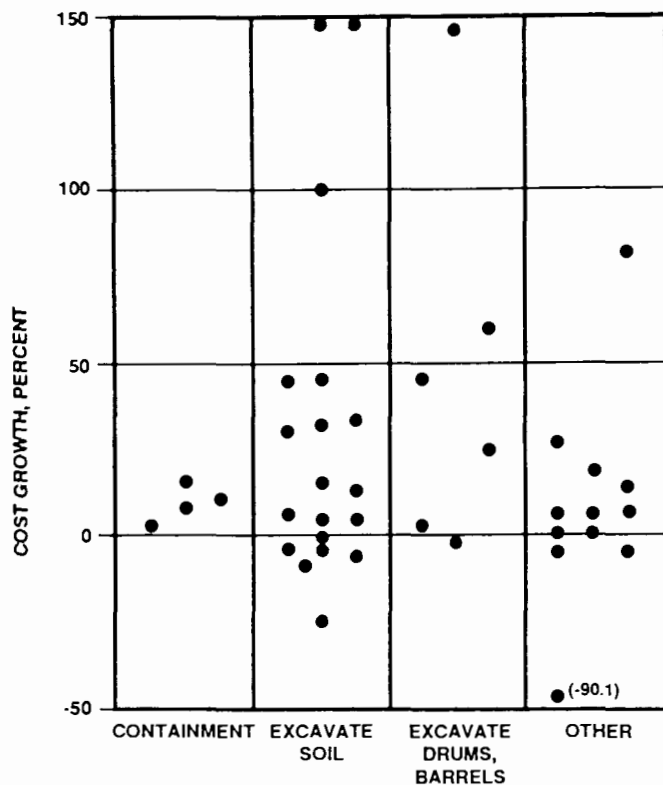
Figure 1
Cost Growth By Remedial Action Type from the
Original Construction Estimate to
Total Construction Cost

Many of the other projects from the GAO report and our research experienced relatively little cost growth. Once project in Table 1 (Del Norte Pesticide in California) experienced a contract which was awarded based on approximately 4-year old groundwater analytical data. After the contractor began mobilization, the monitoring wells were resampled, and constituent levels were below action levels, apparently as the result of natural attenuation. Thus, the contractor's mobilization costs ($137,000) were needlessly expended.

Table 1 also indicates the cost estimate prepared as part of the Record of Decision (ROD) for selected projects.[1] Cost growth from the ROD estimate to total construction cost is shown on Figure 2. As can be seen, this ROD cost growth is generally greater than the cost growth from the original construction price. This result is not unexpected based on the lesser project definition at the ROD stage. However, examination of individual projects indicates no consistent trend in decreased cost growth from ROD to RD stages. This trend apparently results from the significant assumptions implicit at both estimating stages, and particularly the estimate of a contamination volume which may remain consistent in both stages.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are based on the projects presented previously and the combined experience of the three authors.

Excavation-Based Remedial Actions
Pose a Greater Cost Risk Potential

The remedial action projects presented in the previous section demonstrate that projects involving excavation present the greatest risk of cost growth. The cause for this cost growth potential is clear. A typical site assessment, even a well-performed assessment, still represents only an approximation of Figure 2 the volume of contaminated material. Excavation, on the other hand, allows a direct examination of the subsurface and a revelation of previously undiscovered contamination. "Plume

chasing" in these cases leads to significantly higher excavation volumes and disposal/treatment costs, while confirmation testing to meet strict cleanup guidelines assures that the chase will not be prematurely ended. This reason for cost growth should not surprise anyone associated with normal construction excavation or underground construction activities. "Changed conditions" on these projects are the normal course of business. The erratic and elusive nature of contamination only tends to worsen this situation.
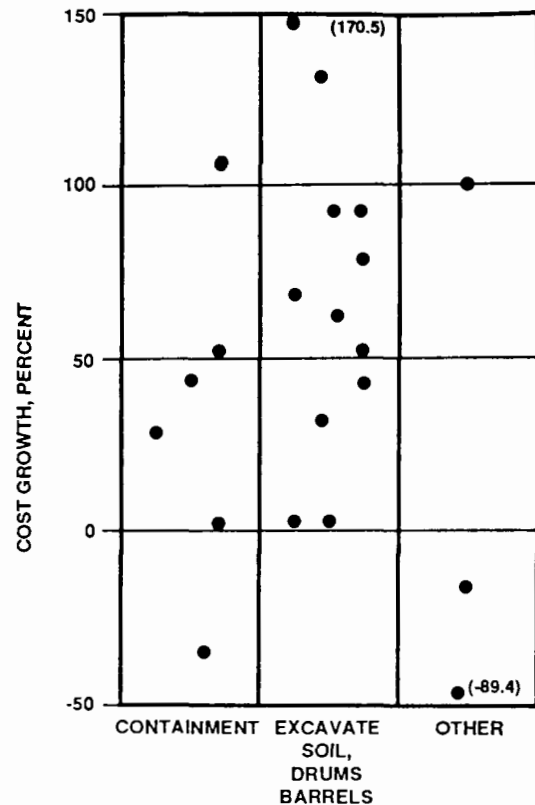
Figure 2
Cost Growth From ROD Estimate to Total Construction Cost

In contrast to projects involving excavation, most other remedial actions assume that the contamination volume has been correctly evaluated as shown conceptually in Figure 3. These types of projects may include pump-and-treat methods, in situ methods (such as biological treatment, vacuum extraction, in-place solidification, etc.) or containment (such as capping or slurry walls). Cost growth on these types of remedial actions is limited to the more typical change orders, etc. However, while in situ projects may not experience significant cost growth during construction, they may exhibit a greater cost risk during the O&M phase. In part, this cost increase occurs because the length of time associated with these projects usually is a rough estimate at best.

The Remedial Investigation

The previous discussion highlights the critical role the Remedial Investigation plays in the potential for cost growth. Remedial Investigations typically are expensive undertakings. Often, it is assumed that a reasonably complete RI will serve all purposes. This often may be the case. However, the previous data indicate that some RIs do not provide sufficient information to accurately estimate costs. We recommend that the RI be tailored to the anticipated remedial action. This tailoring is suggested in the U.S. EPA guidance for RI/FS studies[5] with an integration of the RI and FS activities (Figure 4a). The anticipated remedial action should be identified as early as possible in the FS, with the remaining RI activities geared toward a specific objective. Strictly sequential RI and FS activities should be avoided (Figure 4b).
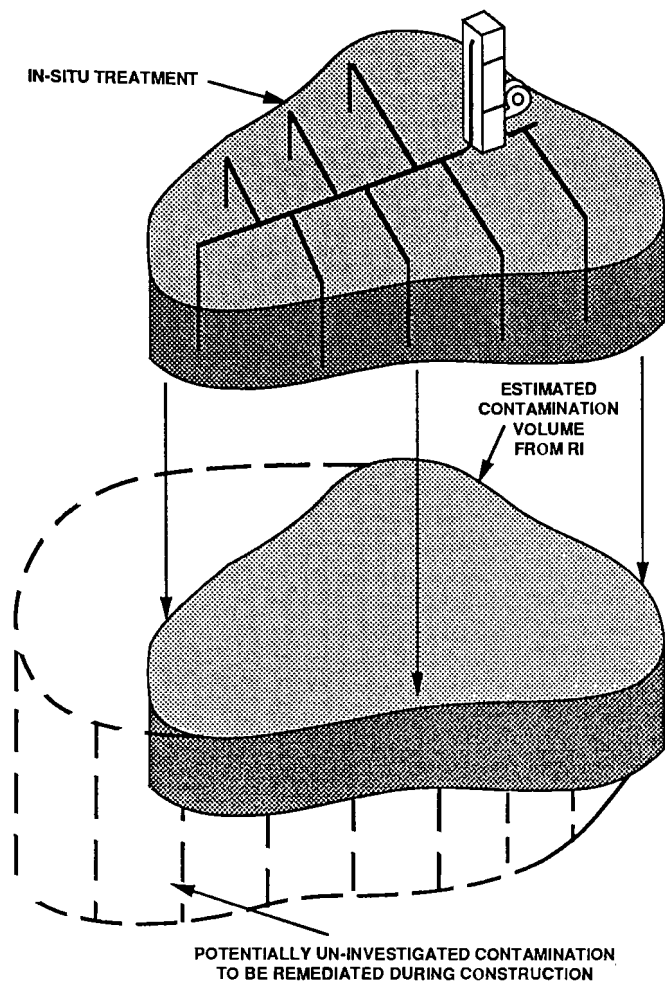
Figure 3
Effect of Contamination Volume on
Excavation vs. In Situ Treatment
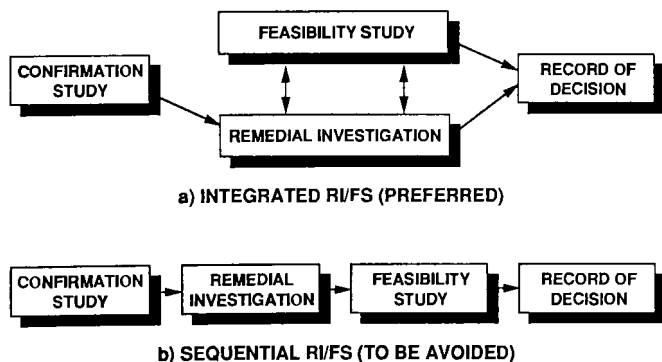
Figure 4
The RI/FS Process and Its Effects on Cost Growth

The question of "How much investigation is enough?" is highly relevant to the potential for cost growth. The hope is that increased investigation will reduce the potential for cost growth, while the fear is that mounting investigation costs will not be recouped during remedial action. A fundamental decision must be made early in the RI/FS process if an excavation-based technology will be used. If so, increased investigation is recommended to adequately estimate the excavation volume for budgeting purposes. However, the goal of this investigation should clearly be understood. The goal is not to precisely define the extent

of contamination, utilizing highly accurate methods with extensive QA/QC methods. These data are unnecessary because the volume of the contaminated soil will be clearly revealed during remedial excavation. Sampling and laboratory- analysis can be performed more accurately and economically while the excavation occurs and provides the community and regulators the requisite information to assure the site is "clean." Rather, the RI goal for an excavation-based technology is to roughly assess the volume of contaminated material for budgeting purposes only. These activities can be conducted using economical field screening and other less precise analytical methods. Using cheaper methods, a greater number of samples can be analyzed for the same or reduced cost as a detailed RI study. More accurate analyses can be conducted after the risk assessment, cleanup goals and appropriate remedial technology are developed. Also, it should be realized that for some projects no reasonable amount of investigation can adequately define the volume of contaminated material. For these projects, the construction contingency should be appropriately increased.

This emphasis on excavation-based versus nonexcavation-based RIs should not obscure the other potential effects of the RI/FS process on cost risk or absolute cost. As discussed previously, in situ remedial methods are typically straight-forward to implement (i.e., little immediate cost risk). However, significant cost growth may occur later if the system is ineffective or takes much longer to achieve cleanup goals than anticipated. Thus, the RI activities must adequately define the volume of contaminated materials (to the satisfaction of the regulators) and provide sufficient information about the complex physical and biological factors needed for an effective remedial design.

Finally, absolute cost, while not the subject of this paper, is an important and closely related subject. The RI/FS process plays a central role in absolute cost determination. Trained and experienced professionals in both the RI and FS areas are necessary to make informed and innovative decisions.

Effect of Quantity Overruns on Contracting Process

Federal policy with regard to construction type contracts has generally recognized that certain risks are potential costs to the government. In developing its contract documents, the federal government has in effect directed the contractor not to include costs to cover certain risks such as: (1) significant changes to the scope of requirements of the contract as a result of the direction of the government; and (2) significant differences in the character or condition of the work site between that which is represented by the contract documents or within the contractor's reasonable ability to determine and the actual condition when the work area is exposed. The reason for this governmental decision is that rather than incur the cost of the successful contractor's assessment of these risks on every contract, the government prefers to incur the cost of the risk only on those projects when the risk is realized. The two contract mechanisms by which this is accomplished are the "changes clause" and the "differing site condition clause" which are a part of almost all federal construction and remediation contracts.

In a typical fixed price remediation project, the contract documents might represent a quantity of contaminated earth to be removed and treated. This quantity has been calculated based on the site investigation data. The contractor relies on the government's representation of the quantity of contaminated earth in preparing his bid. After award of the contract and notice to proceed, it might be discovered that the contamination had been dispersed more widely than the site investigation data suggested. The government's only real choice at this time is to issue a change order to the contractor to remove and treat the additional quantity.

Typically, the contractor would respond to the change order with a price for the additional work, negotiate that price with the government and undertake the work. Generally the government has the right to direct the contractor to continue work on the additional work while the pricing and negotiations take place. If the negotiations are not successful, the government would likely issue a unilateral change order. Often the price for the change is negotiated covering the direct cost of labor, material and equipment only, the contractor reserving the right to claim for ex-

tended overhead and related costs on the completion of the project.

By their nature, remediation projects have high public visibility and are vulnerable to media coverage. As a result, the government often is under pressure to complete the remediation effort without delay. If, in dealing with the contractor, the government is burdened by inadequate contract documents resulting from the inclusion of incorrect quantities, it is quite possible that the completed projects costs will be higher than those originally bid when the final costs of change orders, extended overhead claims and litigation are tallied.

Most remediation projects are bid on the basis of a contract which includes a combination of lump sum and unit price items. Often the Government Contracting Officers, in order to "Tighten up the Contract," place some items whose actual quantities are unknown in the lump sum portion of the contract to reduce the number of unit price items. If during the remediation process, some of those items overrun, the costs of the affected items can be subject to renegotiation under the "changes" or "differing site conditions clauses." If the same items had been contracted as unit price items, they could be handled more simply and at reduced cost to the government.

Because of a desire to achieve "certainty" in the project cost, the government often does not desire to include an appropriate contingency in the final estimate. While this decision is understandable when dealing with Congress and budget agencies, the fact remains that on projects involving excavation, certainty of estimating the final cost is not likely. On projects requiring excavation of soil drums, the contingency factor should be higher than that used on a more standard remedial action project.

Other Factors Affecting Cost Risk

Inaccurate quantities cannot bear the responsibility for all the increases from budgeted costs to actual costs on remediation projects. Realistic costing while the design is taking form requires a quality estimating effort. The estimator needs access to an up-to-date data base which contains line items appropriate to remediation work. The data base needs to include remediation health and safety line items, remediation general conditions line items and the ability to factor conventional line items which occur on remediation projects for loss of productivity due to the presence of contaminants. One such data base is currently under development by the U.S. Army Corps of Engineers.

The Corps of Engineers' Walla Walla, Washington District office has been tasked with developing the data base to supplement the current data bases used on the Corps' Micro Computer Aided Cost Engineering System (MCACES), formerly called the Micro Computer Aided Cost Estimating System. MCACES is a PC based estimating system containing a data base of approximately 20,000 line items which are sensitive to crew size and composition, labor rates, equipment rates and productivity.

Another factor affecting the accuracy of final cost estimates for remediation projects is that the cost estimator rarely has access to the Final bid documents, including special contract provisions, bid item schedule and the time allotted for completion of the project, at the time the final estimate is prepared. These documents usually have not been prepared when the final cost estimate is made. This information, while available to the remediation contractor at the time of bid preparation, can greatly impact the independent government estimate.

Several other factors may play a significant role in the determination of cost risk and absolute cost. Schroeder and Shangraw[3] have prepared a data base with 40 private and public sector remedial action projects. Their conclusions, based on an analysis of this data base, are summarized in Table 2. Note that the table includes both conclusions supported by their analysis and those for which only a general suspicion exists. Also note that the authors cite this as a preliminary study to be modified by future analysis of projects.

Our experience allows us to suggest slight revisions to the preliminary conclusions drawn by Schroeder and Shangraw:[3]

- Clearly the stage of project definition is a factor in cost risk as recognized by the U.S. EPA guidelines of +50/-30 percent for FS studies, compared to higher standards Table 2 for RD level estimates. More

detailed design and more refined cost estimates should be available as the project progresses. However, if the site investigation does not provide a proper foundation for the cost estimate, cost estimating at any stage of project definition presents a significant cost risk. Prior action at a site should also reduce cost risk, as it allows a greater "window on the contamination" than available from typical RI studies.

Table 2
Summary of Schroeder and Shangraw[3] Preliminary
Conclusions on Factors Affecting Cost Risk

FACTOR	EFFECT	COMMENT
Stage of Project Definition (ROD, RD, etc.)	Major	Cost risk decreases with increased definition
Prior Action at Site	Major	Cost risk decreases when prior action has taken place
Types of Contamination	Mostly None	Major cost increase risk when tanks or drums are present
Treatment Technological	None	Slight decrease in risk when containment is employed
Regulatory Events	--	Suspect significant effect
Project Management	--	Suspect major impact
Public versus Private Cleanups	--	Suspect that private sector cleanups have less cost risk

- It appears that this type of contamination should significantly affect cost risk. For example, VOC is very amenable to in situ remediation techniques, whereas inorganic contamination is more likely to require and excavation-based technology. Thus, inorganic contamination should be prone to the greater cost risk related to excavation. This matter directly relates to the next category (technological complexity), as a back-hoe is not complex but represent a large potential for cost risk. Technological complexity as it relates to in situ methods may have more effect on increased O&M costs.

- Regulatory events could have a significant effect on cost risk. The Land Disposal Restrictions and interstate agreements on landfill disposal are of particular concern. Assumptions about transportation and disposal costs could shift significantly from FS or Remedial Design stage to actual implementation.

- The effects of project management and public versus private sector cleanup appear to be significant and interrelated. Many excellent professionals work in the public sector. However, the private sector is more likely to retain experienced project managers and provide them with more resources to allow them to make more consistent and informed choices.

CONCLUSIONS

The most significant factor affecting cost risk is the decision to use an excavation-based remediation technique. Excavation will reveal the full extent of the contamination, previously only estimated by the RI. Thus, greater investigation will be required to provide more confidence in the cost estimate. However, in some cases, no amount of investigation will be enough. Thus, contracting procedures must provide suffi-

cient flexibility to handle the increased cost risk on these projects. This recommendation means the cost estimate should include more unit price items (rather than lump sum) and provide a greater contingency than on other projects. Other factors may also influence cost risk, most notably the state of project definition, the type of contamination, regulatory events, and the skill and resources of the remedial action project manager.

ACKNOWLEDGEMENTS

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Cost Inaccuracies in Superfund Projects: Strategies for Building Better Estimates

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ABSTRACT

Estimates of cleanup costs during the 1980s failed to provide reasonably accurate projections of actual costs. This statement is especially true for federally-led Superfund projects. Two primary approaches have been used to tackle the problem of building better estimates. One approach is the development of computerized cost estimating systems for generating base estimates. The other approach is to build methods to better understand the cost risks for remediation projects. Currently, five major computerized systems are in existence for generating base estimates and two are actively under development. The majority of these systems provide early order-of-magnitude estimates of remedial construction costs. Unfortunately, little effort has been directed at understanding the cost risks of remediation. However, new methods such as Monte Carlo analysis and historically based models are now available that take into account project and site characteristics for assigning contingencies. The cost-estimating lessons learned from the experience of the 1980s demonstrate the need for adjusting estimates by taking into account the unique risks of each site. In addition, there is an ongoing need to collect better cost data and to improve other historically based statistical methods employed for building estimates.

INTRODUCTION

Estimates of the cost of remediating the nation's hazardous waste sites have been characterized by a high degree of uncertainty. Cost estimates for nationwide cleanups have ranged from $8 billion in 1984 to more than $500 billion in 1989.[1] Receiving less attention, but just as notable, has been the poor record of these estimates in predicting the actual costs at the individual project (OU or SWMU) level. Traditional engineering and construction methodologies have failed to provide reasonably accurate estimates for this class of projects.

Through joint funding by a consortium of major chemical and oil companies and the U.S. Department of Energy (DOE), the HAZRISK data base containing detailed information on completed Remedial Investigation/Feasibility Studies and Remedial Design/Remedial Actions (RD/RA) has been compiled. The objective of this paper is to use the HAZRISK data base to describe the cost estimating record of the 1980s, to outline the tools and strategies available and under development for building better estimates and to summarize the lessons learned from the past decade as they relate to building cost estimates for hazardous waste projects.

COST ESTIMATING EXPERIENCE OF THE 1980s

While many remedial actions are just underway, there is enough collective experience across the country to assess the accuracy of cost estimates for this class of projects. Figure 1 graphically depicts the accuracy of cost estimates for more than 50 remedial actions completed over the past decade. The vertical axis measures the percent deviation between actual project cost and estimated cost for the construction stage of a cleanup project. The horizontal axis indicates the stage at which the estimate was made. In theory, the ratio of the actual cost to the estimated cost should average zero with a narrowing band of variability around this ratio towards the completion of the project (shaded region of figure). In reality, however, there is a problem with both estimate accuracy and variability. The figure shows a consistent problem with underestimation, especially at early project stages. In addition, there is a wide variance in the accuracy of the estimates. At early project stages, costs can be underestimated by as much as 53% and overestimated by more than 250%.
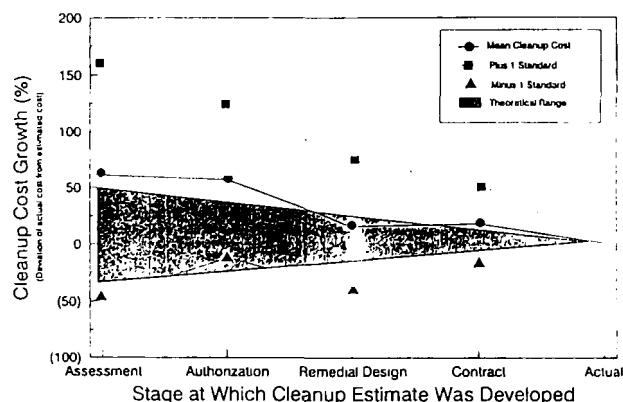
Figure 1
Estimation Accuracy For Remedial Actions

Figure 2 shows the mean and range of cost growth for 51 completed remedial actions by project lead. The figure shows that federally-led Superfund cleanups historically have experienced the largest cost growth on average. At project authorization cost growth averaged 75% for federal-led Superfund cleanups; 41% for cleanups at DOE facilities conducted by the DOE; 25% for state-led Superfund projects; and 15% for a sample of industry-led cleanups. Project authorization is the ROD (Record of Decision) for Superfund projects. For other projects, this is the point at which the project was authorized to proceed with design and construction. It should be noted that both the industry and DOE samples of cleanups were not conducted under CERCLA/SARA. The sample these numbers are based on is large enough to give an indication of the comparative magnitude of the problem facing both the government agencies and the private sector.

Figure 2
Comparison of Cost Growth By Project Lead
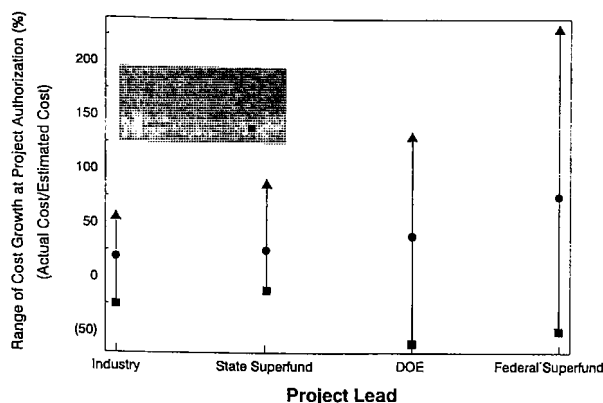
An even more intractable problem than the average cost growth, especially for federally-led and DOE-led cleanups, is the wide range in deviations of actual costs from estimates. While high cost growth can be accounted for with the use of an adjustment factor, the large variability in cost growth is much more difficult to resolve. This result suggests that uncertainties present in cleanups are greater than commonly perceived.

This wide variation also suggests that there is a fundamental problem with current estimating methods for cleanups and a continuing reliance on conventional "bottoms-up" approaches or ad hoc techniques that do not take into account the unique risks and uncertainty associated with this class of projects.

We can conclude that regardless of project leader, estimates of cleanup costs have been largely inaccurate and that costs have not been controlled effectively during project implementation. We can speculate that the far superior estimating performance exhibited by industry-led cleanups is due to a combination of factors. These reasons might include: (1) better project management; (2) more effective contractor selection; and (3) greater control over the choice of the remedy. Perhaps an even more fundamental reason for the difference in project outcomes between the industry and government sample is due to industry's greater motivation to bring cost within budget. In contrast to the government, the private sector is interested in maximizing profits. Thus, cost-effectiveness means that cost-minimization is the number one priority. While achieving a permanent remedy and complying with regulations is important, selection of a remedy is made under the framework of minimizing costs, not vice versa. An analysis of RODs by the U.S. EPA showed that when PRPs lead the remedial action, less innovative and lower cost technologies are chosen.[2] Research has shown that the employment of more complex and innovative remedial technologies are associated with higher cost growth.[3] Moreover, the penalties for a wrong estimate are far greater in industry to both the individual and company than they are in government.

Figure 3 shows that two approaches have been used to tackle the problem of generating better cleanup cost estimates. One approach has been the development of computerized cost estimating systems for generating base estimates targeted exclusively at environmental restoration projects. The other is the development of methods to better understand the cost risks of individual cleanups and thereby assign more appropriate contingencies. Although more attention has been focused on the former approach, the unusually high cost risks associated with cleanup projects have generated increasing interest in the latter.

TOOLS FOR GENERATING BETTER BASE ESTIMATES

The large number of cleanup sites resulted in the development of several computerized cost estimating systems for environmental restoration projects in the latter half of the 1980s. The focus of these systems was primarily on generating better base estimates early in the project cycle for the remedial construction phase of a cleanup. Figure 4 traces the time of introduction of these systems. (It should be noted that this

survey excludes noncomputerized methodologies for estimating environmental restoration costs. We also exclude discussions of generic cost estimating systems such as COSTPRO, G2 and Primavera even though some estimators are using these tools for cleanup projects.) Although there are several other computerized systems in existence that deal with the issue of cost, these are the primary tools for generating base estimates that are currently available or actively under development. The following section contains a brief description of each system.
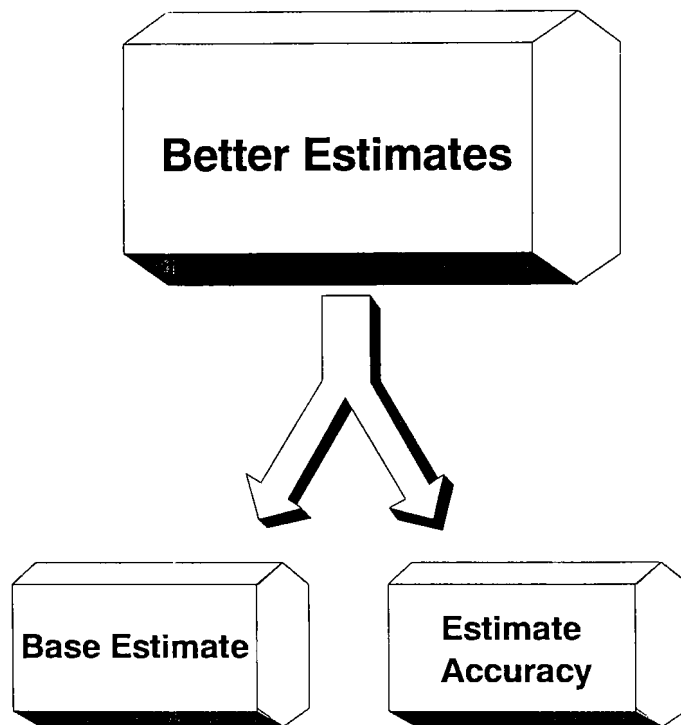
Figure 3
Approaches for Building Better Estimates
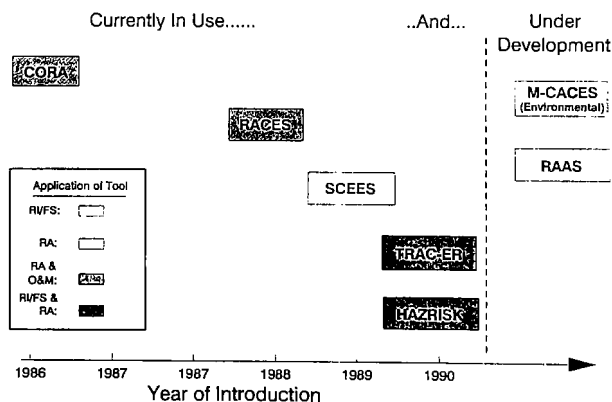
Figure 4
Overview of the Development
in Computerized Cost Estimating Systems

CORA (Cost of Remedial Action)

CORA was developed by CH_2M Hill for the U.S. EPA to estimate the remedial action costs associated with Superfund sites. The U.S. EPA routinely uses CORA to build budget estimates of remedial action costs at Superfund sites. CORA is probably the most widely used cleanup

cost estimating tool and effectively serves as the industry bench mark against which other cost estimating tools are judged.

RACES (Remedial Action Cost Estimating System)

RACES (formerly known as PRACES) was developed by PEI, Inc. for the U.S. EPA Risk Reduction Engineering Laboratory (RREL). A "quasi-design" system, the program allows the user to estimate costs at a component level. The system is structured to cost out remedial technologies and actions at a site on a line-item approach and relies upon a unit cost, cost estimating relationship (CER) and operations and maintenance item data base.

SCEES (Superfund Cost Estimating Expert System)

SCEES was developed by CDM Federal Programs Corporation for the U.S. EPA to estimate the cost of the RI/FS at Superfund sites. SCEES is a menu-driven system that walks the user through the steps of conducting an RI/FS.

HAZRISK

The HAZRISK models were developed by Independent Project Analysis for a consortium of private sector companies and the DOE to estimate the cost, cost risk and schedules for both the RI/FS and RA stages of environmental restoration projects. The models are based on a data base of completed projects and involve the systematic linking of cost and schedule outcomes with project and site characteristics.

TRAC-ER (Project Tracking for Environmental Restoration)

This system, developed by Los Alamos National Laboratories, currently is used to produce definitive base line costs and schedules of RI/FSs. It relies on a unit cost data base that can be augmented with historical unit costs. Currently, this system is in the working prototype stage and is installed at four DOE sites under the Albuquerque Operations Office.

M-CACES (Micro-Computer Aided Cost Engineering Support System)

M-CACES was developed by the Army Corps of Engineers as a detailed "bottoms-up" construction cost estimating tool typically applied to heavy civil projects, new building construction, process plants and rehabilitation projects. CACES is oriented towards lump-sum contracts. The Corps is in the process of building an environmental restoration unit cost library so that both the mainframe and micro-version of CACES can be used for hazardous waste projects.

RAAS (Remedial Action Assessment System)

RAAS currently is under development for DOE's EM-50 (Office of Research and Development) by Pacific Northwest Laboratory. RAAS is designed to be used during the RI/FS stage as a computer based advisory tool to screen and evaluate remedial action alternatives. RAAS will work in tandem with the Multimedia Environmental Pollutant Assessment System (MEPAS) in order to "focus on and prioritize the environmental issues at a waste unit."[4] It will be a total screening advisory tool as it will have the capacity to identify health risks and environmental damage as well as recommend remedial alternatives and estimate the remediation costs associated with a site.

Use of Computerized Cost Estimating Systems

Figure 5 summarizes the tools by the project stage at which they are most appropriately applied, the underlying methodology used by each tool and the applications of the tools. Four of the seven tools listed are used to generate order-of-magnitude estimates. Order-of-magnitude estimates are approximate estimates made without detailed engineering data. Actual costs should be accurate within plus 50% or minus 30% of the estimates. Budget (intermediate) estimates are made at the beginning of the design stage and actual costs should be accurate within a range of plus 30% or minus 15% of the estimate. Definitive estimates are defined as estimates made when engineering may be up to 40% completed. The actual cost should be accurate within plus 15% to minus 5% of the estimate.[5]

Tool	Estimate Generated			Underlying Approach		ER Application			
	Order-of-Magnitude	Budget	Definitive	Unit Cost	Historical	RI & FS	Remedial Construction	O&M Costs	Contingency
CORA	•			•			•	•	
HAZRISK	•				•	•	•		•
M-CACES (Environmental)			•	•			•		
RACES		•		•			•	•	
RAAS	•			•			•		
SCEES	•			•		•			
TRAC-ER		•		•		•			

Figure 5
Summary of Computerized Cost Estimating Systems
for Environmental Restoration Projects

The higher level of effort focused on systems for generating order-of-magnitude estimates probably is a reflection of the fact that this is the area where there is the greatest need for cost estimating tools due to the difficulty in producing reasonably accurate estimates during early stages of a cleanup project. The relative lack of effort devoted to developing tools for the latter stage of a remediation project can be attributed to several factors. First, we are in the middle of the evolution of environmental restoration cost estimating tools. Tools that currently are used for order-of-magnitude estimates may, with later versions, be used to generate intermediate and definitive cost estimates. Second, it is easier to use generic cost estimating tools to estimate cost in the latter stages of a project since a more detailed "bottoms-up" approach is required. These tools provide a framework for generating the estimates and require a unit cost data base for environmental restoration items.

TOOLS AND APPROACHES FOR UNDERSTANDING COST RISK

The only tool in our survey currently available for assessing cost risks and assigning contingencies for environmental restoration projects is the HAZRISK model. Contingency in cost estimates represents an allowance for elements within the project scope that are not included in the detailed estimate. More formally, "it is a cost element of an estimate to cover a statistical probability of the occurrence of unforeseeable elements of cost within the defined project scope due to a combination of uncertainties, intangibles and unforseen/highly unlikely occurrences of future events, based on management decision to assume certain risks for the occurrence of those events."[5] Traditionally, three approaches have been used to assign contingency to cleanup projects. Each is discussed below:

Fixed Percentage

The most commonly used method for assigning a contingency is some fixed percentage of the base estimate. Typically these contingencies are the same as those required for other classes of projects and are in the range of 10 to 15%. With average cost growth across all cleanup projects at 41%, this is generally insufficient to cover the uncertainty associated with these projects. In addition, the use of a fixed percentage can be appropriate for the average project, but for all others it will be inaccurate.

Estimator's Judgement

Unlike the fixed percentage approach, this is defined as a varying percentage or allowance based on the judgement of the estimator. While this method can be fairly accurate if the estimator is familiar with cleanup projects, it also can be inaccurate if the reverse is true. It is also difficult to justify.

Monte Carlo

The Monte Carlo estimating technique is a statistical method that uses sampling theory to calculate a contingency. This method is being

used increasingly for assigning contingencies to all classes of projects. Although it is relatively easy to justify, the results can be highly variable. In addition, assigning the appropriate parameters requires detailed knowledge of cleanup costs and cost drivers.

HAZRISK Models

The HAZRISK models differ from these approaches in that they take into account project and site characteristics. Logically, there are only a few potential causes of cost and schedule estimating problems:

- The cost estimates were developed poorly - not in accord with best practice
- The project changed (project definition) from that envisioned in the cost estimate
- Project implementation was faulty
- The "state-of-the-world" assumed in the estimates changed[6]

Although the causal factors can be sorted this way in theory, in practice the challenge is to identify what contribution, if any, a given factor is contributing to a given result. Obviously, however, the estimator cannot be held accountable for all things that may go wrong in a project. Some events and situations that can have a substantial effect on project costs are not, in fact, predictable by estimators. For example, external factors such as unusually bad weather, labor strikes, shortages of labor, new regulations, equipment and inflation are risks that can only be assessed in a rudimentary way by estimators. The estimator also has little control over the implementation of the project, including planning and definition; design and engineering; and construction.

The HAZRISK model for estimating remedial action contingency concentrates on the controllable aspects of misestimation; estimate error and project definition. Figure 6 graphically shows that three of the primary sources of cost growth in cleanup projects: (1) project definition, (2) technological complexity and (3) media complexity of the site, are controllable by the estimator and accounted for by the HAZRISK model. Conversely, the influence of external factors on cost growth is not assessed by the model. However, Figure 7 shows that external factors only account for at most 29% of the variance in cost growth. By contrast, 71% of the variance in cost growth can be accounted for by the estimator with the model. In other words, the factors which drive cost growth are identifiable before major expenditures are made and can be accounted for in the estimate. Cost growth is largely a result of three systematic and controllable sources: low levels of project definition: poor understanding of the influence of site characteristics on costs; and neglecting the impact of the selected remedial technology on costs. While regulatory and other external factors certainly influence cost growth, they are not the sole or even primary causes of cost growth.
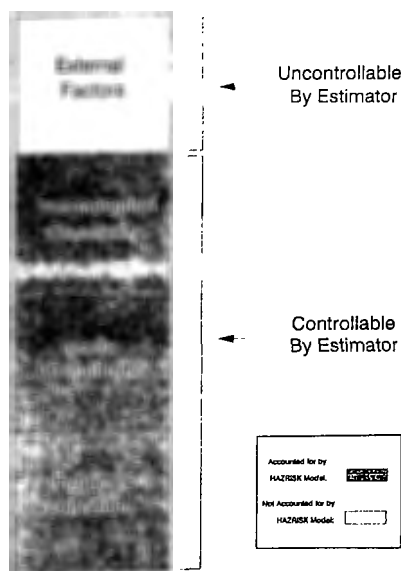
Figure 6
Sources of Cost Growth
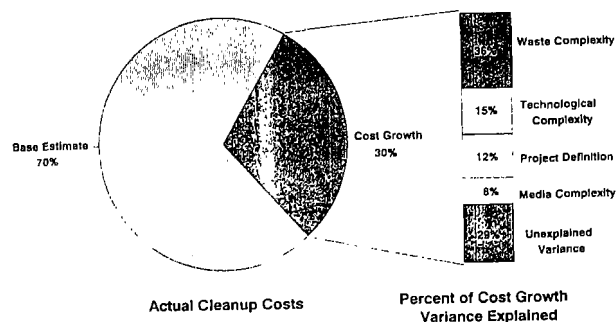
Figure 7
Cleanup Cost Growth Drivers

LESSONS LEARNED: STRATEGIES FOR MORE ACCURATE ESTIMATES

The experience of the 1980s showed that cleanup cost estimation errors are a persistent and serious problem. Data are now becoming available to help improve methods for generating estimates as well as for understanding the unique cost risks of cleanup projects. Figure 8 summarizes the strategies available for generating better base estimates and improving estimate accuracy. The challenge now facing the environmental restoration community is how to translate the experience of the past decade into building more accurate estimates. A few of the primary lessons learned are discussed below.
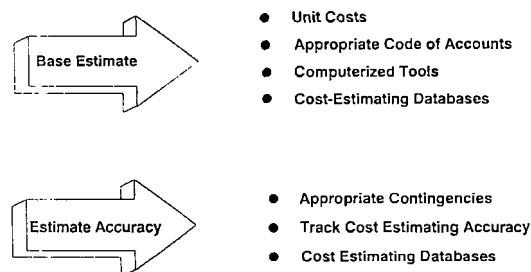
Figure 8
Current Strategies for More Accurate Estimates

Adjust for Uncertainties by Assigning an Appropriate Contingency

Most of the cleanup estimates in our analysis included contingencies intended to cover the costs of unforseen problems. These contingencies rarely exceeded 20% and generally are in the range of 10 to 15%. These contingencies tend to be based on contingencies required for more conventional projects and do not begin to cover the cost risks associated with cleanup projects.

Collect Better Cost Data

Because many estimates will continue to rely on unit cost data, the collection of new data and the routine update and maintenance of a cost estimating library is essential. Gathering data is also critical for building historical based models. Currently, only DOE, of the government agencies, has moved in the direction of developing a historical data base that tracks historical cost estimates as well as actual costs for cleanups and assessments. Without a historical track record documenting the cost and schedule performance of past projects, it is difficult to evaluate the potential of future projects in meeting their performance objectives. The U.S. EPA's CERCLIS data base, for example, does not currently track cost estimates.

The Key Cost and Cost Growth Drivers of Cleanup Projects Can Be Identified Before the Start of a Cleanup

This statement contradicts a prevailing view among NPL site mangers and environmental cost engineers that every site is so different that

attempts at classification are futile. The implication of this view is that we cannot use past experience to assist us in estimating new sites. The HAZRISK models, however, have demonstrated the utility of a historically based approach in checking the reasonableness of base estimates and in assigning appropriate contingencies.

CONCLUSION

Increasingly, tools and methods are becoming available to help improve the accuracy of cleanup cost estimates. By incorporating the lessons learned from completed projects, the cost estimating record of the next decade can be greatly improved.

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U.S. DOE's Program to Better Understand the Cost of Environmental Restoration Projects

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ABSTRACT

This paper summarizes the efforts of the U.S. Department of Energy (DOE) to better understand the cost and cost risks of environmental restoration (ER) projects. DOE is in the early stages of assessing and remediating their sites and therefore has the opportunity to put new systems into place to better manage cleanup projects. Understanding the factors that drive the cost and schedule of environmental restoration projects has been a particularly challenging problem for most of the responsible parties involved in cleanups. DOE recently completed the first phase of a program that included:

- **Developing a cost estimating handbook for DOE personnel.** This handbook provides guidelines for estimating both the assessment and cleanup stages of environmental restoration projects.
- **Organizing the Cost Assessment Team (CAT).** The CAT is composed of representatives from the major operating sites in the DOE complex and includes a mix of cost engineers and environmental professionals. This group serves as a forum for discussing cost issues and for recommending cost and schedule estimating procedures.
- **Initiating a research program in environmental restoration costs.** The research program included a detailed study of the factors that drive the cost and schedule of hazardous waste cleanup projects. The research program also resulted in the development of several cost and schedule assessment tools.

This paper provides insights on the utility of this approach and discusses the results of this program. In addition, future activities to improve cost estimates are identified.

INTRODUCTION

This paper provides an overview of the U.S. Department of Energy's (DOE) activities in developing more consistent and accurate environmental restoration (ER) cost estimates. The program was started in 1985 and recently was transferred from the Division of Planning and Project Management (DP-521) under DOE's Assistant Secretary for Defense Programs to the newly created Division of Program Support (EM-43) under the Office of Environmental Restoration and Waste Management.

DOE has taken a three-part approach to improving ER cost estimates. First, a group was formed to address ER cost estimating issues in the DOE complex (the Cost Assessment Team [CAT]). Second, a handbook was developed to strengthen DOE's ER cost estimates (the *Cost Estimating Handbook for Environmental Restoration*). Third, a research program was inaugurated to study the factors driving ER costs and schedules and to develop tools to assist DOE personnel in developing more accurate cost and schedule estimates (the HAZRISK Study). Each facet of this program is discussed in more detail below.

DOE'S COST ASSESSMENT TEAM

In 1988, DOE initiated a program to assemble a team of both cost estimators and environmental professionals to develop and review cost guidance in the ER area (Fig. 1). This group, known as the Cost Assessment Team (CAT), was designed to serve as a resource for the development and promulgation of tasks, techniques, procedures, data bases and project management activities related to environmental restoration cost estimating. The group first met on March 29, 1989, and the group's first product, the Cost Estimating Handbook for Environmental Restoration, was finalized in September, 1990.
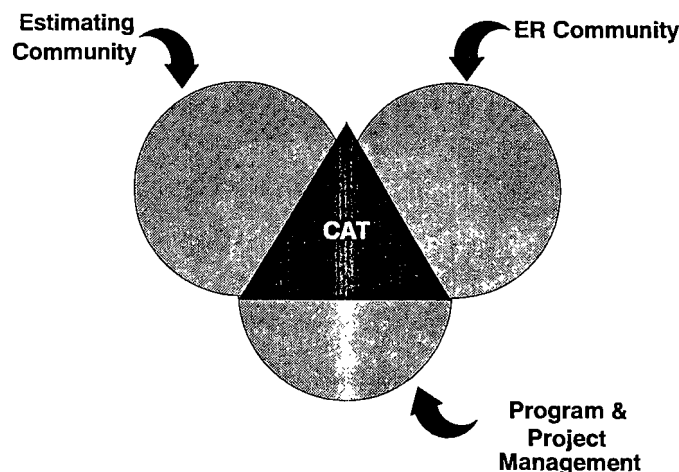
Figure 1
Where Does the CAT Fit?

The CAT was split into seven subtask groups to address cost estimating concerns. These groups were asked to:

- Develop recommendations regarding guidelines for RI/FS, Program/Project Management, Remediation Activities and ED&I
- Develop recommendations regarding guidelines for contingency applications
- Develop recommendations regarding cost estimating formats reflecting reporting and review requirements
- Develop a catalog of ER data bases
- Develop a dictionary of terms
- Develop recommendations regarding guidelines for escalation application

• Develop a catalog of cost estimating techniques and methods relevant to ER

The reports from these seven working groups formed the basis for the *Cost Estimating Handbook* and resulted in a set of issues papers that were forwarded to DOE-EM management.

Over the next several years, the CAT will be a source of cost estimating expertise for ER projects. Individuals on the CAT already serve a gatekeeping role in their home organizations with regard to new approaches and tools for ER cost estimating. Undoubtedly, the CAT can play an important role in improving DOE's learning curve in the cost estimating arena.

COST ESTIMATING HANDBOOK FOR ENVIRONMENTAL RESTORATION

The purpose of the *Handbook* is to assist cost estimators in the preparation of estimates for Environmental Restoration and Waste Management (EM) projects undertaken by DOE. The DOE has, in recent years, seen a significant increase in the number, size and frequency of environmental restoration projects that must be estimated by the various DOE offices. Current projections indicate that the EM program will be the largest nonweapons program undertaken by DOE. These projects create new and unique estimating requirements since historical cost and estimating precedents are meager at best.
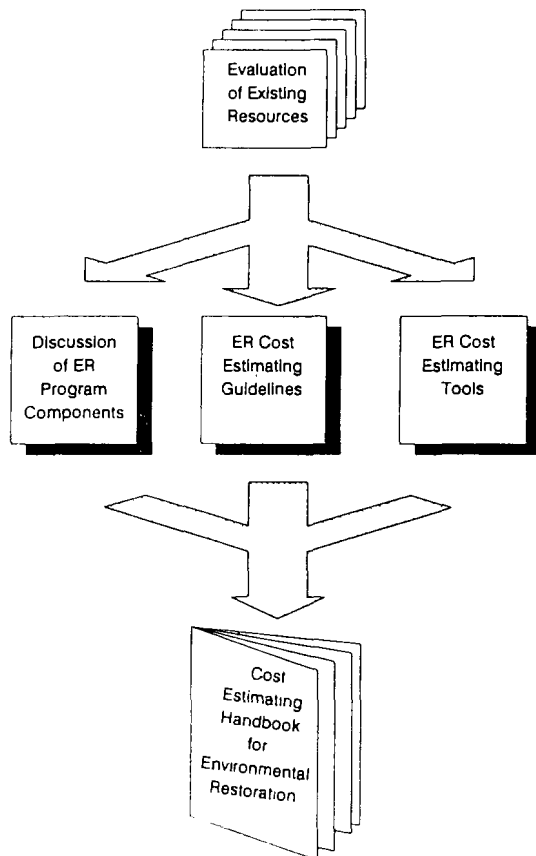
Figure 2
Process for Developing Cost Estimating Handbook

The principal thrust in producing the *Environmental Restoration and Waste Management Cost Estimating Handbook* was to produce a document which could be widely used in the field. This goal meant that the end users would have to be a principal source of the information in the *Handbook*. Therefore, it was prepared by cost engineers with extensive field experience in the DOE process. Further, it was intended to capture, as much as possible, the environmental restoration experience to date within the Department and throughout other government agencies

and the private sector. Figure 2 graphically depicts the process by which the *Handbook* was developed.

The *Handbook* is drawn from existing Department of Energy cost guidelines and orders and from U.S. EPA and Army Corps of Engineers documents, where appropriate. However, much of the *Handbook* was created by the participants based on their expertise, their research and the character of the environmental restoration process. Table 1 summarizes the contents of the *Handbook*.

Table 1
Chapter Summaries of U.S. DOE's Cost Estimating
Handbook for Environmental Restoration

Chapter	Title	Description
Chapter 1	Introduction	This chapter provides an overview of the *Handbook* and describes how the *Handbook* can be used by different audiences.
Chapter 2	Types of Estimates	This chapter describes several different types of cost estimates likely to be developed during the course of an environmental restoration project. Throughout this Chapter, the regulatory terminology for the CERCLA/SARA and RCRA programs is used to provide a baseline for discussing estimate types.
Chapter 3	Basis of the Estimate	A basis of the estimate should be written for each task explaining how the estimate was developed. This chapter outlines the items that constitute the basis of the estimate.
Chapter 4	Guidelines for Developing Cost Estimates	This chapter provides guidelines for estimating costs in each of four categories: Assessment, Cleanup Design, Cleanup Action, and Project and Program Management. These categories correspond to major classes of work within a typical environmental restoration project.
Chapter 5	Work Breakdown Structure	This chapter summarizes the Work Breakdown Structure (WBS) for ER work. The Environmental Restoration Program Work Breakdown Structure provides a framework for all program management functions for a project. The WBS will integrate budget, scope, and schedule through a program oriented hierarchy that begins at the highest level with the DOE Environmental Restoration program and progressively subdivides the work into smaller increments down to the subcategory level (Task Phase).
Chapter 6	Contingency	Environmental Restoration (ER) projects pose unique difficulties and challenges for the estimator. They are characterized by greater uncertainty than typical construction projects since contaminant types, amount of contamination, and the remedial technology are often not known until a detailed assessment has been completed. As a result, traditional engineering and construction estimating methodologies have failed to provide reasonably accurate estimates for ER projects. The purpose of this section is to provide guidance and a standard approach to the DOE community regarding contingency estimating practices for ER projects.
Chapter 7	Escalation	This chapter provides guidance in the application of anticipated economic escalation rates to ER cost estimates.
Chapter 8	Estimator's Checklist	Checklists have been prepared to assist the estimator in evaluating the proposed scope of work for completeness, complexity and accuracy. The checklists are organized to agree with the activities and program phases identified in the WBS and are not intended to be all inclusive, but merely a guide.
Chapter 9	Catalog of ER Databases	The objective of this chapter is to present a catalog of data sources and databases available for the preparation of cost estimates and undertaken as part of the DOE Environmental Restoration and Waste Management (EM) Program. The catalog of data and databases should facilitate the exchange of cost information between DOE estimators that would be unavailable or scarce to some groups and to keep data a current as possible to the actual cost experience.
Chapter 10	Catalog of Computerized ER Cost Estimating Tools	The first section of this chapter describes the cost estimating framework for categorizing the various tools. The second section provides a brief overview of each tool organized by the estimating stage at which it is best applied. The third section looks at other generic cost estimating tools that may be applied to environmental restoration projects. Finally, the conclusion offers recommendations on improvements and changes that are needed for the next generation of tools. A summary sheet on each tool also is included.
Appendices		Acronyms and Abbreviations, Glossary, Background on the Environmental and Waste Management Cost Assessment Team (EM-CAT), Illustrations and Examples, Bibliography

It is anticipated that this *Handbook* will enhance the quality of cost data within DOE in several ways by providing:

• The basis for accurate, consistent and traceable base lines

- Sound methodologies, guidelines and estimating formats
- Sources of cost data and data bases and estimating tools and techniques available to DOE cost professionals

The result will be greater comparability between estimates, reduced risk to projects from under/over estimating, expanded communication of cost drivers and improved capability to successfully meet budget validation requirements.

The *Handbook* was published in September 1990. Given the nature of the environmental restoration field, the *Handbook* will need frequent updates. It is expected that later versions of the *Handbook* will be expanded to include discussions of ER-specific escalation rates and factors, a code of accounts, contracting guidance and indirect cost calculation guidance.

DOE'S COST RESEARCH PROGRAM

Estimating the cost and time required for hazardous waste cleanup projects is a new art with little directly applicable experience. Existing cost and schedule data tend to be thinly scattered among a number of companies and federal agencies, and reliable cost estimating tools are just now emerging on the market. There are well-documented discussions of the ER estimate accuracy problem, including Schroeder's paper in these Proceedings; therefore, this issue will not be revisited in this paper.[1]

A research program was initiated in 1985 to better understand environmental cleanup cost drivers and to build a family of tools aimed at improving the accuracy of ER cost estimates. The early research, conducted by Hackney, concluded that a set of factors known early in the ER project cycle was related to cost overruns in projects.[2] However, in the 1985-1986 time period, there were insufficient data from completed remediation projects to fully test this hypothesis.

In 1988, the DOE along with seven firms in the oil and chemical industries provided support for the HAZRISK Project. Independent Project Analysis, Inc. (IPA) pooled their sponsors' experience and that of many others in order to develop realistic cost estimating, contingency setting and scheduling algorithms to be used for hazardous waste cleanup projects.

IPA's approach involves the systematic linking of cost and schedule outcomes with project characteristics. A HAZRISK project worksheet was developed to capture project information and was reviewed by the corporate sponsors, the DOE and the U.S. EPA. The worksheet organizes project information into the following areas:

- Site characteristics
- Nature and Type Contamination
- Site cleanup history
- Cleanup Funding History
- Cleanup technology
- Project management
- Estimated and actual costs
- Estimated and actual schedules
- Regulatory and external events

The tools are built using parametric statistical techniques such as correlation and multiple regression and have been described in detail in earlier publications.[3,4] These techniques are powerful extensions of the plots and cost-capacity curves familiar to all cost engineers. These methods have been used by DOE and IPA with considerable success to gauge the cost growth, schedule slippage and performance difficulties to be expected in first-of-a-kind process plants, megaprojects and other complex, innovative projects.[5,6]

Two classes of tools were developed during the first phase of the HAZRISK project. These tools:

- Identify and quantify the causes of cost and schedule overruns in environmental assessment projects (RI/FS projects under CERCLA/SARA or RFI/CMS projects under RCRA)
- Identify and quantify the causes of cost growth and schedule slip in environmental cleanup projects (RD/RA projects under CERCLA/SARA or CMI projects under RCRA)

The HAZRISK tools can be used early in the project cycle to evaluate

the riskiness of a project. A sample output from the assessment cost risk model is shown in Figure 3. Project managers can use the tools to build better estimates and to more effectively manage project risk. The HAZRISK project evaluation system also provides DOE with an easily applied set of techniques for checking the reasonableness of estimates generated by other organizations.
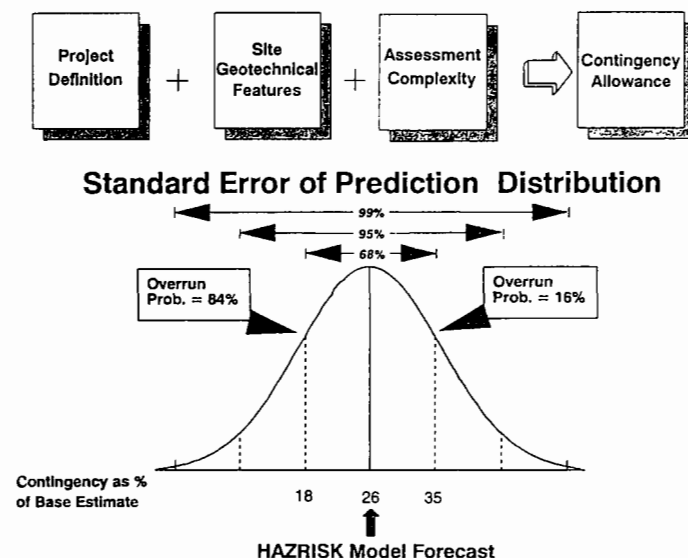
Figure 3
Output from the Assessment Contingency Allowance Model

The primary benefits to DOE of the HAZRISK research are:

- Knowledge of the factors driving cost growth in environmental remediation projects
- Set of models for evaluating and quantifying cost and schedule risks for assessment and cleanup projects
- Method for estimating the percent contingency needed to minimize cost overrun/underrun risks
- Ability to compare project costs and schedules with other cleanup projects around the country
- Capability to independently validate cost and schedule estimates generated by others
- User-friendly software package for evaluating the cost risks of assessment and cleanup projects

The second phase of the HAZRISK Project is underway. Funding has been provided to maintain the models, to validate the tools and to collect additional DOE data as they becomes available.

CONCLUSIONS

It is unfortunate, in some respects, that the activities discussed in this paper were not initiated even earlier. DOE is under a great deal of pressure from Congress and others to document and justify their multibillion dollar estimates of cost to remediate the complex. DOE's recent doubling of cost projections from the previous year simply exacerbates the problem. A well researched, systematic approach to generating cost estimates is likely to pay high dividends in the current cost conscious environment. It is hoped that the three activities described above will play a significant role in initiating improvements in DOE's ability to produce consistent and accurate cost estimates.

ACKNOWLEDGEMENTS

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Selection of a Commercial Hazardous Waste Facility with Minimum Generator Liability

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ABSTRACT

Potential liabilities associated with hazardous waste disposal are related to the waste properties, disposal practices and the threat to people and the environment in case of a potential or existing pollutant release. Based on the regulations, the liabilities are enforceable and long standing.

This paper summarizes a methodology developed to aid hazardous waste generators in selecting a commercial disposal facility with a relatively low risk of potential liability. In this methodology, 35 factors grouped into 9 categories were used. The methodology has two parts. The first part covers factors common to all facilities and the second part deals with the waste and treatment or disposal technology factors. The first part is highlighted in this paper. This two-part evaluation feature enables the user to adapt the methodology, to any type of waste disposal. In determining the scores for the factors used in the evaluation, an unranked paired comparison technique with slight modifications was used to weight the relative importance of the factors. In the methodology it is possible for the user to redefine the factors and change the scoring system.

To make the methodology usage more efficient, a computer program is used. The computer program is user-friendly and is written such that any changes in the methodology can be readily adapted. In addition to the basic evaluation, the computer program also has the capability for record-keeping related to waste disposal information.

INTRODUCTION

The current problem in hazardous waste management is that companies or agencies that generate hazardous waste, either as an ultimate product of a handling method or an intermediate process, must find the best disposal alternative.[7] Alternative handling methods for hazardous wastes include reuse, recycling, exchange, minimization and/or disposal. The waste disposal category includes treatment and/or direct land disposal.

Waste disposal in an environmentally sound manner could occur on-site or off-site. On-site disposal involves sizable environmental risks and liabilities and it has numerous regulatory compliance requirements.[2] Off-site disposal requires the selection of facilities that show full regulatory compliance, in addition to necessary investments in facilities, equipment and personnel to protect the generator from liability.

This study involved the development of a methodology which could be used to assess the potential liability associated with an off-site commercial hazardous waste treatment, storage and disposal facility (TSDF). The methodology is based on a thorough literature review of treatment and disposal considerations for hazardous waste and on existing methodologies (manual and computerized) that can be used to assess potential risks associated with hazardous waste handling and disposal. In the evaluation of potential liabilities, considerations related to a facility's financial strength (in terms of the company which owns the facility), regulatory compliance, business handling methods, management methods and technical ability are evaluated.

DESCRIPTION OF METHODOLOGY

The methodology we have developed has nine categories and 35 factors to evaluate the TSDF (Table 1). The categories are divided into two parts; the first part contains eight categories with 30 factors, while the second contains one category with five factors. The emphasis in this paper is on the facility evaluation in Part I.

According to their perceived relative importance, the categories and factors were assigned weights using an unranked paired-comparison technique.[4] Then each factor was assigned possible occurrence or

Table 1
Categories and Factors in the TSDF Evaluation Methodology

Part I: Eight Categories with 30 Factors Common to All Facilities

Category 1: Company's Financial Strength

 (F1) Financial Size
 (F2) Growth Pattern
 (F3) Average Annual Growth
 (F4) Ratio of Assets to Net Worth
 (F5) Revenue from Hazardous Waste
 (F6) Years in Hazardous Waste Business

Category 2: Facility's Legal Status

 (F7) Permit Status
 (F8) Insurance Coverage
 (F9) Closure and Post Closure Costs
 (F10) Provisions for Closure Costs and Post Closure Costs

Category 3: Facility's Business Status

 (F11) Number of Generators Using a Facility
 (F12) Types of Waste Handled

Category 4: Facility's Waste Handling Methods

 (F13) Waste Identification
 (F14) Record Keeping
 (F15) Waste Shipment

Category 5: Facility's Management Attitude

 (F16) Personnel Technical Training
 (F17) Process Technical Control
 (F18) Management Location

Category 6: Facility's Site Characteristics

 (F19) Population Pattern
 (F20) Flood Vulnerability
 (F21) Depth to Ground Water
 (F22) Vadose Zone Permeability

evaluation scores which represent varying degrees of potential risk (and, in turn, potential liabilities). A relative liability score can be obtained for each facility being evaluated by multiplying the importance weights by the scores and aggregating the products. The facility with the highest overall numerical score is considered to offer the least potential liability.

To aid in using the methodology, a user-friendly computer program was developed by the Environmental and Ground Water Institute (EGWI).[3] The basic structure of the methodology and the program are parallel. The program has a built-in flexibility to accommodate changes in the factor scoring. In addition, the program can retrieve facility information in the data base in different formats and it can be used to keep records of waste disposal information.

Category 1: Company's Financial Strength

The financial strength of a company is one indicator of an ability to adapt to changing regulations and advancing technologies. More importantly, it may be the best indicator of a firm's ability to finance facility repair or maintenance and to correct any facility deficiencies or releases. The rationale used in reaching this conclusion assumes that a company with greater financial strength offers lower liability to the firm using it for the wastes disposed of through its facility(ies). It is assumed that the financial strength of a facility is represented by the financial strength of its parent company, since a company could have more than one facility. A company here represents the company which exists today. It is assumed that present financial strength is more important than the financial history of the company.

Financial strength in the methodology is assessed in terms of six factors: (1) financial size in terms of a company's total assets and the profits in the latest fiscal year; (2) growth pattern over the last five years; (3) average annual growth over the last five years; (4) ratio of company's total fixed assets to the company's net worth during the latest fiscal year; (5) number of years in the hazardous waste disposal business; and (6) percentage of revenues obtained from hazardous waste management during the latest fiscal year.

Category 2: Facility's Legal Status

In terms of potential liability, a facility's legal status is very important. Legal status can be determined by the evaluation of four indicator factors: (1) permit status and the ratio of number of citations to the number of visits for site inspections; (2) insurance coverage; (3) closure costs; and (4) provisions for meeting closure costs. A facility with the maximum legal status category score is assumed to offer the least liability.

According to Section 3006(c) of the RCRA, state regulations must be equivalent to, or more stringent than, the federal regulations. State programs must be consistent with the federal programs and must ensure adequate enforcement. Therefore, while evaluating a facility for legal status, both federal and state regulations must be considered.

Category 3: Facility's Business Status

Under business status, the potential liability associated with a commercial hazardous waste facility is analyzed by considering possible causes of a release event and the possibility of reducing the impact of the liability in case of such events. The business status is determined by two indicator factors: (1) the number of hazardous waste generators using a facility; and (2) the types and quantities of wastes handled at a facility. Considering the fact that there is always some degree of uncertainty associated with hazardous waste handling (fear of "something going wrong somewhere"), it is to the generator's advantage to send the wastes to a facility: (1) where there is a relatively lower possibility of a release event occurrence; and (2) in case of an event, where there is a responsibility for equitable apportionment of the liability between the contributors.

Category 4: Facility's Waste Handling Methods

Liability based on waste handling at a facility is determined by three factors: (1) waste identification; (2) record-keeping; and (3) waste location. By regulation, a waste must be analyzed prior to treatment, storage and disposal in order to obtain sufficient information on the

waste being handled.[7] Waste analyses include both detailed physical and chemical analyses using U.S. EPA-approved methods. For an unknown waste, an analysis can be performed following a set of steps specified in the regulations.

Once a waste is analyzed, it is assigned for a proper treatment, storage, or disposal method either on-site or off-site. In case of an off-site disposal (i.e., when the appropriate method for handling is not available at a facility), the waste may be sent to another facility operated by the same owner/operator or to a different facility. According to regulations,[7] there must be proper waste manifesting and record-keeping of all the waste analysis results and the ultimate treatment and/or disposal. The ease with which the details of a disposal of waste can be traced at a facility is also an important measure of the potential liability.

Category 5: Facility's Management Attitude

Good management practices at a facility are assumed to be indicative of lower risks and less associated liability. Management practices in terms of potential liability can be determined by three factors: (1) technical training imparted to the personnel; (2) technical quality control implemented in the treatment process; and (3) ease with which the top management can be reached (management location) in case of an emergency.

Some of the good management practices identified in different methodologies include:[4] (1) employment of personnel with proper training to accomplish a quality job; (2) the presence of a special advisory committee for waste management; (3) use of special facility environmental auditing; (4) provisions for tight facility security; (5) proper worker protection equipment and insistence on proper use of the equipment; (6) medical surveillance programs; (7) presence of a well-trained on-site emergency rescue team; (8) periodic drills for fire and other kinds of emergency situations; and (9) good public and customer relations. A facility with all or most of these good management practices is assumed to exhibit minimum liability.

Category 6: Facility's Site Characteristics

In addition to the management/operational practices (covered under management attitude) at a facility, site physiographic demographic, hydrogeologic and water use characteristics are important in terms of risks to the environment or human health resulting from the potential release of a pollutant. This potential impairment could be through any one of four possible pathways (air, water, soil and direct contact). Direct contact could occur due to poor operational practices at a facility, lack of proper security measures to warn and advise the nearby public to keep away from facility operations or emergencies such as fires or accidental spills. Evaluation of the management attitude category has taken into account possible liability associated with direct contact.

In terms of site characteristics at a TSDF, impairment through direct contact and water pollution (both surface and groundwater) are the most important and often lead to large potential liabilities. Therefore, factors such as (1) population pattern, (2) flood vulnerability, (3) depth to groundwater, (4) vadose zone permeability, (5) class of the aquifer underlying a facility and (6) surface waste use at a facility are considered for indirectly evaluating potential liability. A site with a nearby dense population pattern will offer a greater potential liability than a facility surrounded by less dense population patterns. Water pollution is evaluated based on the following factors: (1) flood vulnerability of a facility; (2) depth to shallow groundwater table; (3) permeability of the vadose zone; (4) class of the major aquifer underlying the site; and (5) surface and groundwater use near the site.

Category 7: Facility's Monitoring Program

Monitoring of facility operations based on several parameters is required under regulations. Some of these monitoring parameters include: (1) regular personnel health examinations; (2) training on performing various facility operations (including security); (3) impact of biota; (4) air emissions; (5) surface water discharges; and (6) contamination of groundwater and the vadose zone. Monitoring requirements under each of these parameters are different; but, in a generic sense, each of these monitoring programs must have a well-documented monitoring plan.

According to the plan, a monitoring system to obtain information/samples is required. Also, a detection system is needed. Proper management (record-keeping, maintenance and operation) of the monitoring and detection systems is a must.

Potential liabilities associated with the monitoring programs related to personnel health, facility operations and impact of biota are covered under other factors (such as management attitude). Therefore, in this evaluation, it is assumed that only the programs related to monitoring of pollution pathways such as air emissions, surface water discharges and groundwater contamination need to be considered. It is assumed that poor monitoring of any one or more of these pathways will result in potential liabilities. The monitoring programs can be evaluated based on three factors: (1) detection system; (2) monitoring system; and (3) management of monitoring system.

Category 8: Facility's Deficiencies

According to regulations, facility deficiencies are inadequacies in a facility's design, operations and/or management. Deficiencies have the possibility of causing damage to human health or the environment. The damage could be due to a sudden or accidental (acute) release or a slow (chronic) release of a pollutant. Once a pollutant is released, the impact of damage varies according to the magnitude and type of the pollutant. Facility deficiencies are determined by evaluating three factors: (1) nature and type of a release; (2) impact of a release; and (3) the response of a facility to a release. These considerations cover both existing and past deficiencies. However, in considering past deficiencies, only those that have long-term impacts are considered.

Description of Factor Evaluation for Four Selected Factors

Detailed information on the evaluation of the 35 factors in the methodology is contained elsewhere.[4] Four examples will be included herein for illustration purposes: (1) insurance coverage; (2) personnel technical training; (3) surface water use; and (4) monitoring system management.

Insurance Coverage

The liability to a hazardous waste generator is, to some extent, reduced by liability insurance coverage for injury and property damage. This insurance is required under Subpart H of RCRA (40 CFR 264.147 and 265.147) for the owners and operators of TSDFs. The owner or operator must demonstrate financial assurance for liability coverage of third-party damage for as long as the facility remains in operation.[5] The U.S. EPA[7] specifies the actual amount of coverage required for each occurrence. For sudden accidental occurrences, a TSDF has to have liability coverage of at least $1 million per occurrence with an annual aggregate of at least $2 million, exclusive of legal defense costs. For non-sudden accidental occurrences, a land treatment, storage and disposal facility must have at least $3 million per occurrence with an annual aggregate of at least $6 million, exclusive of legal defense costs. The coverage can be through Comprehensive General Liability-CGL (covering sudden accidental occurrences) insurance or through Environmental Impairment Liability-EIL (covering both sudden and non-sudden accidental occurrences) insurance. Insurance coverage bought by a company can cover more than one facility owned by the company.

Considering the limited availability of insurance, according to Tenusak and Bailey[5], the U.S. EPA is studying alternative insurance mechanisms that could provide adequate protection. These alternatives can be: (1) pure captive, that is, owned and controlled by one company; or (2) group captive, that is, owned and controlled by a number of companies. A risk retention group is a kind of group captive that can only offer coverage to companies or professionals with similar exposure. Even though a TSDF with secure management practices offers low liability, liability coverage is considered here to reinforce the concept of the need for management. This point is emphasized by the fact that insurance coverage is difficult to obtain unless the management practices are sound and offer very low potential risk for the insurer.

The section dealing with financial instruments under the Hazardous Waste Data Management System (HWDMS) of the U.S. EPA lists all the financial instruments implemented at different RCRA facilities. The information on the financial instruments also can be obtained from facility documents, annual and other reports and state and federal regulatory offices. The selected scoring for the insurance coverage factor is as follows:

Insurance Coverage	Grade
Covers more than required using CGL/EIL	A
Covers adequate amount using CGL/EIL	B
Covers more than required using financial instruments other than CGL/EIL	C
Covers adequate amount using financial instruments other than CGL/EIL	D
There is no adequate coverage	E

Personnel Technical Training

With the increasingly sophisticated technologies and equipment being employed in hazardous waste management, it is important to employ highly qualified, well-trained and skilled technical personnel in order to obtain acceptable results. Required technical skills can be imparted to properly qualified employees by periodic training. Training is especially crucial when one considers the evolving nature of hazardous waste regulations and technologies. SARA regulations (OSHA-promulgated rules) clearly define the specific requirements of personnel in terms of qualifications and training in hazardous waste handling. Therefore, facility management which promotes good personnel training practices is assumed to offer minimum liability.

This factor is evaluated based on regulator site inspection findings on personnel training (in accordance with 40 CFR 264.16). The selected scoring for this factor is shown below.

Technical Training	Grade
Approved training plan and positive findings for the requirements under 40 CFR 264.16 or the state equivalent	A
Approved training plan and positive findings for most of the requirements (except for a few minor requirements) under 40 CFR 264.16 or the state equivalent	B
Approved training plan and negative findings for most of the requirements under 40 CFR 264.16 or the state equivalent	C
No approved training plan	D

Surface Water Use

Potential liability associated with a release to surface water is anticipated because of the relative risks to the people, resources and environment surrounding a facility. According to the revised Hazard Ranking System (HRS), a release to the environment can threaten drinking water, the human food chain, recreation and the environment.[8] The surface water source near a facility could be a stream, river, pond or lake.

The potential liability threat from surface water is determined by considering the distance to the nearest surface water source and the actual use of the surface water. The boundaries of the factor alternatives are fixed by applying the divisions used in the revised HRS's distance to surface water factor. In the revised HRS, the factor value is calculated to determine the potential of release by overland flow. In calculating the distance to the nearest surface water body, the high water level of the water body is used. The selected scoring for the surface water use factor is shown below:

Surface Water Use	Grade
Present at a distance > 2 miles but not used for human consumption or recreational purposes	A
Present at a distance > 2 miles but used for human consumption or recreational purposes	B
Present at a distance from 1 to 2 miles but not used for	

Table 2
Computer Input Data for Four Selected Cases

Factors	Facility Name EPA ID	Best Facility AAAAAA000001	Worst Facility BBBBBB000001	Moderately Better CCCCCC000001	Real Facility OKD005438300
Company Financial Strength					
	Financial size	FISA	FISD	FISB	FISA
	Growth pattern	FGPA	FGPD	FGPC	FGPA
	Average annual growth	AAGA	AAGD	AAGB	AAGA
	Ratio of assets to net worth	DCFA	DCFD	DCFB	DCFB
	Revenue from hazardous waste	RHWA	RHWD	RHWB	RHWA
	Years in hazardous waste business	YIBA	YIBD	YIBB	YIBC
Facility Legal Status					
	Permit status	PERA	PERE	PERB	PERA
	Insurance coverage	INSA	INSE	INSC	INSA
	Closure and post closure costs	CLCA	CLCD	CLCB	CLCC
	Provisions for closure/post closure costs	PRVA	PRVD	PRVC	PRVA
Facility Business Status					
	Number of generators using a facility	NOGA	NOGD	NOGB	NOGB
	Types of waste handled	TYWA	TYWE	TYWB	TYWD
Facility Waste Handling					
	Waste identification	WASA	WASC	WASC	WASA
	Record keeping	WRKA	WRKC	WRKC	WRKA
	Waste shipment	WLOA	WLOD	WLOB	WLOA

Factors	Facility Name EPA ID	Best Facility AAAAAA000001	Worst Facility BBBBBB000001	Moderately Better CCCCCC000001	Real Facility OKD005438300
Facility Management Attitude					
	Personnel technical training	TTRA	TTRD	TTRB	TTRA
	Process technical control	TCOA	TCOE	TCOC	TCOA
	Management location	MGLA	MGLE	MGLB	MGLA
Site Characteristics					
	Population pattern	SPPA	SPPE	SPPB	SPPA
	Flood vulnerability	SFVA	SFVE	SFVC	SFVA
	Depth to ground water	DGWA	DGWE	DGWB	DGWA
	Vadose zone permeability	PUFA	PUFE	PUFB	PUFA
	Aquifer classification	AQCA	AQCE	AQCC	AQCA
	Surface water use	WTUA	WTUE	WTUB	WTUA
Facility Monitoring Program					
	Detection system	DETA	DETE	DETB	DETA
	Monitoring system	MNTA	MNTE	MNTC	MNTA
	Monitoring system management	MSMA	MSMD	MSMB	MSMA
Facility Deficiencies					
	Release to environment	RELA	RELE	RELB	RELB
	Release impact	RIMA	RIME	RIMC	RIMB
	Reponse to release	RESA	RESE	RESC	RESB

[a]The letter codes in the table correspond to factor evaluations described in detail elsewhere (Pendurthi, 1990).

human consumption or recreational purposes   C

Present at a distance from 1 to 2 miles but used for
human consumption or recreational purposes   D

Present at a distance < 1 mile but may or may not be
used for human consumption or recreational purposes   E

Monitoring System Management

Monitoring system management refers to the periodic and/or daily maintenance of equipment, stations, wells and laboratories. The monitoring system management factor also addresses the use of the best available field and/or laboratory sampling, analytical and statistical techniques.

The performance of monitoring system management is indicated by: (1) effective record-keeping; (2) adequate monitoring data; (3) high quality laboratory analysis based on an approved QA/QC program; and (4) proper maintenance of monitoring equipment. In addition, efforts at a facility to improve the monitoring system are considered to be good management practice. These efforts might include: (1) improving personnel skills through participation in a round-robin conference and periodic training (in-house, through a university or U.S. EPA workshops); and (2) improving the process through the use of state-of-the-art equipment. Information on monitoring system management practices can be obtained by a site inspection. The selected scoring for the management performance factor is as follows:

Monitoring System Management	Grade
No construction or maintenance deficiencies in equipment/stations/wells; full compliance with data/information record-keeping; full compliance with the U.S. EPA's or state monitoring QA/QC program; periodic training related to laboratory analysis.	A
No construction or maintenance deficiencies in equipment/stations/wells; full compliance with data/information record-keeping; full compliance in providing sufficient monitoring data; full compliance with U.S. EPA's or state's monitoring QA/QC program; lack of periodic training related to laboratory analysis.	B
No construction or maintenance deficiencies in equipment/stations/wells; minor/major non-compliance with data/information record-keeping and/or minor/major non-compliance or compliance in providing sufficient monitoring data; full compliance with the U.S. EPA's or state monitoring QA/QC program; lack of periodic training related to laboratory analysis/presence of periodic training.	C
No construction or maintenance deficiencies in equipment/stations/wells; compliance or minor/major noncompliance or compliance in providing sufficient monitoring data; non-compliance with the U.S. EPA's or state's monitoring QA/QC program; lack of periodic training related to laboratory analysis/presence of periodic training.	D
There are construction or maintenance deficiencies in equipment/stations/wells; compliance or minor/major non-compliance with data/information record-keeping and/or minor/major non-compliance or compliance in providing sufficient monitoring data; compliance or non-compliance with U.S. EPA's or state's monitoring QA/QC program; lack of periodic training related to laboratory analysis/presence of periodic training.	E

HYPOTHETICAL EXAMPLE

A hypothetical example of the use of Part I of the relative potential liability evaluation methodology described earlier is summarized herein, while detailed information is contained elsewhere.[4] Four cases are used in the example: three are fictitious and one is real. The three fictitious cases were framed such that they represent best, worst and moder-

ately better facilities in terms of potential liability. Computer input data for four selected cases are tabulated in Table 2. The data were evaluated using the computer program developed for this methodology.[3] The modified unranked paired comparison technique was used in the evaluation and the relative ranking category weights and factor scores used in the computer program are presented elsewhere.[4]

The results of the Part I scores indicate that there is a possibility of obtaining maximum and minimum scores of 5000 and 980. The breakdown of the category scores (for these four cases) into factor scores is presented in Table 3. The breakdown of the total scores (for these four cases) into category scores is presented in Table 4. The real facility had a score of 4590 in Part I. Incidently, this case was ranked as the best of eight large United States hazardous waste facilities by the Council on Economic Priorities (Council on Economic Priorities, 1986).

Table 3
Factor Scores for Each Category

Financial Strength Scores*

EPAID	F1	F2	F3	F4	F5	F6	Financial Strength
OK OKD005438300	100	100	100	100	120	20	540
IN AAAAAA000001	100	100	100	130	120	50	600
CA BBBBBB000001	20	20	20	25	25	10	120
MN CCCCCC000001	80	40	80	100	100	40	440

*F1 = Financial size   F4 = Ratio of assets/net worth
F2 = Growth pattern   F5 = Revenue from hazardous waste
F3 = Average annual growth   F6 = Years in hazardous waste business

Legal Status and Business Status Scores*

EPAID	F7	F8	F9	F10	Legal Status	F11	F12	Business Status
OK OKD005438300	240	240	40	240	760	160	40	200
IN AAAAAA000001	240	240	80	240	800	200	100	300
CA BBBBBB000001	50	50	20	40	160	40	20	60
MN CCCCCC000001	200	150	60	80	490	160	80	240

*F7 = Permit status   F10 = Provisions for closure/post closure costs
F8 = Insurance coverage
F9 = Closure and post   F11 = Number of generators using a facility
   closure costs   F12 = Types of waste handled

Waste Handling and Management Attitude Scores*

EPAID	F13	F14	F15	Waste Handling	F16	F17	F18	Management Attitude
OK OKD005438300	133	134	133	400	150	150	100	400
IN AAAAAA000001	133	134	133	400	150	150	100	400
CA BBBBBB000001	25	25	25	75·	30	30	20	80
MN CCCCCC000001	25	25	100	150	120	90	80	290

*F13 = Waste identification   F16 = Technical training

F14 = Record keeping
F15 = Waste shipment
F17 = Technical control
F18 = Management location

Site Characteristics Scores*

EPAID	F19	F20	F21	F22	F23	F24	Site Characteristics
OK OK4005438300	210	100	140	190	190	170	1000
IN AAAAAA000001	210	100	140	190	190	170	1000
CA BBBBBB000001	30	20	30	35	35	35	185
MN CCCCCC000001	165	60	110	155	110	140	740

*F19 = Population pattern
F20 = Flood vulnerability
F21 = Depth to ground water
F22 = Vadose zone permeability
F23 = Aquifer classification
F24 = Surface water use

Monitoring and Deficiencies Scores*

EPAID	F25	F26	F27	Monitoring Program	F28	F29	F30	Deficiencies
OK OKD005438300	165	165	170	500	200	340	250	790
IN AAAAAA000001	165	165	170	500	250	420	330	1000
CA BBBBBB000001	30	30	35	95	50	85	60	195
MN CCCCCC000001	135	100	140	375	200	250	180	630

*F25 = Detection system
F26 = Monitoring system
F27 = Monitoring system management
F28 = Release to environment
F29 = Release impact
F30 = Response to release

Table 4
Total Scores for all Categories

EPAID	Fin	Legl	Busn	W. Han	Mgmt	Site	Mont	Defi	Total
OK OKD005438300	540	760	200	400	400	1000	500	790	4590
IN AAAAAA000001	600	800	300	400	400	1000	500	1000	5000
CA BBBBBB000001	120	160	60	75	80	185	95	195	970
MN CCCCCC000001	440	490	240	150	290	740	375	630	3355

Total Scores for Part I

CONCLUSIONS

The methodology described in this paper can be used to evaluate a selected TSDF or several TSDFs for which information is available,

based on factors covering financial, regulatory, business, management, location, legal and technical aspects. If several facilities are evaluated, whichever facility scores the highest can be assumed to offer the minimum potential liability.

When an individual facility is evaluated, the relative potential liability offered by a facility can only be estimated based on the experience of the user with the methodology. The methodology uses only such factors for which identified/identifiable sources of information exist. It is assumed that information gathering would not require facility inspection, although this could be done as part of the selection process.

Existing methodologies (parallel to the one described herein) on risk or liability assessment mostly cover only limited aspects of a hazardous waste facility. Here, the methodology covers a broad spectrum of important aspects of a facility. For better usage of the methodology, the following observations and comments are in order.

- Even though it is possible to relatively compare and evaluate different facilities with insufficient information, a user should give priority to those factors which have a relatively high weighting in the evaluation (e.g., in fixing the scores for the methodology, it is realized that site characteristics are the most important category of factors).
- More elaborate methodologies (similar to the present) can be developed covering individual categories of factors, which can be assembled to fit a particular user's needs. This gives a user more flexibility in the evaluation.
- The present methodology does not cover liability in terms of risks associated with hazardous waste transport; this deserves an exclusive and exhaustive evaluation. Therefore, similar methodologies can be developed to cover related aspects of the transport of hazardous waste.
- The methodology could be updated based on information obtained from a thorough review of previous liability law suits in the hazardous waste business.
- In the future, attempts could be made to connect existing state, federal and other data bases to evaluate the facilities, thus reducing the present need for special data collection requirements.

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Reduce Liability with Quality Data:
A Risk Management Approach

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ABSTRACT

In recent years, litigation has too often been the means of resolving incidents involving inappropriate measurements based upon inaccurate laboratory data. Remediation activities begun unnecessarily or false positive results of athletes' drug tests may both incur considerable costs, not solely financial, for the responsible party.

Since environmental monitoring data are being used on a more frequent basis as proof in legal actions, it is no longer sufficient that the data be accurate, precise, representative and complete. In addition, analytical results must be obtained by appropriate procedures (or methods) and must be carried through an unbroken chain-of-custody to eliminate the possibility of intentional contamination of or tampering with the samples. In certain cases, the analytical results may be completely invalid depending upon the amount of time by which the holding time for sample preparation or analysis has been exceeded.

Clients unwilling to pay for the analysis of recommended (and often required) QC samples, which can be both extensive in scope and expensive in price, bear the risk of receiving unreliable data. When key decisions are based upon such data, those making the decisions expose themselves and their organizations to potential losses of any of the following key elements:

- Net income
- Personnel
- Property
- Freedom from liability

By taking appropriate risk control measures before exposure to loss of one or more of these elements occurs, both the frequency and the severity of potential losses may be reduced.

INTRODUCTION

All too often everyday, activities have legal actions which revolve about them. Occurrences that twenty years ago would have been resolved equitably between the parties involved are now being protracted into years of court battles, with each successive ruling being appealed by the party against whom the decision was made.

Not only has this litigious trend created a significant increase in available work for lawyers, it also has necessitated more careful and specific contract negotiations between parties before any services are performed or products are delivered. The focus of this paper is to discuss methods which environmental laboratories and users of these analytical laboratories may use to reduce the potential for incurring liability. By its nature, this paper is intended to highlight the general topics to be considered in reducing liability; it is not meant as a specific examination to be applied exclusively to any organization.

Although the concept of Risk Management has been in existence for several decades, it traditionally has been associated with underwriters and the insurance profession. Now, however, the basic premise of risk management is being applied to almost every kind of business, particularly chemical analytical services, where site investigation and remediation decisions hinge primarily on the results of sample analyses from the laboratories. As the responsibilities and, in turn, costs of being named a potentially responsible party increase, so do the stakes involved in the event of litigation.

The Risk and Insurance Management Society defines risk management in its glossary as "a management discipline whose goal is to protect the assets and profits of an organization by reducing the potential for loss before it occurs... and financing the remaining exposures so that in the event of a major loss, the organization can continue to function without severe hardship to its financial stability."[1] Risk management can be subdivided into three categories: (1) risk assessment, (2) risk control, and (3) risk financing. (This paper is only concerned with the first two categories, the third being a world unto itself, usually addressed by the curriculum of a business school).

DISCUSSION

Risk assessment, the first area of risk management, involves identifying exposures to loss, examining feasible alternative procedures to be implemented for the identified losses and then selecting the apparently best risk management technique or combination of techniques to be used.

Identifying the exposures to loss inherent in any organization means examining every aspect of the business from material holdings and real estate to intangible images of the company, such as public relations and long-term employment potential for the employees. In general, there are four areas into which potential losses may be grouped:

- Net income
- Property
- Liability (legal action)
- Personnel

For example, a poor or sudden downturn in the image of the company as perceived by the general public could result in a loss of net income due to a decrease in patronage and, therefore, sales. This is what happened to Exxon following the Valdez oil spill. On the other hand, a company may own a piece of real estate which is found to be the source of groundwater contamination in a suburban area. This problem would decrease the value of that property as well as incur considerable cost to the company if it is found responsible for cleanup. Regardless of whether or not he or she is an employee, if an individual is injured on the company's property, or because of an oversight on the part of the company, a lawsuit may be filed against the organization, incurring significant costs, not just in the settlement of the claim but in legal fees as well.

Feasible Risk Management Procedures

Examining feasible alternative risk management procedures to those already in existence can be accomplished in one of two ways. A risk manager, or some internal management-level person with an appropriate background, may review the options. This method is usually most effective when only a few elements are lacking or need updating in an organization's risk management structure. For instance, if risk management has been an established aspect of a corporation's structure, and some real estate is being considered for acquisition by the company, the prudent risk manager might have a background check done on the history of the site. A few soil and water samples could be taken for analysis if contamination is suspected. Based on the findings of a preliminary investigation of this sort, a recommendation could be made regarding purchase of the property. If the property had merits in spite of a likelihood of some minimal degree of contamination, the property could be purchased by a subsidiary of the parent company. With the benefit of specific legal conditions written into the contract, in the event of a lawsuit, only the subsidiary and its assets would be subject to legal action, rather than the whole organization.

The second means of examining feasible alternative risk management techniques is to have a full evaluation done on the corporation by an independent consultant, who would also assist in implementing a corporate-wide risk management program. This option is most appropriate for a business without an existing risk management structure or with one in need of major revision or updating.

Selecting Risk Management Techniques

Once a comprehensive examination has exhausted the possible alternative risk management techniques available to the organization for each of the four major categories of potential loss, selection of the best technique or combination of techniques is the obvious next step. This phase of the process is individually tailored to meet the specific needs of each corporation; therefore, in each instance, the technique or techniques chosen will be different. However, the decision-making process should be conducted on the corporate level involving upper level management if it is to be far-reaching in scope and is to affect the entire organization (or a large part of it). If, on the other hand, only one department, division or single process in the whole corporate structure is likely to be affected, these decisions should include the input of that department or section manager.

Risk control, the second area of risk management, involves implementing the risk management measures which have been selected as the best possible alternative measures in order to avoid exposure to loss, prevent exposure to loss or reduce exposure to loss. In reality, it is often neither practical nor possible to avoid any exposure to potential losses since this would necessitate doing no business at all. Therefore, the most that can be done is to either prevent or reduce exposure to loss. Preventing exposure entails reducing the probability, or frequency, of the occurrence of a particular loss, but does not eliminate it entirely. Reducing exposure is accomplished by implementing any measures which diminish the severity of any losses which do occur.

Environmental Data

One of the best ways to ensure that environmental data are of adequate quality to meet the stated objectives for which the samples were originally collected is to practice risk control measures which will reduce exposure to loss. This process entails employing the necessary quality control components associated with the analytical method appropriate for evaluation of the samples, as well as some more general quality control practices which need to be followed regardless of the analytical testing procedure used.

Precision, accuracy, completeness and representativeness are the usual quality control elements that an analytical method is expected to provide in order to be considered appropriate for a given purpose. Three additional elements, method detection limit, comparability and data usability, are equally important considerations which determine a method's suitability.

Method Detection Limit

The analytical method needs to be chosen based upon the quantitative objective for detection of the analytes specified by the data collection activity, not vice versa. More simply stated, the objectives should be written first and the analytical methods then chosen in order to meet those objectives. The objectives should not be written based upon the capabilities of a particular method. For instance, it should first be determined that groundwater samples are to be analyzed to the part per billion level for trace metals; then a method may be selected that is capable of detecting trace metals in water to that level.

Comparability

Comparability is a qualitative measure which expresses the measure of confidence with which data are found to be equivalent to data generated at other times and places by different scientists using the same procedures. Evaluating the comparability of data sets indicates the degree of equivalence the data set has to others in terms of the measurement of a specific parameter or group of parameters. This requirement is particularly important when data sets for a specific parameter are interpreted in regard to action levels, permit limits or regulatory standards.[2]

Data Usability

Whether or not a data set is sufficiently complete and meets the quality criteria defined in terms of the specific objectives of the data collection activity determines its usability. The specific objectives, defined in quantitative and qualitative terms, are the criteria for evaluating the usability of the data. There are additional quality control measures which can be practiced to control the risk inherent in analytical work and which can and should be followed regardless of the analytical method employed. An experienced sampling team should always collect the samples according to the procedures and at the specific locations and depths prescribed in the work plan. Obviously, the data will be meaningless if the sample is collected at a depth of two feet at a location where waste is suspected to exist below eight feet.

Chain-of-Custody

From the moment the samples are collected, an unbroken chain-of-custody needs to be maintained. This requirement means that when not in direct sight of the responsible individual, the samples must be secured such that access to them cannot be gained by unauthorized personnel. These limited access measures prevent tampering with the samples and ensure that the analytical results are from the samples collected at the actual site location designated. Each time the samples are transferred from one person to another, both the individual relinquishing the samples and the individual receiving them are to sign the chain-of-custody form. A properly maintained chain-of-custody form provides a record of every person who has come into contact with the samples, including shipping agencies.

Analysis

Once the samples arrive at the sample receiving area of the laboratory, holding time becomes important. The time period between sample receipt and completion of the sample preparation process is critical to the viability of the sample. While it may be argued that a sample found to contain benzene at 200 parts per million even though the holding time has expired would have shown even more benzene had it been prepared and analyzed within the holding time, problems arise when the reported concentration approaches the detection limit or an action limit. Also, the possibility is strong that target compounds which were present in low concentrations in the sample may be reported as nondetectable if the holding time is exceeded.

Finally, it is critical that appropriate methods be used for preparation and analysis of the sample, depending upon the matrix, the analyte(s) of concern and the method detection limit. Equally important in obtaining meaningful analytical results are the instrumentation used for detection and, therefore, the analytical method chosen.

Once these various risk control techniques, in the form of specific and general quality control measures, have been implemented, the results need to be monitored. Both project specific measures and overall program implementations of these practices need to be evaluated and modified as necessary. No quality control measure or program is able to sustain itself once initiated without any attention or adjustment to make the system work. Quality control is a living system, not a perpetual motion machine.

CONCLUSIONS

Quality control should not be thought of as extraneous or as an "add on" at the end of a project or procedure. The purpose of quality control measures can be thought of as "insurance," not against things going wrong, which is sometimes inevitable, but against the data being worthless or meaningless when problems do occur. Blanks help locate possible sources of contamination, for example; however, they do not eliminate the contamination. The blank results may change the way in which the data are interpreted in light of contamination that is known.

The same results might be interpreted in a completely different manner, possibly incurring needless exorbitant costs to the party involved, if the blank results were not available because blanks had not been prepared and analyzed. Quality control is therefore a worthwhile expenditure as a form of insurance policy against some of the considerably more costly risks that are reducible or preventable.

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Structuring Environmental Cleanups

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ABSTRACT

The U.S. EPA in its recent report, *A Management Review of the Superfund Program*[1] — the "90-day review" — pledged to rely on an "enforcement first" strategy that seeks cleanup funding from responsible parties at hazardous waste sites and turns to the Superfund only as a last resort. This strategy already shows promise: recent EPA reports indicate that responsible parties now bear the cost of more than half the studies and cleanups underway nationally. But even as potentially responsible parties (PRPs) come to accept Superfund liability, they face a renewed assault on corporate finances as the average cost of cleanup grows.

Because of increasing costs, realistic and innovative mechanisms for PRPs to finance cleanups have become more important than ever. Recognizing this need, the U.S. EPA recently agreed for the first time to accept a PRP's use of a structured settlement — payments over time in lieu of a lump-sum settlement, usually funded by an annuity — to pay for portions of cleanup at a Superfund site.

The structured settlement offers a proven means of covering large, long-term payments, combining an initial, cash payment with periodic payments in the future, usually funded through an annuity or similar financial instrument purchased from a qualified life insurer. Such an arrangement takes advantage of the "time value" of money — in other words, earns interest through investments — so that the initial expense for PRPs is less than a traditional lump-sum payment, providing an added inducement to settlement. The U.S. EPA itself in a 1988 study[2] cited structured settlements as the most promising alternative means of achieving settlement between the Agency and PRPs.

The structured settlement is used routinely by private industry in settling wrongful death and bodily injury cases and recently has been applied in at least four hazardous waste cleanup settlements where remediation costs ranged as high as $6 million.[3] The first use of the structured settlement in a federal Superfund cleanup was in some respects unconventional — rather than the common steady stream of payments stretching over a number of years, the structured settlement in this case will return a one-time payment 17 years in the future. But the U.S. EPA's decision to accept this financing alternative marks an important first step in more routine use of the structured settlement in hazardous waste cleanups and other environmental areas.

This paper briefly reviews alternative methods of cleanup funding, describes the structured settlement and examines the U.S. EPA's first use of the structured settlement. The paper concludes by summarizing the views of responsible parties, the life insurance industry and structured settlement specialists on applying the concept to Superfund sites and reviews possible next steps.

ALTERNATIVES FOR FUNDING CLEANUP

As the number of potential hazardous waste sites grows and the average

cost of cleaning up a single site climbs past $25 million, the U.S. EPA, PRPs and insurers alike will turn to alternative financing mechanisms. Traditional methods such as lump-sum cash payments or trust funds could be complemented by alternative means such as annuities, surety bonds, letters of credit, financial tests or corporate guarantees.

The traditional arrangement in Superfund settlements has been the lump-sum cash payment, usually to compensate for past, present and future cleanup costs. But lump-sum payments have at times proven difficult to negotiate because of the complexity of issues involved and the high cost associated with Superfund cleanups. In addition, the U.S. EPA cannot directly receive cost reimbursement; instead, recovered funds revert to the Superfund at the U.S. Treasury, so the U.S. EPA cannot guarantee that recovered funds will be returned to assist in continuing cleanup at the site where they were spent.[4]

TRADITIONAL USE OF THE STRUCTURED SETTLEMENT

The search for innovative cleanup financing methods has until recently overlooked a tried and proven approach that, while not a universal cure, could benefit both the regulated community and the government.

In a structured settlement, the plaintiff agrees to accept payments for damages over time in lieu of a single lump-sum payment from the defendant. The payments can be funded in several ways, but the most common method is an annuity issued by a life insurance company. The structured settlement offers a method of financing that lowers the PRP's initial cost, offers other benefits to the PRP, its insurers and U.S. EPA and provides a "coalescing" factor leading to successful negotiations for past, present and future cleanup costs.

First applied to settle thalidomide cases involving bodily injury during the 1960s, the structured settlement came into greater use during the early 1970s. Structured settlements initially were limited to serious bodily injury cases, although they have been used increasingly in other liability settlements involving both catastrophic and less serious liability claims and have moved from exclusively private sector to include government settlements. The most recent (1988) U.S. Department of Justice estimate indicates that the federal government has used the structured settlement to resolve approximately 500 claims.[5] In addition, at least 16 states now permit — or even require — their use in settling liability claims that meet certain criteria.

STRUCTURED SETTLEMENTS AND ENVIRONMENTAL CLEANUPS

The structured settlement is increasingly moving into the environmental arena. Representatives of the life insurance and structured settlement industries report that cleanup costs for at least four private hazardous waste sites will be financed by structured settlements.[6] The cleanup sums involved have ranged from $1 million to $6 million. In addition, the U.S. EPA recently accepted what appears to be the first-

ever structured settlement to fund portions of cleanup at an NPL site. This settlement is more fully discussed later in this paper.

Briefly, the structured settlement can reduce the initial cost to PRPs by taking advantage of the time value of money and yet still ensures the U.S. EPA of full recovery of the agreed-upon sum. A 1988 U.S. EPA study[7] of existing and alternative financing mechanisms found that structured settlements showed great promise for promoting Superfund settlements.[8] Of the mechanisms studied — lump-sum payments, traditional trust funds, liens on PRP assets and alternative means including surety bonds, letters of credit, financial tests and corporate guarantees — structured settlements alone showed promise in lowering the settlement cost to PRPs without interrupting planned response activities.

The study found that structured settlements may promote CERCLA settlements because they can: (1) reduce PRPs' settlement cost compared to a lump-sum payment, (2) provide a secure source of funds for cleanup, (3) help ensure the timely completion of the U.S. EPA or PRP response actions, (4) provide payments in excess of the estimated response costs, perhaps providing incentive for the U.S. EPA or PRPs to settle, (5) serve as a no-cost coalescing factor between PRPs and the U.S. EPA and (6) contain special features to encourage PRPs to settle. A test case in the U.S. EPA study showed that the structured settlement could have reduced PRPs' initial expense by 34 percent at one Superfund site.

The concept may be seen initially as applying predominantly to long-range actions involving as future costs, including operations and maintenance — its application in the case is discussed later in this paper. The structured settlement may be best suited to the remedial action (cleanup) phase because the remedy is well defined and the PRPs' extent of liability and ability to pay are more clearly understood.[9,10]

CASE STUDY

The process for negotiating a structured settlement generally proceeds as follows. The plaintiff, as recipient of the annuity payment, agrees to accept a stream of periodic payments instead of a lump sum from the defendant.[11] (The Superfund structured settlement will differ here because the U.S. EPA as plaintiff agrees only that PRPs may fund cleanup through a stream of periodic payments instead of a lump sum. The U.S. EPA is not the "recipient" of the payments.) Annuities[12] issued by life insurance companies provide the funding mechanisms because of their security, flexibility and ability to lower initial costs.

The settling parties confer with a structured settlement specialist to design a schedule of payments tailored to meet the needs of a specific case. The specialist is an annuity broker, financial consultant and third-party negotiator. Specialists generally are not compensated directly for time spent in negotiations; instead they receive a commission from the life insurer selected to issue the annuity.

A life insurance company the U.S. EPA deems qualified issues the annuity used to fund the structured settlement. The defendant — in a Superfund settlement, the PRP — buys the annuity for a single premium. The life insurer or its affiliate then makes payments to the party the settlement designates and is legally bound to deliver the payments to the specified party according to the terms of the annuity policy.

The U.S. EPA recently accepted a proposal by a group of PRPs to provide for a Superfund cleanup partially funded by a structured settlement. The agreement involves the Liquid Disposal, Inc. site in Shelby Township, Michigan.[13] The original consent decree for Liquid Disposal was signed in May 1989 and entered in December 1989; parties first broached the concept of a structured settlement to fund cleanup in January 1990 and agreement was reached in March 1990.

It is important to note that this application of the structured settlement differed from the traditional method in that, rather than supplying the conventional stream of payments over time, the annuity purchased will provide a one-time payment for operations and maintenance in 2007. In addition, this case is simple but illustrates the advantages of the structured settlement.

The 6.8-acre Liquid Disposal facility was used mostly to incinerate combustible liquid organic wastes. Since the site's inclusion in September 1983 on the NPL, the U.S. EPA has completed four removal actions

at the Liquid Disposal site. The ROD for the site calls for solidification and fixation of soils, installation of a slurry wall and groundwater extraction and treatment with long-term operations and maintenance. Operations and maintenance, to begin about 17 years from the date of the agreement, are projected to cost about $6.1 million.

Parties to the $24.5-million settlement include about 500 de minimis settlers not included in the structured settlement[14] and 27 major parties that will perform the Liquid Disposal site cleanup. The site consent decree required establishment of a separate operations and maintenance trust fund; this fund will be financed through an annuity or structured settlement payment.

The U.S. EPA agreed to the 17-year annuity term as coming 16 years after groundwater treatment began. But the U.S. EPA retained power to review and change the structured settlement. In addition, the U.S. EPA wanted to avoid assuming responsibility for the selection of the company that issued the annuity. Therefore, the U.S. EPA would only "not disapprove" of the selected annuity fund.

Although the Liquid Disposal case represents a simple application of the structured settlement, it illustrates the concept's advantages. Significantly for the PRPs, the annuity premium — the total cost to PRPs for operations and maintenance — represented less than 25 percent ($1.5 million) of the $6.1-million total fund that will be required for operations and maintenance over the life of the cleanup. Under a traditional lump-sum agreement, the entire $6.1 million. Such cost savings provide a powerful economic incentive for PRPs and their insurers to settle with the U.S. EPA. Yet the U.S. EPA is assured that full funding will be available when needed to complete operations and maintenance activities. Furthermore, the Liquid Disposal case demonstrates the flexibility of the structured settlement. Rather than the traditional stream of payments, the structured settlement in this case was tailored to the needs of the U.S. EPA by providing a one-time payment many years in the future. If needed, the structured settlement also could have been tailored to accommodate uncertainties such as cost overruns or remedy failure.

PRIVATE INTEREST AND USE GROW

Over the past several years, PRPs, their representatives, structured settlement specialists and life insurers have shown growing interest in applying the structured settlement to Superfund cleanups. To date, at least four private cases, with a total annuity value exceeding $10 million, have been resolved by structured settlements.

Since its 1987 study, the U.S. EPA has investigated the possible application of structured settlements to Superfund cleanups; the private sector also has taken steps toward their more routine application. In informal conversations held over the past year, specialists, life insurers and representatives of private parties said they regarded the structured settlement as a useful tool in Superfund settlements and predicted continued rapid growth in its use. The following general points emerged from these conversations:

- Although the structured settlement usually has been applied to high-cost settlements, the concept may be useful for long-term cleanups involving small, less financially stable PRPs. The PRP may declare bankruptcy, go out of business or in some other way become inaccessible as a source of funding when cleanup is under way. The structured settlement, however, ensures that cleanup funding is available when needed. In addition, the structured settlement provides a sort of double guarantee to the U.S. EPA that funding will be available when needed; unless the PRP is released from further liability, it stands as guarantor to the annuity.
- The structured settlement as applied to Superfund has certain unusual features such as the potentially large number of parties. In addition, apportionment of liability may complicate the settlement process, as it does with all variants of Superfund settlements.
- The structured settlement may be useful in other environmental areas as well, although many members of the industry concede they have yet to explore these options in much depth. For example, some have suggested that structured settlements may be equally suited to corrective actions under the RCRA and to commercial real estate transactions that involve a high degree of environmental exposure.

- Generally, the advantages offered by structured settlements increase with the size of the cleanup and the time involved. Some facets of hazardous waste cleanup are more predictable than others and these areas are probably better suited to this approach. Where the process is less predictable, the structured settlement still may be suitable as a partial settlement to reduce the overall cost of the work.

- Some barriers remain to the widespread use of structured settlements in environmental cleanups. First, parties to a settlement need to understand the potential financial, substantive and security advantages of this type of settlement. Second, some public resistance to structured settlements could be encountered. Citizens, believing that the parties who created the pollution should pay a penalty, may object on the basis that the structured settlement allows the responsible parties to lower their cost.

- Even among PRPs, the largest contributors may balk at a structured settlement. They may want to retain the "time value" of money for themselves. In addition, as the number of PRPs grows, such issues as accounting for interest income, costs associated with the separate vehicle and even simple bookkeeping become obstacles.

- Finally, federal and state governments could play a role in promoting the concept simply by endorsing it and encouraging its early consideration among PRP groups without necessarily making a policy statement for that particular site.

- The structured settlement can be applied to any situation where periodic payments satisfy the requirements, both cost and payout, of the settling parties. Current United States tax codes are, however, favorable only in cases involving physical injury or illness.

NEXT STEPS

The first step in successfully applying structured settlements to hazardous waste site cleanups that involve the U.S. EPA as a party is building consensus within the structured settlement community. In addition, structured settlement specialists who decide to enter the environmental field must operate on common ground, underscoring the importance of consensus within the industry. The concept also would benefit from the early design of products that can be tailored to site-specific circumstances and easily understood by private parties already facing myriad complex technical and legal issues. The structured settlement industry should attempt to anticipate the many contingencies that must be accommodated in hazardous waste cleanups, such as the possible need for changes in cleanup plans or the potential for remedy failure. The expertise that already exists in the industry should, however, enable structured settlement specialists to overcome such obstacles.

If the structured settlement is to come into routine use, the hazardous waste defense bar and especially outside counsel to PRPs, should continue its process of self-education on the financial aspects of hazardous waste cleanups. For PRPs and their attorneys, liability as an issue typically takes precedence over the method of financing that will best meet the needs of private parties and the government. In addition, as structured settlements initially are applied in a sporadic manner, transaction costs may be high and PRPs may only reluctantly embrace the structured settlement. Therefore, real gains in this area will come only when PRPs and their representatives are convinced that the structured settlement is a viable and workable option for financing cleanup.

The technical and legal intricacies native to the traditional uses of structured settlements may be dwarfed by the complexities in the environmental area. The structured settlement industry will find that federal and state governments (and their environmental agencies) will become more receptive to this and other innovative concepts as the industry becomes versed in environmental cleanup issues, programs, regulations and requirements.

DISCLAIMER

The opinions and conclusions in this paper are the authors' alone and do not necessarily reflect those of the U.S. EPA. Mention of company, trade, or product names is not intended as an endorsement.

CONCLUSION

The structured settlement could become an important element in the nation's effort to clean up an unanticipated and still growing array of environmental problems. Issues such as tax ramifications and institutional reluctance both in the public and private sectors continue to hinder its widespread use. But as government and industry begin to realize the advantages this concept can provide in the environmental field, quicker, more financially secure cleanups at lower cost will occur.

ENDNOTES

1. U.S. EPA, *A Management Review of the Superfund Program*, see for example Chapter II, 1989.
2. U.S. EPA Office of Waste Programs Enforcement, *An Analysis of Alternative Cleanup Financing Mechanisms for Their Potential Application to CERCLA Settlements*, Feb. 1988.
3. Based on informal conversations with representatives of life insurance companies, Mar. 1990.
4. The U.S. EPA is developing guidance on management of "special accounts" for cashouts that will enable the Agency to receive money directly for response work to be performed by the U.S. EPA or PRPs. A cashout to the U.S. EPA will generally result from one of the following circumstances:
   - *De minimis* PRPs settle for a cash payment to the U.S. EPA
   - Marginally viable prps make payments commensurate with their ability to pay
   - Major settlers agree to fund a U.S. EPA response in lieu of conducting the response themselves.
5. Correspondence from Jeffery Axelrad, Director of the Torts Branch, Civil Division of the U.S. Department of Justice, revised July 19, 1988. Cited in Hindert, Dehner, Hindert, *Structured Settlements and Periodic Payment Judgements*, p. 1-16.
6. Based on informal conversations with PRP representatives, life insurers, and structured settlement specialists, Oct. 1989 to Jan. 1990.
7. U.S. EPA Office of Waste Programs Enforcement, *An Analysis of Alternative Cleanup Financing Mechanisms*, cited as ref. 2.
8. Mason, R.J., and Johnson, M.F., 1989, "Structured Settlements: A New Settlement Incentive" *Superfund '88: Proc. of the Ninth National Conference*, HMCRI, Silver Spring, MD.
9. It also has been suggested, but not demonstrated, that the structured settlement could be considered for short-term actions such as remedial investigations/feasibility studies.
10. Despite its advantages, the structured settlement generally may not be useful when the sum involved is small or the repayment period is brief. Structured settlement specialists cite four additional potential drawbacks, although these primarily relate to structured settlements in cases involving personal bodily injury:
    - A minor but real level of financial risk in accepting payments over time
    - Limited lack of the amount of the award
    - Potential misperception of the amount of the award
    - A new level of complexity in settlement
11. The U.S. EPA, for example would continue to require past costs as a lump sum.
12. The annuity is an investment that yields a level or varied stream of cash flows for a defined period in exchange for payment of a premium.
13. The following was based on conversations with parties to the settlement.
14. Liquid Disposal also represents the first de minimis settlement for U.S. EPA Region 5.

Development of a Real-Time Air Monitoring Technique for Dimethyl Mercury

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ABSTRACT

Many forms of organic and inorganic mercury are pervasive in the environment, and both natural and industrial sources contribute to the total environmental mercury burden. Mercury can be biologically metabolized to form various organo-mercurials such as dimethyl mercury (DMM). Dimethyl mercury is approximately ten times more toxic and 10,000 times more volatile than elemental mercury. In biologically active areas where an organic or inorganic source of mercury is present, DMM represents a potential health risk via the air route of exposure because of its high volatility and toxicity.

Mercury-contaminated soils and sediments are frequently biologically active and have been demonstrated to contain DMM. If left undisturbed, emissions of DMM will be related to the biological generation rate of DMM as well as the emission rate through the soil or sediments as regulated by porosity, temperature, pressure and other physical-chemical factors. However, when the soils are disturbed, as in a remedial action at a waste site, the potential for elevated emissions of DMM increases. This increased potential for emissions raises numerous concerns from an industrial hygiene point of view.

Due to DMM's high volatility and toxicity, real-time monitoring, in conjunction with confirmatory sampling, is the preferred method of quantifying any health threat. Recent research conducted by the U.S. EPA's Environmental Response Team (ERT), with the support of the Response, Engineering and Analytical Contract (REAC) Roy F. Weston Inc., has resulted in a potential real-time monitoring technique.

Concerns over the potential health threat represented by the excavation of mercury-contaminated soils prompted the ERT/REAC team to examine both real-time monitoring techniques and time, weighted average sampling methods for DMM. This paper will address the real-time methods examined, while focusing on the technique which appears to have the most potential.

INTRODUCTION

The U.S. Army Corps of Engineers had been conducting a cleanup of mercury-contaminated soils at the Nyanza Chemical Site in Ashland, Massachusetts. However, site remediation was suspended due to the potential for dimethyl mercury (DMM) emissions and the lack of a real-time air monitoring method. The suspension of remediation activities was costing the government an estimated $10,000 per day.

In response to a request for assistance from the Army Corps and U.S. EPA Region I, ERT and Weston/REAC conducted a preliminary investigation. This investigation involved a site examination and literature review. The site examination provided information regarding topography and contaminant distribution. The literature review indicated that DMM could conceivably be present in the soils, especially in swampy areas where anaerobic activity is prevalent.

BIOLOGICAL TRANSFORMATION OF ENVIRONMENTAL MERCURY

Mercury in the environment is primarily inorganic in form. Inorganic mercury may be methylated through the action of bacteria; methyl mercury compounds have a high affinity for living tissue and are readily taken up by organisms. Methylation via aerobic pathways is a common means of methylation; however, anaerobic methylation is not uncommon.

One widely accepted metabolic pathway for transferring methyl groups to mercury involves the transfer of a methyl group from a methyl corrinoid, for example, methyl cobalamin. Methyl cobalamin (Vitamin B_{12}) is a common constituent of microorganisms. The following reaction is one possible route:

$$\begin{array}{ccccc} CH_3 & & & & H_2O \\ | & & & & | \\ Co^{+3} & + \; Hg^{+2} & ----> & CH_3Hg^+ & + \; Co^{+3} \\ | & & & & | \\ R & & & & R \end{array}$$
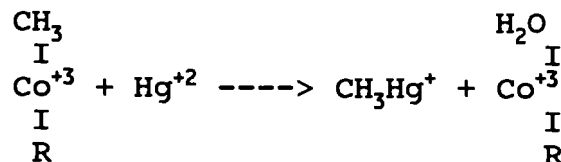
REVIEW OF REAL-TIME PORTABLE INSTRUMENTS FOR DETECTING DMM

The criteria established in this study for selecting a real time instrument for monitoring DMM were quite restrictive. First, the instrument had to be portable and permit operation by non-technical personnel. Second, it had to provide real time or semi-real-time monitoring capabilities. The third and final requirement was that it had to be specific to organo-mercurials.

Several instruments met the first two criteria. However, upon preliminary examination, none appeared to meet the final criterion. Previous experience with elemental mercury sampling indicated that silver-coated Chromosorb was an excellent sorbent for elemental mercury. This finding suggested that the silver-coated Chromosorb might be employed as a pre, scrubber to remove elemental mercury while allowing DMM to pass unimpeded to the monitoring instrument. Some experiments indicating the effectiveness of this process will be discussed later in this report. In summary, these experiments indicated that the silver-coated Chromosorb effectively removed the elemental mercury while allowing the DMM to pass through.

A literature review indicated that the primary methods for detecting elemental mercury were atomic adsorption/UV detection and gold film technology. The UV detectors appeared to have a number of interferences such as H_2O, O_3, SO_2 and a variety of organic compounds.

Gold film detectors are also cross-sensitive to sulfide compounds. However, the use of an internal sulfide trapping pre-filter negates this cross, sensitivity. The gold film technology thus appeared to have the greatest potential for the required application and so a gold film mercury vapor analyzer was selected for detailed review.

GOLD FILM TECHNOLOGY

The Arizona Instruments (formerly Jerome Instruments) Model 411, Gold Film Mercury Vapor Analyzer was selected as the instrument of choice. The Model 411, originally developed for monitoring elemental mercury in air, operates on the principle that mercury will form an amalgam when it contacts a gold film. The formation of the amalgam causes a change in the resistance of the film which can be quantified by the instrument.

The Model 411 detects the presence of mercury by passing a stream of air across a thin gold film. As the mercury in the air contacts the film, an amalgam is formed; this amalgam is simply a mixture of gold and mercury. The amalgamation causes an increase in the electrical resistance of the film proportional to the mass of mercury in the sample—that is, the higher the concentration of mercury, the greater the increase in resistance of the gold film. The change in resistance is then compared to a reference gold film across a Wheatstone bridge circuit. The instrument then integrates the increase in resistance with a precise volume of air contacting the gold film. The difference in resistance is magnified by an amplifier and processed by a microprocessor to provide a digital read-out of mercury concentration in mg/m^3.

The adsorption or amalgamation of mercury with the gold film is a surface phenomenon and it is not within the scope of this paper to enucleate surface chemistry. However, it should be noted that the reaction is reversible. Heating the film to approximately 250°C and subsequently passing a stream of mercury-free air across the film desorbs the mercury and restores the film to its baseline resistance. In order to eliminate the necessity of thermally desorbing the gold film after each use, the Model 411 employs a microprocessor which allows the instrument to operate over a wide range of resistances while remaining balanced with the reference film. Therefore, thermal desorption of the gold film is required only after it becomes so saturated with mercury that the microprocessor can no longer compensate for the difference in resistance between the sample and the reference film.

EXPERIMENTS WITH SILVER-COATED CHROMOSORB

Since DMM may be metabolized from elemental mercury, the assumption was made that both DMM and elemental mercury might be present during air monitoring. Elemental mercury would interfere with the detection of DMM in monitoring air, therefore, a means to remove the elemental mercury from the sample without affecting the DMM concentration was required. Silver-coated Chromosorb was subsequently tested as a prescrubber.

First, the silver-coated Chromosorb was tested to determine if it could adequately remove elemental mercury from the Model 411 monitoring stream. This experiment involved monitoring for elemental mercury with the Model 411 using a silver-coated Chromosorb tube prescrubber within a test vessel containing elemental mercury in which the vapor pressure had reached equilibrium. Thirty samples of the mercury-saturated air were collected without breakthrough occurring from the silver, coated Chromosorb tube. The breakthrough study was terminated at this point because ambient air mercury levels approaching the saturated concentrations present in the test chamber were not likely to be encountered.

The next test of the silver-coated Chromosorb prescrubber required that it allow DMM to pass through it. This was accomplished by preparing a DMM standard and measuring the concentration with and without the silver-coated Chromosorb pre-scrubber. As Table 1 indicates, the test results for the analysis with and without the pre-scrubber are essentially the same.

Since the air volume sampled by the Model 411 is required for the conversion of the change in resistance of the gold film to mg/m^3, it was necessary to determine if the flow rates of different silver-coated Chromosorb tubes were consistent. This evaluation was accomplished by randomly selecting silver-coated Chromosorb tubes from a single lot of tubes and measuring the flow rates of each. The Model 411 was utilized as the air moving device and a primary air flow measuring standard (bubble meter) was employed to determine the tube flow rates.

Table 1
Comparison of Arizona Instruments Model 411 Response With and Without a Silver-Coated Chromosorb Pre-Scrubber to 4.8 ppb-v and 24.6 ppb-v Standards of DMM

DMM Standard Concentration ppb-v	Date Run	Jerome Meter Response (unit less) without Pre-Filter	Jerome Meter Response (unit less) with silver-coated Chromosorb Pre-Filter
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.003	0.002
4.8	7/25/89	0.003	0.003
4.8	7/25/89	0.004	0.003
4.8	7/27/89	0.003	0.003
4.8	7/27/89	0.004	0.003
4.8	7/27/89	0.004	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.001	0.002
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.003
4.8	7/28/89	0.002	0.002
4.8	7/28/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.002	0.002
4.8	8/01/89	0.003	0.002
4.8	8/01/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.002
4.8	8/03/89	0.002	0.003
24.6	7/25/89	0.012	0.016
24.6	7/25/89	0.011	0.012
24.6	7/25/89	0.010	0.009
24.6	7/25/89	0.015	0.011
24.6	7/25/89	0.016	0.011
24.6	7/25/89	0.014	0.011
24.6	7/25/89	0.012	0.011
24.6	7/27/89	0.013	0.013
24.6	7/27/89	0.013	0.011
24.6	7/27/89	0.012	0.011
24.6	7/27/89	0.011	0.011
24.6	7/28/89	0.011	0.009
24.6	7/28/89	0.009	0.009
24.6	7/28/89	0.009	0.008
24.6	7/28/89	0.010	0.008
24.6	7/28/89	0.008	0.008
24.6	8/01/89	0.010	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.011	0.010
24.6	8/01/89	0.010	0.009
24.6	8/03/89	0.009	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.008	0.008
24.6	8/03/89	0.009	0.009

First, the flow rate was set to approximately 850 cm^3/min on the Model 411. Next, six individual tubes were randomly selected from the same manufacturer's lot. Then, five flow measurements were recorded for each tube. The flow rate population standard deviation was then determined for each tube. The flow rate population standard deviation never exceeded 1.2 for the six tubes tested. Subsequently, five additional tubes from the same manufacturer's lot were tested for flow variation among different tubes. A population standard deviation of 6.9 was obtained when five flow rate measurements were compared between five separate tubes.

PREPARATION OF DMM STANDARDS

A significant problem encountered while conducting research for this study was that of obtaining certified DMM in air standards. None of the specialty gas manufacturers routinely produces DMM. In fact, a vendor could not be located to custom mix and certify a DMM standard in the time-frame available. Therefore, it was necessary to prepare DMM standards in-house.

DMM standards were prepared in Summa passivated canisters by injecting a measured volume of DMM and methanol solution into the canister. This process was accomplished by injecting the DMM solution into a heated (60°C) stainless steel "Tee" which connected the Summa canister to a cylinder of Ultra-High Purity Nitrogen. The nitrogen simultaneously flowed through a heated stainless steel transfer line into the Summa canister at a flow rate of 200 cm³/min so as to pressurize the Summa. The Summa canisters were then pressurized to between 30 and 40 psig. Knowledge of the initial concentration of the DMM solution, the volume of liquid injected and the final pressure of the Summa canister in psig, allowed the DMM concentration to then be calculated. This calculation is represented by the following formula:

$$\frac{DMM\ (g)}{Total\ vol\ (L)} * \frac{1\ mole\ DMM}{M.W.\ DMM\ (g)} * \frac{molar\ volume\ (L)}{1\ mole\ DMM} * 10^9\ ppbv\ (l)$$

This formula assumes that temperature and pressure are corrected for, the total air volume is exact and that all of the DMM is transferred from the syringe to the Summa canister. Due to uncertainties in this procedure, DMM standards were subsequently confirmed by select ion gas chromatography and mass spectra analysis.

USE OF THE MODEL 411 FOR DETECTION OF DMM

Once the Model 411 was selected, the manufacturer was contacted for additional information on its applicability for detecting DMM. The manufacturer, Arizona Instruments, indicated that the Model 411 was indeed capable of detecting DMM. However, they also stated that very little was known regarding the instrument's response factor and linear range for DMM.

Initial experiments conducted with the Model 411 (configured as per manufacturer's specifications) provided erratic results and an inadequate detection limit for DMM. The manufacturer was again consulted, this time for methods to increase the instrument's sensitivity as well as for a means to quantitatively detect DMM. The modifications suggested included increasing the sampling period and air sample flow rate as well as adjusting the gold film detector sensitivity potentiometer. After these modifications, the instrument could be reliably calibrated to DMM by adjusting the display potentiometer until the meter display yielded the correct reading.

The Arizona Instrument's Model 411 was modified as follows:

- The detector resistance was increased from approximately 60 ohms to approximately 98 ohms
- The instrument's sample flow rate was increased from 720 cm³/min to 866 cm³/min
- The sampling duration was doubled from 10 to 20 seconds
- A silver-coated Chromosorb tube was utilized as a pre, scrubber to remove elemental mercury
- The calibration switches were adjusted to calibrate the instrument to a known concentration of DMM

SENSOR STATUS DRIFT IN THE MODEL 411

One phenomenon observed while developing this monitoring method was that the Model 411's sensor status would first increase after the instrument detected DMM, then decrease after a period of time. The sensor status is an indication of the percent gold film saturation. The increase and subsequent downward drift in sensor status was not encountered with elemental mercury. This finding suggests that the DMM/gold amalgamation process is somehow different. It appears that DMM forms a transient amalgam with the gold film.

The authors propose that the methyl groups preclude the formation of a true amalgam. The sensor status drift, which was encountered, affected the instrument readings by disrupting the balance between the sample gold film and the reference film. This phenomenon resulted in the instrument indicating readings lower than actual concentrations. The sensor status drift was corrected for by allowing the instrument to balance the Wheatstone bridge between the sample gold film and the reference film prior to monitoring another sample. It is postulated that the transient amalgam dissipates during this period. This process was accomplished by drawing four, 20-second samples into the instru-

ment through an iodized charcoal filter. The filter effectively adsorbs organic and inorganic mercury resulting in mercury free sweep air. The number of mercury free air sweeps required to permit the instrument to reestablish base line was determined empirically to be four.

LINEAR RANGE OF THE MODEL 411 FOR THE DETECTION OF DMM

The linear range of the Model 411 for the detection of DMM was determined by diluting a 13.70 ppb-v DMM standard down to approximately one half the Threshold Limit Value (TLV) of mercury of 0.01 mg/m³. Dilutions were made to 0, 0.64, 6.40 and 13.70 ppb-V. The DMM concentrations were validated by GC/MS analysis. The DMM standards were tested by the Model 411 by:

- Filling a 1-L Tedlar bag with a standard air sample
- Sampling from the bag with the Model 411 with the silver-coated Chromosorb pre-scrubber in-line and the instrument configured as previously indicated (98 ohms, 866 cm³/min...)
- Recording the meter response
- Purging the instrument four times with a zero air (iodized carbon) filter in-line
- Repeating steps 1-4 three times for each concentration
- Determining the average meter response at each concentration (Table 2)

Table 2
Arithmetic Mean and Linear Regression Values
for the Model 411 as Related to Dimethyl Mercury Concentration

DMM CONC. (ppb-V)	METER RESPONSE
0	0
0.64	0.008
6.40	0.043
13.70	0.126

Linear regression values:

R^2 = 0.98
y intercept = 0.00220
Standard error of y = 0.010048
Slope = 0.008959
Standard error of x = 0.000911

These data were then utilized to generate a calibration curve (Fig. 1). The calibration curve was found to be linear, with a critical correlation coefficient (R^2) of 0.98. This accuracy was deemed to be an acceptable linear range for this work effort.
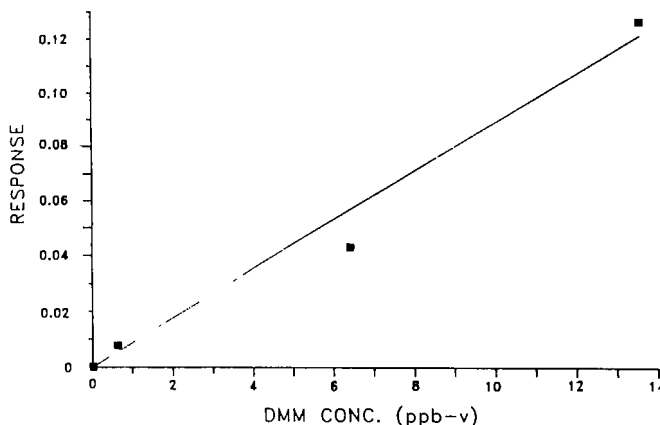
Figure 1
Plot of Model 411 Response Versus
Dimethyl Mercury Concentration (PPB-V)

CONCLUSIONS

This study indicates that gold film mercury vapor detectors have definite potential in determining air concentrations of DMM. The Arizona Instruments Model 411 analyzer appears promising because of its simplicity, stability and ease of use. Initial testing indicates that the Model 411 is an effective screening tool. However, as with any screening device, it should not be relied upon exclusively. Rather, it should be incorporated into a multi-tiered sampling and monitoring program. The multi-tiered sampling and monitoring program should include: screening work areas with the Model 411 as well as a time weighted average sampling method utilizing an appropriate sorbent tube with subsequent analysis.

A reliable source for DMM air standards remains to be located and the stability of these standards determined. The method for producing DMM standards must be described in this study is inappropriate for an in-depth research project because the volume of standard produced per batch is insufficient to carry out multiple experiments.

Further experimentation is required to confirm the results of this study. This monitoring method relies heavily on the selective removal of elemental mercury by silver-coated Chromosorb This selective exclusion technique has been found by others[1,2,3] to be of dubious reliability when applied to field conditions. That is, the silver amalgamation of elemental mercury may be negatively impacted under field conditions by the presence of chlorine and sulfur dioxide because of the following reactions:

$$Cl_2 + 2AgCl = 2AgCl$$
$$SO_2 + 6Ag_2S + Ag_2O$$
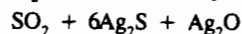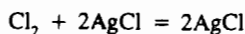
These reactions reduce the collection efficiency of the silver proportionally. As yet, no adequate means of selectively isolating DMM from other organo-mercury species has been tested for application in this monitoring technique. Therefore, other organo mercury compounds such as phenylmercuric acetate would be reported as DMM. This monitoring method requires further field testing and the determination of a correlation between Model 411 readings and sorbent tube analysis.

The results obtained in this study should be scrutinized further and confirmed or refuted. The sensitivity of the gold film detector may be further increased through the use of advanced electronics and a means to obtain direct readings should be developed. It was not within the scope of this study to specifically develop a complete air monitoring method for DMM. Rather, this study attempted to bring forth a method which others might bring to fruition.

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Field Analytical Support Project (FASP) Use in a Site Characterization for Removal: On-Site Laboratory Support to Optimize Use of Analytical Results for Subsurface Sampling and Monitoring Well Placement

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ABSTRACT

Brown and Bryant, Inc., an inactive pesticide formulating facility in Arvin, California, was listed on the NPL in June 1989. Due to concerns about the groundwater contamination potential of the site, a 90-day study was initiated under the Technical Assistance Team (TAT) contract to determine what short term removal actions were necessary under the NCP.

Existing site data showed $\mu g/kg$ to percent levels of halogenated volatile fumigants and the herbicide dinoseb. To provide cost-effective analytical support with rapid turnaround, an on-site laboratory was used to support the drilling operation. The laboratory analyzed both surface and borehole soil samples for six fumigants of concern and provided results to the project manager within 12 hours of sample collection. The on-site laboratory analyzed 536 soil samples; 15% of the samples were sent to an off-site laboratory for confirmatory analysis. The on-site analytical data were instrumental in an early site characterization; field analytical results agreed with off-site confirmatory analyses. As a direct result of the field analytical support, drilling costs were more than 40% under U.S. EPA's budget, monitoring well placement was optimized in a single field effort and the site assessment was completed within 90 days.

INTRODUCTION

Brown and Bryant, Inc. (B&B) is located at 600 South Derby Road, Arvin, Kern County, California. Beginning in 1960, the 5-acre site was used for the formulation of agricultural chemicals, including various pesticides and fertilizers. Due to the improper waste management practices used in spill management, equipment and container washdown and on-site liquid waste disposal, the operator came under State enforcement scrutiny in 1985. The operator was required to bring waste management practices into compliance and to conduct environmental assessments of surface and subsurface contamination. The operator went out of business in 1988, before fully investigating the extent of contamination in the soil and groundwater. However, the preliminary data revealed serious and widespread contamination in on-site subsurface soils and groundwater. Based on the release of dinoseb into the regional aquifer below the site, B&B was added to the NPL.

In April 1989, the Agency for Toxic Substances and Disease Registry of the United States Public Health Service (ATSDR) conducted a preliminary health assessment at the site and concluded that B&B was a potential health concern because of possible human exposure to hazardous substances at concentrations that may result in adverse health effects (the major public supply well is 1,700 feet downgradient of the site). ATSDR recommended further site characterization and downgradient drinking water well monitoring.

In July 1989, a preliminary assessment by the U.S. EPA and the Region 9 Ecology and Environment, Inc. (E & E) Technical Assistance Team (TAT) determined that the existing groundwater monitoring system was inadequate to monitor contaminants and it could not be determined if the NCP criteria for a removal action had been satisfied. A comprehensive site assessment was required, including soil borings for geotechnical and chemical analyses, the installation of an effective groundwater monitoring system both on- and off-site, aquifer testing and treatability studies. The goal of the site assessment was to determine if a removal should be conducted and what type of on-site treatment would be feasible.

SCOPE OF WORK

For the B&B site assessment, chemical contaminant concentrations and locations and physical characteristics such as horizontal and vertical permeability were necessary to provide information concerning groundwater quality and soil characteristics at the site. Existing site data were available from two 50-foot borings in areas suspected to be the most highly contaminated, based on past site practices (Table 1). Thirty boreholes were scheduled to be drilled on the 5-acre site to determine the design and placement of on-site and off-site monitoring and extraction wells, to retrieve representative samples of subsurface soils for lithological descriptions and geotechnical parameters bearing on contaminant migration through the vadose zone and to characterize the extent of fumigant and dinoseb contamination. Samples were to be collected at regular intervals for laboratory analysis of contaminants of concern. The high levels of the dinoseb (percent levels) and the fumigant ethylene dibromide (EDB) detected established the need to perform all on-site activities in Level B protective clothing.

Although the project was allocated more funds for subcontracting than a typical removal assessment ($500,000), it was estimated that the drilling costs for 30 boreholes and the laboratory analysis for geophysical parameters would require all the budgeted funds. Off-site laboratory support for analysis of the volatile contaminants and dinoseb was projected to be very costly; these costs would either cause the project to go over budget or compromise the drilling effort. Additionally, the shortest possible turnaround time for the analytical results was critical in optimizing the drilling location depths and borehole sampling plans which would aid in controlling project cost. Data available within 24 hours also would be used to support site safety decisions. However, quick turnaround analyses would drive the analytical cost up as much as 100%. To provide cost-effective analytical support for the site assessment with rapid turnaround, an on-site laboratory was employed. The mobile laboratory was provided by the Region 10 Field Analytical Support Project (FASP).

Table 1
Historical Results of Soil Sample Analysis for Some Detected Organic Compounds at Brown and Bryant

Sampt Interval Feet b.l.s.	Dibromo- chloro- propane mg/kg	1,2- Dichloro- propane mg/kg	1,2,3- Trichloro- propane mg/kg	1,1- Dichloro- propane mg/kg	Dibromo- chloro- propane (µg/kg)	1,2- Dibromo- ethane (µg/kg)
Boring A						
	71	1.000	4,006	40	1,600	770
	330	111	445	38	620,000	11,000
	54	410	350	15	310,000	14,000
	4.6	1,360	285	60	640,000	45,000
	33	4,600	1,700	130	610,000	28,000
	<0.4	16	3	<0.9	500	540
	<0.4	6	2	<0.3	346	130
	<0.4	12	4	<0.3	220	200
Boring B						
	21	<0.3	<0.3	<0.3	18	120
	<0.4	4	2	<0.3	71	130
	<0.4	3	0.4	<0.3	<5	<5
	<0.4	2	2	<0.3	190	140
	<0.4	4	4	<0.3	160	140
	<0.4	1	3	<0.5	240	160
	<0.4	2	2	<0.3	170	15
	<0.4	3	2	<0.3	160	<5
	<0.4	2	0.9	<0.3	110	100
	<0.4	1	0.6	<0.3	17	62

feet bls - feet below land surface
(<) - Less than; numerical value is limit of detection for that compound
(mg/kg) - milligrams per kilogram
(µg/kg) - micrograms per kilogram

FASP

FASP was developed and implemented by E & E in 1983 under the U.S. EPA Field Investigation Team (FIT) contract. E & E has developed a series of analytical options—documented as Standard Operating Guidelines (SOGs)—that form the basis for matching FASP analytical support capability with project Data Quality Objectives (DQOs). SOGs for many analyte groups (VOCs, chlorinated pesticides, nitrogen/phosphorus pesticides, phenoxy herbicides, PCBs, polycyclic aromatic hydrocarbons, phenols and selected metals) in various matrices (soil, water, air, soil gas and oil) have been developed in response to specific needs within the Superfund program.

The Region 10 FASP laboratory had the expertise and instrumentation available to support the Region 9 site assessment; therefore, the loan of Region 10 FIT FASP to Region 9 TAT was effected for on-site laboratory support.

DATA QUALITY OBJECTIVES

To generate data that would meet the project needs, it was imperative that the DQOs at B&B be established clearly. The site DQOs were established through coordination of FASP, TAT and U.S. EPA personnel. The project DQOs at B&B were required to determine the level of analytical support necessary to provide decision-makers with sufficient confidence to support a removal action. In general, choices of specific analytical options for a project may be determined by:

- Health-based concerns
- Sample analysis costs
- Statutory compliance needs
- Analytes of concern or target/indicator analytes
- Regulatory action levels that dictate method detection limits
- Sample matrices
- Sample collection, handling and storage requirements
- Statistical uncertainty in the qualitative identification of analytes and the errors associated with the quantitation.

All of the above considerations must be weighed to determine the appropriate analytical level for the project data. Rarely, if ever, will a single level of information provide the best technical information and the most cost-effective solution to address all concerns at a site.[1]

At the B&B site, initial DQOs were based on the following considerations:

- The need to minimize sample analysis cost
- The need to analyze 30-60 samples per day and to generate contaminant information at 6-inch intervals down each borehole

- The need for the fastest possible turnaround to guide placement of boreholes

Based on the need for cost control and the initial DQOs listed above, it was determined that field analytical laboratory support for the site assessment at B&B would be appropriate.

FASP IMPLEMENTATION

The Region 10 FIT FASP group was approached with the project DQOs and the "wish list" of analytes shown in Table 2 in February 1990. After discussion about the information required to guide on-site decisions, the target analyte list was modified to the parameters shown in Table 3. On-site analytical data generation was restricted to the fumigants—halogenated VOCs that could be determined with a single analytical system and with rapid turnaround. Based on studies of the existing data, project managers determined that information about fumigant contaminations would be sufficient to determine the extent of off-site contamination and the degree to which contaminants had migrated towards the shallow and the deeper aquifers. It was expected that these compounds would migrate the furthest distance from spill locations. Although the dinoseb contaminant distribution was considered to be critical to the site assessment, turnaround in the on-site laboratory would not be fast enough to guide borehole placement. Additionally, the FASP effort would have increased significantly, reducing the cost-effectiveness of the on-site analysis. Dinoseb analysis was performed by a commercial laboratory on the samples chosen for confirmatory volatile analysis.

Table 2
Brown and Bryant Initial Target Analyte Limit List for Soil Samples

Analyte	Required Detection Limit (mg/kg)
DBCP	0.005
DNBP	3.9
BEN	10
DDE ⎫	
DDD ⎬ total	1.0
DDT ⎭	
EDB	0.005
2,4-D	2.0
Prowl	?
DCP	0.1
Temik	?
Zn (total)	500
Zn (soluble)	250
As (total)	5.0
As (soluble)	0.5
Chloroform	0.1
Benzene	0.07
Toluene	10.0
Xylene	62.0
PCNB	0.09
1,2,3-Trichloropropane	?
Ethyl Benzene	68
DEP	?
Disulfoton	0.07
Ethion	3.5
Ethyl Parathion	3.0
Phonate	0.07
Dinitrophenol	7.0
Other analytes to be determined	

? - Not established.

Table 3
Brown and Bryant FASP Target Compound List

Volatile Organic Compound	Required Quantitation Limit (µg/kg)
Chloroform	20
1,2-Dichloropropane	20
1,3-Dichloropropane	20
1,2-Dibromoethane	20
1,2,3-Trichloropropane	50
1,2-Dibromo-3-chloropropane	20

FASP methodology for the volatile fumigants was developed prior to mobilization. Existing methodology for chlorinated VOC analysis was modified to meet site DQOs (i.e., positive quantitative identification was compromised for very short analytical run times to accommodate the need for quick turnaround of reported results [2 hours] and the potentially large sample load). These data were to be used only to screen to select samples to be sent to an off-site laboratory for analysis.

After further evaluation of the dynamics of the drilling operation, it became apparent that 12-hour sample data turnaround (rather than 2-hour) would be sufficient to guide borehole placement. The project manager determined that samples collected at 5-foot intervals rather than 6-inch intervals would generate enough data to meet the project DQOs; the sample load on-site would be reduced to 15 to 20 samples per day. The reduced sampling effort in each borehole would allow more field effort to be directed towards drilling, as sampling in Level B was slow and labor-intensive. Rather than using FASP data as a screening tool, it would be used to aid in site characterization, which eliminated the need for off-site laboratory fumigant analysis with 12-hour turnaround. Confirmatory data with standard turnaround were easily available commercially and much less expensive. Consequently, the FASP method was revised prior to the fieldwork to provide more qualitatively accurate results. The field analytical results would be used directly to guide drilling. The on-site phase of the site assessment was initiated in the first week of March 1990.

FASP METHODOLOGY

Sample Preparation

Soil samples were collected in the field in preweighed 22-Ml glass vials. Approximately 0.5-gram samples were collected in each vial; four vials were collected for each field sample.

In the laboratory, the 22-Ml vial was connected directly to the sparging apparatus of the Tekmar system. Internal standard solution was added to the soil volume immediately prior to analysis. Samples with target analyte concentrations greater than 2,000 μg/kg were extracted with methanol prior to analysis.

Instrumentation

Two gas chromatograph (GC) systems were employed on-site: (1) a Tekmar LSC-2000 Liquid Sample Concentrator, coupled to a Varian 3400 GC with a Tracor Photoionization detector (PID) connected in series to a Tracor Electrolytic Conductivity (Hall) detector; and (2) a Tekmar LSC-1 Liquid Sample Concentrator coupled to a Shimadzu GC Mini-3 with an O.I. Corporation Hall detector. Data processing and storage was accomplished using Nelson Analytical PC Integrators. Specific parameters are listed in Table 4.

Table 4
Brown and Bryant Volatile Organic Analysis

Instrument Parameters	
Extraction	
Instruments:	Tekmar LSC-2000 Liquid Sample Concentrator and Tekmar LSC-1 Liquid Sample Concentrator
Sample Trap Columns:	Silica Gel/Tenax and 34% Silica Gel/65% Tenax/1% SP1000
Purge Gas:	Ultrapure helium – flow 40 mL/min
Trap Column Temperature:	Purge at ambient temperature: preheat trap to 60°C. Desorb 4 minutes at 225°C; bake 5 minutes at 225°C
Analysis	
Instruments:	Varian 3400 gas chromatograph (GC) with a Tracor Photoionization Detector (PID) connnected in series to a Tracor Electrolytic Conductivity (Hall) detector and a Shimadzu GC Mini-3 with an O.I. Corporation Electrolytic Conductivity (Hall) detector
Integrators:	Nelson Analytical PC Integrators with dual channel interfaces and 30MB hard disk drives for data storage
Columns:	J&W 30 meter x 0.53mm fused silica capillary with DB-624 phase
Carrier Gas:	Ultrapure helium – flow approximately 10 mL/min
Makeup Gas:	Ultrapure helium – flow approximately 40 mL/min

Oven:	Initial temperature – 50°C
	Initial time – 5 minutes
	Ramp rate 1 – 10°C/minute
	Final temperature 1 – 100°C
	Ramp rate 2 – 20°C/minute
	Final temperature 2 – 150°C
	Final time – 5 minutes
Detector/Injector:	150°C

Instrumentation and all auxiliary equipment were stored and operated in the Region 10 mobile laboratory.

Analysis

Qualitative identification and quantitation of target analytes were based on both detector selectivity and relative retention time as compared to known standards, using the internal standard method. An initial five-point calibration curve was generated using serial dilutions of a standard mix prepared from NBS traceable individual standards. Standard analyte concentrations ranging from 40 μg/kg to 800 μg/kg (Shimadzu system) or 2,000 μg/kg (Varian system) were used to establish detector linearity (Fig. 1). Daily calibrations and method blanks were performed and required to meet established QC protocols. Matrix spike and duplicate analyses were performed on 10% of the samples to evaluate system performance on the specific site matrix. Representative results for matrix spike and duplicate analyses at the B&B site are presented in Tables 5 and 6.
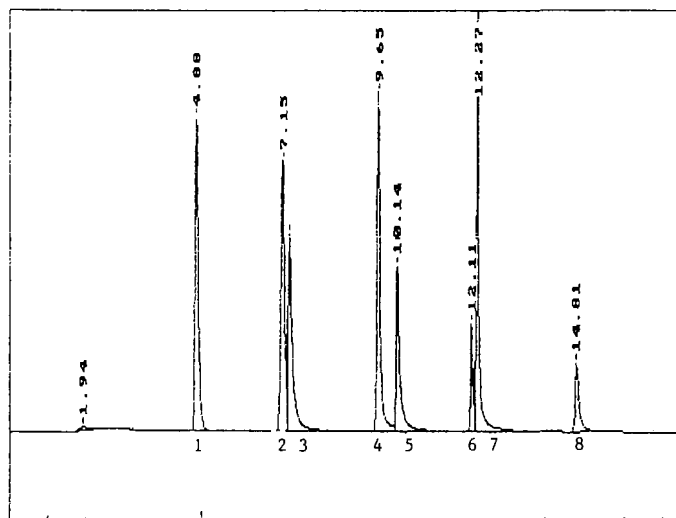
1) Chloroform
2) 1,2-Dichloropropane
3) Dibromomethane (Internal Standard)
4) 1,3-Dichloropropane
5) 1,2-Dibromoethane
6) p-Bromofluorobenzene (Internal Standard)
7) 1,2,3-Trichloropropane
8) 1,2-Dibromo-3-chloropropane

Figure 1
Example of a Selected VOC Chromatogram

ANALYTICAL PERFORMANCE

The FASP laboratory analyzed 536 samples, including quality control samples. Approximately 15% of the samples were sent to an outside laboratory for confirmatory analysis. An initial data set was sent for quick turnaround analysis by a commercial laboratory to provide confirmation data at the start of the field project; a summary of detected volatile analytical results is presented in Table 7. All subsequent volatile analyses were performed by the U.S. EPA Region 9 laboratory; the first set of results is presented in Table 8. Approximately 70 additional samples were analyzed by the U.S. EPA laboratory. A summary of the comparison of FASP results and U.S. EPA results for the 70 samples is presented in Table 9.

Table 5
Matrix Spike Results (Soil) Selected Volatile Organic Compound FASP Analysis

Compound	Spiked Sample	Sample Results	Amount Spiked	Percent Recovery
Field Sample Number AC2QE				
Chloroform	141 F	11.1 UF	228	124
1,2-Dichloropropane	246 F	11.1 UF	278	89.2
1,3-Dichloropropane	289 F	11.1 UF	278	104
1,2-Dibromoethane	293 F	11.1 UF	278	105
1,2,3-Trichloropropane	328 F	17.7 F	278	111
1,2-Dibromo-3-chloropropane	346 F	11.1 UF	278	124
Field Sample Number AD33E				
Chloroform	157 F	5.92 UF	174	90.4
1,2-Dichloropropane	173 F	5.92 UF	174	99.6
1,3-Dichloropropane	135 F	5.92 UF	174	77.7
1,2-Dibromoethane	126 F	5.92 UF	174	72.6
1,2,3-Trichloropropane	137 F	5.92 UF	174	78.6
1,2-Dibromo-3-chloropropane	142 F	5.92 UF	174	81.5
Field Sample Number BD9DC				
Chloroform	71.5 F	4.29 UF	96.2	74.3
1,2-Dichloropropane	110 F	4.29 UF	96.2	114
1,3-Dichloropropane	119 F	4.29 UF	96.2	124
1,2-Dibromoethane	103 F	4.29 UF	96.2	107
1,2,3-Trichloropropane	117 F	4.29 UF	96.2	122
1,2-Dibromo-3-chloropropane	114 F	4.29 UF	96.2	119

U - The material was analyzed for, but was not detected. The associated numerical value is a contractual quantitation limit, adjusted for sample weight/sample volume, extraction volume, percent solids, and sample dilution.

F - Data have been generated using Field Analytical Support Project methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

Table 6
Duplicate Results (Soil) Selected Volatile Organic Compound FASP Analysis

Compound	Sample Results	Duplicate Results	Relative Percent Difference
Field Sample Number H010D			
Chloroform	9.01 UF	7.63 UF	0
1,2-Dichloropropane	397 F	403 F	1.50
1,3-Dichloropropane	18.0 UF	15.3 UF	0
1,2-Dibromoethane	11.1 F	7.63 UF	N/C
1,2,3-Trichloropropane	114 F	122 F	6.78
1,2-Dibromo-3-chloropropane	18.0 UF	15.3 UF	0
Field Sample Number H024D			
Chloroform	7.58 UF	7.81 UF	0
1,2-Dichloropropane	90.7 F	160 F	55.3
1,3-Dichloropropane	15.2 UF	15.6 UF	0
1,2-Dibromoethane	7.58 UF	7.81 UF	0
1,2,3-Trichloropropane	324 F	350 F	7.72
1,2-Dibromo-3-chloropropane	15.2 UF	15.6 UF	0
Field Sample Number C010D			
Chloroform	25.0 UF	23.8 UF	0
1,2-Dichloropropane	25.0 UF	23.8 UF	0
1,3-Dichloropropane	25.0 UF	23.8 UF	0
1,2-Dibromoethane	25.0 UF	23.8 UF	0
1,2,3-Trichloropropane	70.4 F	93.1 F	16.5
1,2-Dibromo-3-chloropropane	25.0 UF	23.8 UF	0

U - The material was analyzed for but was not detected. The associated numerical value is a contractual quantitation limit, adjusted for sample weight/sample volume, extraction volume, percent solids, and sample dilution.

F - Data have been generated using Field Analytical Support Project methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

Field analytical results for all analytes agree on a presence/absence basis in greater than 85% of the samples. Of the 15% of the results out of agreement, approximately half of the analyte concentrations reported are below the quantitation limits of the laboratory reporting nondetected results.

Labor Hours and Project Costs

As of September 1, 1990, a total of 9,247 E & E (FIT and TAT) labor hours were charged to the B&B site assessment. Of this time, 1,871 resulted from field laboratory support—project planning and management, method development, mobilization/demobilization activities, on-site analyses and preparation of the FASP deliverables. The hours invested in on-site analyses can be partially offset by the 85% reduction in on-site labor hours dedicated to the documentation and shipping of samples sent for off-site laboratory analysis.

Table 7
Brown and Bryant Summary of Detected Analyte Results for FASP Laboratory and Commercial Laboratory

Sample Number	Analyte	FASP (ug/kg)	Off-Site Laboratory (ug/kg)
(B026D) BB0471	1,2-Dichloropropane	1,300 F	1,400
	1,2,3-Trichloropropane	270 F	ND (50U)
(B04SC) BB0515	1,2-Dichloropropane	1,700 F*	1,200
	1,2-Dibromoethane	47 F	ND (50U)
	1,2,3-Trichloropropane	820 F*	480
(M025C) BB0719	1,2-Dichloropropane	1,200 F**	4,500
	1,2,3-Trichloropropane	1,800 F	560
	1,3-Dichloropropane	48 F	NA
	1,2-Dibromoethane	130 F	ND (50U)
	1,2-Dibromo-3-chloropropane	41 F	ND (50U)
(L35C) BB0694	1,2-Dichloropropane	4,500 F	8,400
	1,2-Dibromoethane	54 F	ND (50U)
	1,2,3-Trichloropropane	2,200 F	990
	1,2-Dibromo-3-chloropropane	43 F	ND (50U)

*   Outside QC criteria
** Extracted

NA - Not analyzed for
ND - Not determined

U - The material was analyzed for, but was not detected. The associated numerical value is a contractual quantitation limit, adjusted for sample weight/sample volume, extraction volume, percent solids, and sample dilution.

F - Data have been generated using Field Analytical Support Project methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

Table 8
Brown and Bryant Summary of Detected Analyte Results for FASP Laboratory and U.S. EPA Laboratory

Sample Number	Analyte	FASP (ug/kg)	EPA (ug/kg)
(B060C) BB0271	1,2-Dichloropropane	35 UF	7.11
(C000C) BB0164	1,2,3-Trichloropropane	36 UF	31.8
(C044D) BB0210	1,2,3-Trichloropropane	48 UF	9.61
(E000C) BB0297	1,2-Dichloropropane	17 UF	40.7
	1,2-Dibromoethane	7 UF	6.9
	1,2,3-Trichloropropane	330 F*	394.7
	1,2-Dibromo-3-chloropropane	910 F*	326.7
(E005C) BB0318	1,2,3-Trichloropropane	26 F*	7.45
	1,2-Dibromo-3-chloropropane	1,100 F*	ND

*   Outside QC criteria

ND   Not determined

U   The material was analyzed for, but was not detected. The associated numerical value is a contractual quantitation limit, adjusted for sample weight/sample volume, extraction volume, percent solids, and sample dilution.

F   Data have been generated using Field Analytical Support Project methodologies. Analytes are tentatively identified and concentrations are quantitative estimates.

Expendables purchased for the B&B laboratory support totaled approximately $8,500; no instrumentation purchases were required. The cumulative dollars charged to the site assessment by TAT, FIT and subcontracts to date total approximately $808,000. Of this total, 30% ($242,800) represents "drilling dollars." Clearly, drilling costs drove the project, primarily due to the complications of working in Level B.

It was estimated that it cost $60,000 to set up/breakdown the drilling operations. This cost consideration greatly influenced the decision to not follow the traditional approach of:

Mobilize → Drill some boreholes; Demobilize ↑ → Commercial laboratory analysis → Review results; Make decisions ↓

————————————— Remobilize
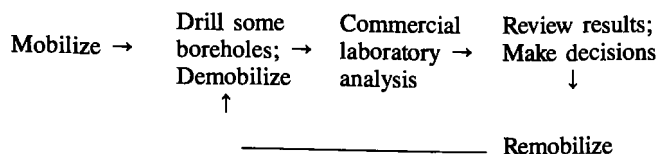
Table 9
Comparison Summary of Results from
FASP and U.S. EPA Laboratories

	Chloroform	1,2-Dichloropropane	1,3-Dichloropropane	1,2-Dibromoethane	1,2,3-Trichloropropane	1,2-Dibromo-3-chloropropane
Percent of non-detect results, both laboratories	89	22	83	68	27	46
Percent of positive detect results, both laboratories	0	60	6	21	62	29
	--	$(.960)^1$	$(.952)^1$	$(.918)^1$	$(.988)^1$	$(.987)^1$
Percent of positive detect FASP results with non-detects in EPA results	2	10	6	2	6	14
Percent of non-detects in FASP results with positive detect results from EPA	9	8	6	9	5	11

* Based on results from 73 co-located samples

[1] Linear regression correlation coefficient for positive results

The field laboratory's quick turnaround results allowed continuous review of the borehole placement, optimizing drilling time, with only one setup/demobilization throughout the assessment. The U.S. EPA's original project estimate was $500,000 for drilling and geophysical analysis subcontracts. Actual costs total approximately $300,000. The $200,000 cost savings were attributed to field analytical support at the project.

CONCLUSIONS

The B&B site assessment was allocated 90 days to determine appropriate short-term removal actions. The TAT and FIT (FASP) teams were on-site approximately 30 days after the project was initiated; on-site activities continued for 55 days. At the end of that time, enough information had been gathered to describe the site geology and map on-site contaminants. Field analytical data were instrumental .in generating on-site data to support the accelerated time-table of an emergency removal.

It was anticipated that 30 boreholes would be drilled on-site; 37 boreholes actually were drilled based on decisions made from the results provided by the on-site laboratory. The boreholes ranged from 30 feet to 130 feet in depth.

On-site analytical results demonstrated that fumigant migration was much deeper than anticipated. The field analytical data allowed the project manager to revise the drilling plan to trace the fumigant migration pathway deeper, without a remobilization of the drillers at a later date. Off-site contamination was more extensive than anticipated; this off-site migration also effected a change in the original sampling scheme, preventing the need for remobilization to determine the extent of off-site migration.

The B&B site assessment demonstrated how field analytical support can be implemented to guide a site assessment—drilling costs were minimized and borehole placement yielded enough information to support the removal decision.

REFERENCE

1. U.S. EPA, *Data Quality Objectives for Remedial Response Activities*, Volume 1, U.S. EPA 540/6-87/003A, U.S. EPA, Washington, DC.

Determination of Hexavalent Chromium in Soil Samples

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ABSTRACT

A field screening method for hexavalent chromium [Cr(VI)] in soils was developed and evaluated. The method uses soil extraction and colorimetric Cr(VI) determination with 1,5—Diphenylcarbohydrazide.[1] Determination of Cr(VI) in soils at concentrations down to 0.5 ppm is accomplished within 30 minutes. A simple, inexpensive test kit was assembled, this kit includes convenient, prepackaged reagents and a hand-held color comparator which does not require electrical power. This lightweight kit is easily transported to and used in the field. For laboratory analysis, the system can utilize various equipment to increase efficiency.

In performance testing against TCLP and other extractants, this method demonstrated significantly higher recovery of Cr(VI) in a wide variety of samples. Because of the wide variety of reactions possible between Cr(VI) and soils, no method was capable of recovering 100% of the Cr(VI) in all of the soil samples. However, the Hach method delivered superior results in a short time, which makes it ideal for field screening and site mapping purposes.

INTRODUCTION

Hexavalent chromium is an especially hazardous oxidation state of chromium, because of both its toxicity and its mobility. Cr(VI) is a known carcinogen and irritant,[2] as well as a powerful oxidizing agent. Cr(VI) has been reported to reduce plant growth at soil concentrations as low as 5 ppm.[3] It can be very mobile due to the solubility of some forms in water. These properties make the detection and monitoring of Cr(VI) contamination a very important task.

Unfortunately, determination of Cr(VI) generally is not a simple undertaking. Most current instrumental methods, such as atomic absorption, X-ray fluorescence and mass spectrometry, are not suitable for use in screening for Cr(VI). Some of these methods are unable to separate Cr(VI) from other Cr species, while others are not useful as field methods because they are not very rugged, require stable power sources or must be operated by highly skilled personnel. All of these methods are much more costly than the method proposed here.

The extraction of Cr(VI) from soil samples is also a difficult process. While some forms of Cr(VI) are highly mobile in aqueous solution, other Cr(VI) compounds are insoluble and therefore are not recovered by extraction with water. In addition, Cr(VI) can be adsorbed by soils under some conditions.[3,4] Adsorbed Cr(VI) is removed best by basic solutions,[3] but many forms of Cr(VI) are insoluble in basic solutions. Acidic extractants can recover substantial amounts of Cr(VI), including some forms which usually are insoluble in basic solutions, but acidic solutions also can cause the loss of Cr(VI) because of the tendency of Cr(VI) to be reduced by organic matter under acidic conditions.[3,4] This problem was noted with some extractions during the comparative study conducted for this paper. The extractant developed for the method discussed in this paper overcomes these problems and consistently recovers more Cr(VI) than any of the other methods tested.

EXPERIMENTAL WORK

Soil samples for this comparison are listed in Table 1. Samples included both contaminated site soils and uncontaminated soils with Cr(VI) added. The contaminated soil samples (SS) are listed as SS 1 and SS 2. The origin of SS 1 was unavailable due to confidentiality agreements; SS 2 was obtained from a contaminated site near an engraving company.

The spiked soils were chosen to cover a large range of soil types and compositions. They include samples from Ohio (pH = 6.95, 3.71% organic matter), Oklahoma (pH = 8.15, 0.2% organic matter), Iowa (pH = 6.47, 6.32% organic matter) and Arizona (pH = 8.10, 0.1% organic matter). The spiked samples simulate different degrees of Cr(VI) contamination and extraction difficulty. Samples 1002 and 1004 provide good conditions for extraction, the soils are alkaline and there is little organic matter present. This leaves little chance of Cr(VI) reduction. Samples 0051, 1001, 2001 and 4001 present somewhat more difficult conditions. There is organic matter present, but not in large quantities. This, along with the nearly neutral pH, results in a better chance of Cr(VI) loss through reaction with the organic matter. The final spiked soil, sample 1003, has high organic matter content and a slightly acidic pH. When compared with the other soils tested, this soil provides the best conditions for the reduction of Cr(VI).

The soils which were spiked had been dried and sieved to pass a 20 mesh screen. $PbCrO_4$ and Na_2CrO_4 were added to simulate insoluble and soluble Cr(VI) species. The amounts of the two compounds added were calculated to provide 20% of the Cr(VI) as easily soluble Na_2CrO_4 and 80% as insoluble $PbCrO_4$. After the addition of Cr(VI), each of the spiked soils was mixed with a kitchen mixer for several hours. The low standard deviations obtained in the analyses suggest that the spiked soils were well mixed during the preparation. All of the soil samples used to prepare the spiked soils were analyzed to determine the Cr(VI) blank value, but none contained significant amounts of Cr(VI).

Hach Method

The extractant solution is prepared by dissolving one Cr(VI) Extractant Powder Pillow in 40 mL of deionized water. This solution is then added to a soil sample in a disposable sample cup. The cup is covered and placed on a mechanical shaker for 15 minutes. The soil/extractant mixture is then filtered and an aliquot of the filtrate is analyzed colorimetrically for Cr(VI) using the ChromaVer 3 reagent. The Cr(VI) concentration of the filtrate is used to calculate the amount of Cr(VI)

Table 1
Soil Characteristics

Sample	Origin	% Organic Matter	pH	Cr(VI) Source
0051	Ohio	3.7	6.95	Spiked Soil
1001	Ohio	3.7	6.95	Spiked Soil
2001	Ohio	3.7	6.95	Spiked Soil
3001	Ohio	3.7	6.95	Spiked Soil
4001	Ohio	3.7	6.95	Spiked Soil
1002	Okla.	0.2	8.15	Spiked Soil
1003	Iowa	6.3	6.47	Spiked Soil
1004	Ariz.	0.1	8.10	Spiked Soil
SS 1	Unknown	7.6	4.29	Contaminated Site
SS 2	Engraving Company	0.7	9.39	Contaminated Site

in the original soil sample.

During the laboratory testing of the methods, a Hach DR/3000 spectrophotometer was used to determine Cr(VI) in the extractant solutions. The kit designed for field use utilizes a color comparator to determine the concentration of Cr(VI). This conclusion device measures Cr(VI) in the soil extract by a visual comparison of the sample with ChromaVer 3 added against a calibrated color wheel. A direct evaluation of the color comparator with the DR/3000 shows that the two measurement methods produce similar results. This is demonstrated by the following comparison of results obtained using Cr(VI) standard solutions (Fig. 1). Each standard was analyzed once using the DR/3000 and once using the color comparator. The agreement between the two methods is excellent over the entire range of the ChromaVer 3 reagent.
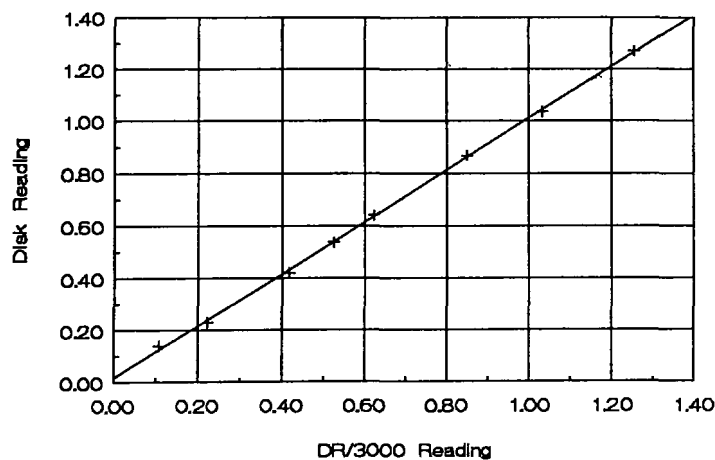
Figure 1
Color Comparator vs. DR/3000 Comparison

The results also are very similar when evaluating soil samples by both the mechanical and manual methods. In Figure 2, each soil sample was evaluated twice, once using a mechanical shaker and DR/3000 and once using hand shaking and a color comparator. The results are expressed as recovery percentage of the spiked soils.

Extractions

A sample of soil (1-10 g) is placed in a disposable sample cup with 40 mL of extracting solution. The cup is covered and placed on a mechanical shaker for 15 minutes. The solution is then filtered through filter paper and the filtrate is analyzed colorimetrically for Cr(VI) using the ChromaVer 3 reagent and DR/3000 spectrophotometer. The concentration of Cr(VI) in the soil is then calculated.

TCLP

The Toxicity Characteristic Leaching Procedure (TCLP) was performed as detailed in U.S. EPA Method 1311(5), with the exception that
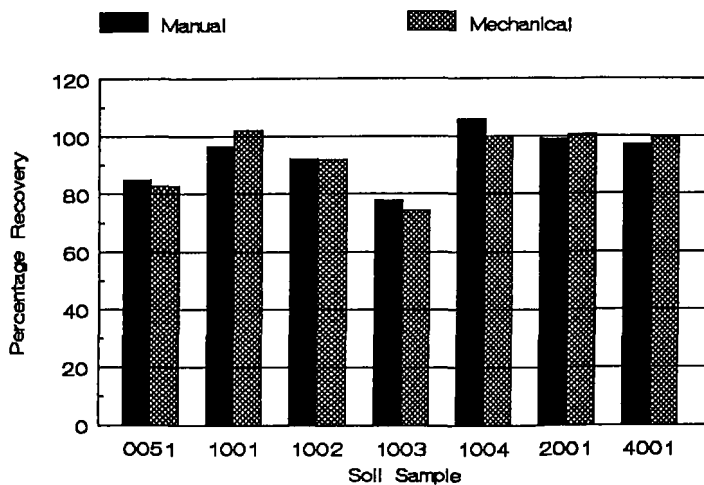
Figure 2
Manual vs. Mechanical Extraction and
Determination Spiked Soil Samples

Table 2
Analysis Results

Soil Sample	Extractant Solution	Cr(VI) Added	Cr(VI) Recovered	Average Recovery	Manual Analysis
0051	Hach	50 ppm	41.5 ± 1.8 ppm	83.0 %	84.8 %
0051	1 N HCl	50 ppm	1.3 ± 0.2 ppm	2.5 %	
0051	DI H$_2$O	50 ppm	5.6 ± 0.6 ppm	11.5 %	
0051	TCLP	50 ppm	18.6 ppm	------	
1001	Hach	1000 ppm	1022 ± 1 ppm	102.2 %	96.7 %
1001	1 N HCl	1000 ppm	716 ± 57 ppm	71.6 %	
1001	DI H$_2$O	1000 ppm	160 ± 6 ppm	16.0 %	
1001	TCLP	1000 ppm	180 ppm	------	
1002	Hach	1000 ppm	918 ± 13 ppm	91.8 %	92.3 %
1002	1 N HCl	1000 ppm	900 ± 49 ppm	90.0 %	
1002	DI H$_2$O	1000 ppm	186 ± 32 ppm	18.6 %	
1002	TCLP	1000 ppm	202 ppm	------	
1003	Hach	1000 ppm	744 ± 95 ppm	74.4 %	77.7 %
1003	1 N HCl	1000 ppm	299 ± 12 ppm	29.9 %	
1003	DI H$_2$O	1000 ppm	182 ± 12 ppm	18.2 %	
1003	TCLP	1000 ppm	169 ppm	-----	
1004	Hach	1000 ppm	1001 ± 14 ppm	100.1 %	105.8 %
1004	1 N HCl	1000 ppm	954 ± 31 ppm	95.4 %	
1004	DI H$_2$O	1000 ppm	253 ± 54 ppm	25.3 %	
1004	TCLP	1000 ppm	176 ppm	17.6 %	
2001	Hach	2000 ppm	2014 ± 66 ppm	100.7 %	99.2 %
2001	1 N HCl	2000 ppm	1464 ± 136 ppm	73.2 %	
2001	DI H$_2$O	2000 ppm	406 ± 82 ppm	20.3 %	
2001	TCLP	2000 ppm	366 ppm	------	
4001	Hach	4000 ppm	3980 ± 172 ppm	99.5 %	97.2 %
4001	1 N HCl	4000 ppm	3608 ± 176 ppm	90.2 %	
4001	DI H$_2$O	4000 ppm	776 ± 156 ppm	19.4 %	
4001	TCLP	4000 ppm	724 ppm	------	

Soil Sample	Extractant Solution	Cr(VI) Added	Cr(VI) Recovered	Average Recovery	Manual Analysis
SS 1	Hach	------	2757 ± 123 ppm	------	2760 ppm
SS 1	1 N HCl	------	2456 ± 140 ppm	------	
SS 1	DI H$_2$O	------	128 ± 12 ppm	------	
SS 1	TCLP	------	228 ppm	------	
SS 2	Hach	------	157 ± 3.2 ppm	------	170 ppm
SS 2	1 N HCl	------	5 ± 4.6 ppm	------	
SS 2	DI H$_2$O	------	142 ± 5.5 ppm	------	
SS 2	TCLP	------	124 ppm	------	

the extractions were performed at onehalf volume and sample size (1 L extractant and 50 g soil rather than 2 L extractant and 100 g soil). The solution was rotated in a plastic bottle at 30 RPM for 18 hours using a Lightning Rotary Blender, the solution was then filtered and the filtrate was analyzed colorimetrically using the ChromaVer 3 reagent. Using the Cr(VI) concentration of the filtrate, the apparent amount of Cr(VI) in the soil was calculated.

Each soil sample was analyzed once using the TCLP procedure and in triplicate using each of the other three extracting methods. The average and standard deviation of the recovery percentages [Cr(VI) concentrations for TCLP data] was calculated and is listed with the data in Table 2.

REAGENTS AND APPARATUS

Reagents used for the determinations:

Cr(VI) Extractant
ChromaVer 3 Reagent
TCLP Extractant, prepared from:
  Glacial Acetic Acid
  1.0 N NaOH
HCl
Deionized water
Apparatus and instruments used in the experimentation:
Balance
Color Comparator
  Chromate Color Disk
  Long Path Viewing Adaptor
DR/3000 Spectrophotometer
pH Meter
Mixer
Rotary Blender
Shaker Table

Graphing the average recovery percentage of the four extracting procedures for the spiked soil samples shows that the Hach extractant delivers superior recovery and consistency (Fig 3).
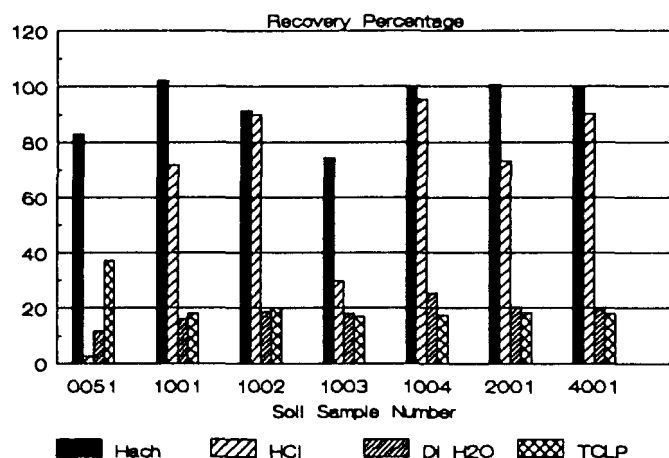
Figure 3
Extractant Comparison: Spiked Soils

In Figure 3, our extractant is shown to extract from 74.4% to 102.2% of the Cr(VI) which was added to the soils. This variation probably is due to the oxidation and reduction of Cr(VI) under the varying soil conditions. It does not appear that oxidation occurred during these trials. Although recoveries of greater than 100% were noted, these excesses are small and the values all are within one standard deviation of 100%. The exception is sample 1001, which was close to 100%, but had an extremely small standard deviation. However, oxidation of Cr(III) to Cr(VI) is a possibility under certain conditions. This oxidation can occur by several mechanisms, including oxidation by atmospheric O_2,[6] or by Mn present in the soil.[6,7]

The low recoveries in some samples can be explained by the reduction of Cr(VI). Reduction can occur through the action of organic matter on some ions, including S^2 and Fe^{2+}.[7] This is the most likely explanation for the low recoveries in two of the samples, 0051 and 1003. Sample 1003 contains a large amount of organic matter, which probably caused the reduction of some Cr(VI). In sample 0051, there is a loss of approximately 7 ppm Cr(VI), which is a significant portion of the

50 ppm originally present. This result would appear to be an indication of a problem with this extraction, since other spiked samples prepared from this same soil (1001, 2001 and 4001) did not show any significant Cr(VI) loss. However, it is more likely that each of these samples was subject to a small amount of Cr(VI) loss, but that the only sample in which this loss was noticeable was sample 0051, due to its low Cr(VI) content. In this case, the actual amount of Cr(VI) reduced is small, but quite often the loss of Cr(VI) by reduction appears to be the main source of error in determining Cr(VI). Therefore, it is most important to minimize the loss of Cr(VI) by avoiding conditions which are conducive to this process.

Figures 4 and 5 present a comparison of several extracting methods which were used to evaluate the contaminated site soils, SS 1 and SS 2. Again, our extractant outperformed the other methods tested.
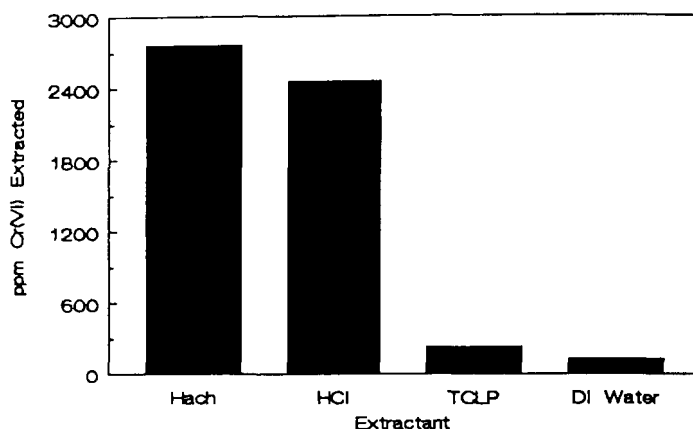
Figure 4
Extractant Comparison: SS 1
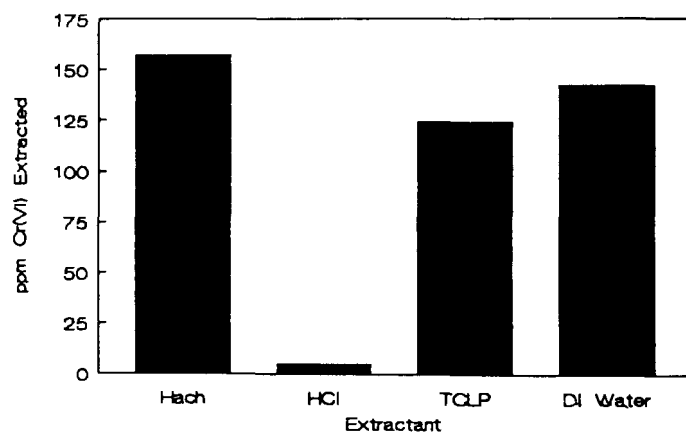
Figure 5
Extractant Comparison: SS 2

When using the TCLP extraction procedure, 18 hours is required to complete the extraction. With our method, the extraction of Cr(VI) is mostly completed within a short time and so longer extraction times are not necessary to obtain useful results. In a comparison of HCl, water and our extractant over an 8 hour extraction, the results obtained are shown in Figure 6.

Our extractant quickly removes the Cr(VI) while consistently outperforming the other extractants, even after long extraction times.

DISCUSSION

Determination of Cr(VI) in soils is a difficult task under the best of situations. The accepted techniques involve lengthy extraction periods prior to analysis. These methods are also designed to determine
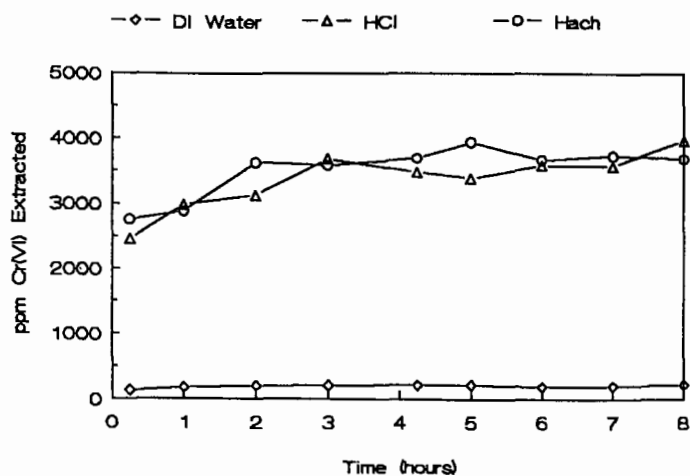
Figure 6
8 Hour Extraction: SS 1

leachability and often ignore a large portion of the Cr(VI) which is present. This problem is demonstrated in the extraction method comparison, Figure 3. TCLP analysis generally recovered only the easily soluble portion of the Cr(VI) which was added to the soils. This may be acceptable if applied to containment of waste, but TCLP provides very little information about the actual amount of Cr(VI) in a soil sample. The TCLP also uses an acidic extractant leading to reduction of Cr(VI) and is less efficient at removing adsorbed Cr(VI). In addition, the TCLP cannot be considered a field-portable method because of problems with time and equipment.

The other extractants tested all have the potential to be applied to a field method. They have a short extraction time and do not require any bulky equipment for analysis. The differences among these solutions are found in their ability to consistently extract different forms of Cr(VI).

Deionized water will extract the easily soluble Cr(VI) species, but is unable to extract insoluble forms. From the comparison data, it appears that deionized water achieves approximately the same results as the TCLP procedure.

HCl is sometimes able to extract a large portion of the Cr(VI), but it also can cause the reduction of Cr(VI) to Cr(III) when there is organic matter present. This appears to be the cause of the varying recovery percentages for HCl shown in Figure 1. The samples which resulted in low Cr(VI) recoveries were those with considerable organic matter present. HCl also failed to recover most of the Cr(VI) in sample SS 2. Again, reduction of Cr(VI) is the most probable cause.

Our extractant was developed with this possible reduction of Cr(VI) in mind and therefore utilizes a buffering system to prevent the development of acidic conditions during the extraction. The use of a basic extracting solution, however, does not generally allow the recovery of insoluble, sparingly soluble or adsorbed Cr(VI) species. This required the addition of several components to solubilize the Cr(VI) in basic solution, which has resulted in an extractant which has been shown to recover more Cr(VI) than the other methods examined.

The extractant is packaged as a dry powder for easy transportation. When extractant solution is needed, the powder is dissolved in 40 mL of deionized water to produce the correct amount of extractant for one soil sample. With its specialized extractant and portability, this analytical method delivers accurate estimates of Cr(VI) contamination on-site without the use of bulky equipment or the expenditure of valuable time. In addition, with prepackaged reagents and simple procedures, there is no need for the highly skilled operators which are necessary with more complicated instrumental methods. All of these factors, limited equipment, simple procedures, accurate results and on-site analysis, combine to deliver useful results in a short time at a cost which is much lower than any other available method.

Another area of interest when testing for Cr(VI) is groundwater, which can be analyzed by the 1,5—Diphenylcarbohydrazide method. This test kit can also be used to determine Cr(VI) in groundwater at levels as low as 20 ppb.

This flexibility makes our Cr(VI) test kit a valuable tool for Cr(VI) site mapping and contaminant estimation. The use of a field method has been shown to greatly reduce the expenditure of time and funds when evaluating possibly contaminated sites.[9] Currently, the field method of choice is X-Ray Fluorescence, but this method is not able to determine Cr(VI). Our proposed analytical method fills this need for a Cr(VI) field screening and site mapping test.

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Site-Wide, Real-Time Air Monitoring During Remediation

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ABSTRACT

The Brio Refining Superfund site is an abandoned refinery and petrochemical recovery operation located immediately adjacent to a 300-home subdivision. From October 1989 to December 1989, refinery structures, tanks, buildings and process equipment were dismantled and removed from the site. To ensure that any air emissions escaping the work zone were immediately detected, five air monitoring stations (AMSs) were installed upwind and downwind of the dismantlement area. Each transportable AMS consisted of a Byron 301 total hydrocarbon analyzer, two sample intake ports (five feet and fifteen feet above grade) and a one-liter, stainless steel grab sample bottle.

Methane and nonmethane hydrocarbon (NMHC) concentrations were transmitted from each analyzer to a system controller where the upwind and downwind nonmethane hydrocarbon concentrations were compared. An alert sounded when the downwind NMHC concentration was 0.5 ppm greater than the upwind reading and an alarm sounded when the downwind NMHC concentration was 1.0 ppm greater than the upwind concentration. Under alarm conditions, an air sample was collected automatically.

During dismantlement, operations were modified to reduce or eliminate emissions when NMHCs were greater than 1 ppm above background at the downwind fence line. Currently, the system is collecting ambient air quality data in preparation for the planned excavation and treatment of 80,000 yd^3 of organic-containing soil, sludge and liquids.

INTRODUCTION

The Brio Refining Superfund site, ranked 183 on the NPL, is a 58-acre abandoned oil refinery and petrochemical recovery plant located approximately 15 miles south of downtown Houston, Texas. From 1957 to 1978, the plant recycled petrochemical process residues to recover ethylbenzene and other salable products. Raw materials, primarily styrene production byproducts, were stored in a series of earthen impoundments which were closed under state order between 1976 and 1979. During closure, pumpable liquids were removed, nonpumpable liquids were stabilized with sand, clay or calcined clay and the remaining pit was filled with clay soil. Refinery dismantlement and excavation and treatment of 80,000 yd^3 of organic-chemical-contaminated soil, sludge and liquid were selected in the ROD as the primary remedial measures for the site.

Fence-line monitoring was required by the U.S. EPA during the RI/FS to insure that emissions resulting from test trenching, soil boring and other investigatory activities did not have an off-site impact. If downwind fence-line organic concentrations, as measured by a photoionization detector (PID), were more than one ppm above background, invasive investigatory procedures were discontinued. PID concentrations

at the downwind fence line were remeasured every 10 minutes after that until concentrations returned to less than 1 ppm above background. Work then resumed and fence-line monitoring continued. If another exceedance occurred, all work at that location was discontinued and the hole or trench was backfilled immediately to prevent further emissions.

Dismantlement at the Brio Refining site and the adjacent Dixie Oil Processors site, carried out between October and November 1989 under an administrative order issued by the U.S. EPA, created a large potential for emissions as process vessels, tanks, piping, etc., which might contain organic liquids or sludges, were decontaminated and salvaged or cut up for scrap. Prior to the start of work, a real-time air monitoring system (AMS) was installed to measure fence-line air quality during refinery dismantlement. The purpose of this system was to insure that work-zone emissions did not leave the site. This goal was accomplished by cessation or modification of work activities when downwind fence-line nonmethane hydrocarbon (NMHC) concentrations were 1 ppm greater than upwind fence-line NMHC concentrations.

AIR MONITORING SYSTEM

Station Locations

Five air monitoring stations were installed at the site during September 1989: (1) AMS-1 at the southern property line, (2) AMS-2 adjacent to the southern side of Dixie Farm Road (a heavily travelled commuter road), (3) AMS-3 adjacent to the northern side of Dixie Farm Road, (4) AMS-4 in the northwestern quadrant of the site and (5) AMS-5 in the northeastern quadrant of the site (Fig. 1). Station locations were selected on the basis of the prevalent north/south winds, the proximity of potential receptors and the area of the site to be dismantled. Generally, winds in the Houston area come from the south off of the Gulf of Mexico. The next most prevalent wind direction is from the north.

AMS-1 was the upwind, background concentration station when the wind was from the south (Table 1). When the wind was from the north, AMS-1 monitored the impact of site activities both north and south of Dixie Farm Road. Located between the southern fence line of the site and the area to be dismantled, a distance of twenty feet or less, this station was impacted by the site even when the wind was from the south. For that reason, the sample intake port was extended 60 feet to the south and terminated at the property line.

AMS-2 and AMS-3 were placed on opposite sides of Dixie Farm Road to determine the impact of vehicular emissions on ambient air quality. For southerly winds, AMS-2 was the upwind station and AMS-3 was the downwind station. With northerly winds, AMS-3 became the upwind station and AMS-2 was the downwind station.

AMS-4 was the upwind monitor when the wind was from the north

through northwest and the downwind monitor when the wind blew from the south through southwest (Table 1). AMS-5 became the upwind station for winds from the north through northeast quadrant and the downwind station for winds from the south through southwest quadrant. The upwind/downwind stations for southerly and northerly wind conditions are shown on Figure 1.
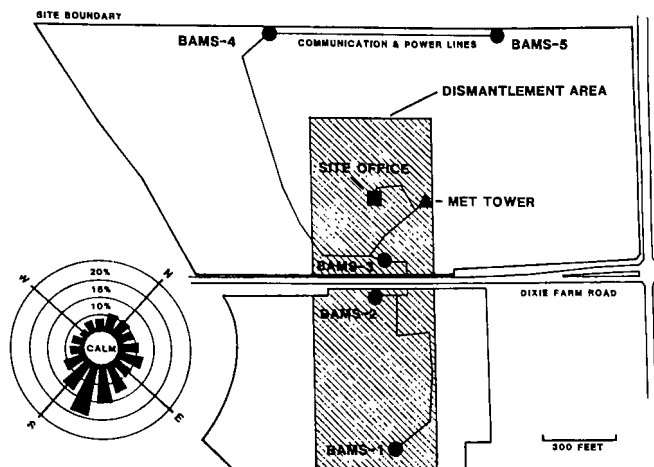
Figure 1
Air Monitoring Station Locations

Table 1
Upwind/Downwind Air Monitoring Station Selection

Wind Direction (Quadrant)	Wind Direction (Degrees)	Upwind Station	Downwind Station
Northerly	54 to 312	BAMS-5	BAMS-1
Easterly	54 to 132	BAMS-1	BAMS-4
Southerly	132 to 222	BAMS-1	BAMS-5
Westerly	222 to 312	BAMS-4	BAMS-1

Note: Wind direction is the direction the wind is from.

Each air monitoring station was mobile. Mounted on steel skids, the location of any station could be readily changed to any point along the power and signal cable network.

Station Configuration

Each station consisted of two sample intake ports, a total hydrocarbon analyzer, a grab sampler and a particulate sampler (Fig. 2). Air samples were drawn from two intake ports: (1) a low-level intake at five feet above grade and (2) a high-level port fifteen feet above grade. Samples were taken from the five-foot intake on a routine basis to monitor breathing-zone air quality. The fifteen-foot level port was sampled for 15 minutes every two hours to insure that any air deflected upwards by fences or other obstructions, such as buildings, tanks, etc., was monitored.

Air was drawn into the total hydrocarbon analyzer through a heated, stainless steel intake line by a diaphragm pump. Heating the intake line was necessary to prevent condensation from forming when moist outside air entered the climate-controlled instrument enclosure. Capillary tubing was used to route a small amount of air to the hydrocarbon analyzer.

Byron 301 Hydrocarbon Analyzers were installed in air-conditioned, weatherproof equipment enclosures at each station. Cylinders for fuel gas, span gas and calibration gas were mounted outside the enclosures;

however, the gas regulators were located inside the enclosure. The analyzer was a laboratory-grade instrument which used a short GC column and a flame ionization detector to analyze methane and nonmethane hydrocarbons. Instrument cycle time was three minutes, so the analyzer was capable of up to 20 analyses/hr providing continual but not continuous analyses of ambient air concentrations. Instrument ranges were 0 to 2, 0 to 5, 0 to 10, 0 to 20, 0 to 50 and 0 to 100 ppm. Analyzer accuracy was 1% of full-scale. Since on-site nonmethane hydrocarbon concentrations were not known in advance of system installation and regional total hydrocarbon concentrations of 20 ppm or more were known to occur, the analyzers were operated on the 0 to 100 ppm scale. A mix of 80 to 90 ppm methane and 80 to 90 ppm propane was used as calibration gas.
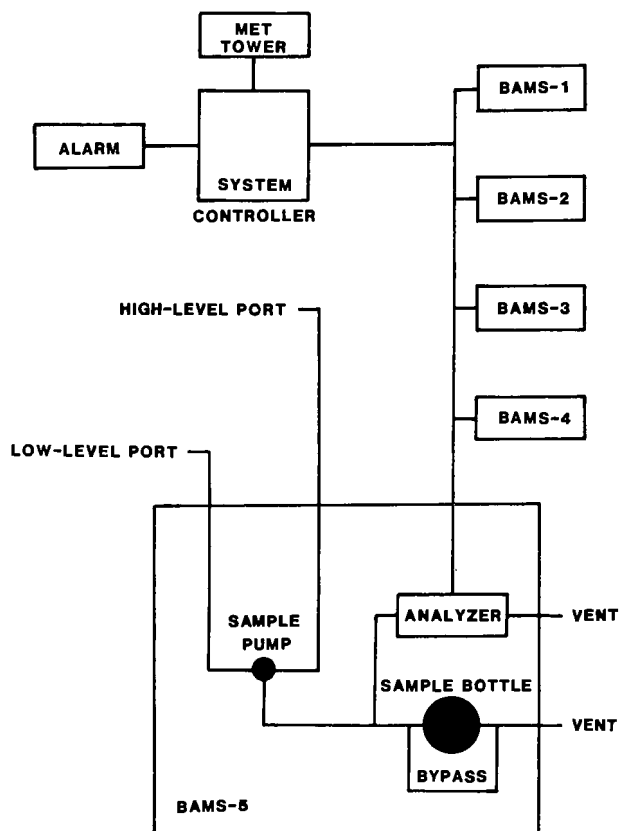
Figure 2
Air Monitoring System Schematic Diagram

At each station, a stainless steel sampling cylinder was mounted as a flow-through portion of the sample intake line. By closing solenoid-operated valves at each end of the sampling cylinder, a sample of ambient air was trapped until removed for VOC analysis. When these valves were closed, air flow was diverted to a bypass line and routed around the sampling cylinder. This sampling system allowed collection of ambient air samples whenever a threshold concentration above background was reached. Initially, the sampling threshold was set at one ppm above background, but it was later changed to five ppm above background.

A General Metal Works GMWS-2310 high-volume particulate sampler was also installed on the same transportable platform as the hydrocarbon analyzer. Total Suspended Particulate samples were taken every day during equipment dismantlement.

System Controller

Communication cable was used to transmit methane and nonmethane hydrocarbon concentrations, hi-vol sampler flowrate and meteorological

parameters from each of the air monitoring stations and the meteorological tower to the system controller. The system controller, an XT-compatible computer equipped with a 20 megabyte hard disk, acquired the data from the individual air monitoring stations and meteorological tower (wind speed, wind direction, etc.), calibrated the hydrocarbon analyzers, controlled the operation of the hi-vol samplers and displayed real-time data in the site office. Instantaneous and one minute, 15 minute and hourly average values of methane and nonmethane hydrocarbons, wind speed and wind direction were displayed on the monitor. These data were stored on the hard disk for later processing and analysis and also printed every 15 minutes to provide hard copy on-site.

SYSTEM OPERATION

During dismantlement, the system controller constantly polled the meteorological tower to determine wind direction, selected the upwind and downwind air monitoring stations based on the direction the wind was blowing from (Table 1) and determined the difference between downwind and upwind nonmethane hydrocarbon concentrations. Alert conditions existed when the NMHC concentration downwind of the site was 0.5 ppm higher than the base line NMHC concentration detected by the upwind air monitoring station. An alert level of notification was provided to give advance warning of an increase in NMHC concentrations. Alarm conditions existed when the NMHC concentration downwind of the site was 1.0 ppm higher than the base line NMHC concentration detected by the upwind air monitoring station. Different audible and visual alarms were used to distinguish between the alert and alarm conditions in the site office. The dismantlement contractor was notified of these conditions and activities were modified to reduce or eliminate any hydrocarbon emissions resulting from this work.

A number of problems were encountered during system startup, most of them associated with transmission of commands from the system controller to the air monitoring stations and data from the remote air monitoring stations to the system controller. First, varying soil resistivity between the stations and the system controller produced large differences in ground potential. During thunderstorms, a frequent occurrence in the Houston area, these potential differences were so large that the short-haul modems used to transmit data from each AMS to the system controller would burn out even with surge protection. Changing the method of connecting the communication cables to the earth solved part of the problem in the early stages of dismantlement. However, modem burnout was not solved until after dismantlement was completed when more sophisticated, transformer-isolated modems were substituted for the short-haul modems.

Second, a Houston-area radio station induced enough radio frequency interference (RFI) in the communication system to cause errors in data transmission and random activation of the analyzer's zero and span calibration controls. RFI was controlled by installation of line filters and modification of system programming to provide more rigorous error checking. This problem was not be eliminated entirely because there were periods of the day when the station operated at high power levels and the potential for data transmission errors increased. Intelligent data loggers, capable of two-way error checking, will be installed to eliminate the problem with RFI. Random activation of zero and span calibration cycles was controlled by switching from automatic, system-controlled calibration to manual activation of analyzer calibration. When the transformer-isolated modems and intelligent data loggers are installed, the system will be returned to automatic daily calibration.

Another problem with system operation was selecting the analyzer operating range. The manufacturer's recommended start-up calibration gas concentration was 80 to 90 ppm methane and 80 to 90 ppm propane which required analyzer operation on the 0 to 100 ppm scale. Regional air monitoring indicated total hydrocarbon concentrations of 20 ppm or more could occur in the area of the site. Since the range of emissions potentially resulting from dismantlement was unknown and calibration gas concentrations were 80 ppm, the operating range of the analyzers was kept on the maximum scale of 0 to 100 ppm after start up. As mentioned above, alerts were sounded when downwind NMHC concentrations were more than 1.0 ppm above background. With an accuracy of 1 ppm when the analyzers were operated on the 0 to 100 ppm scale (1% of full-scale), instrument drift alone caused alarms to be sounded even during evening and early morning hours when no work was being done at the site. Alarms were always responded to during working hours. However, to avoid constant sample bottle replacement, the ambient air sampling algorithm was changed so that a bottle sample was collected when any NMHC concentration was five ppm higher than the upwind NMHC concentration instead of the 1 ppm difference originally programmed into the system. In the future, this problem will be eliminated by changing the calibration gas concentration and operating the system on the 0 to 20 ppm scale.

CONCLUSIONS

The Brio Air Monitoring System provided a real-time method of determining whether or not dismantlement activities were adversely affecting air-quality at the boundaries of the site. When combined with work zone monitoring, this system provided the assurance that any emissions leaving the work zone were detected at the site fence-line in time to stop or modify the activities causing the releases.

Accurate, On-Site Analysis Of PCBs In Soil
A Low Cost Approach

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ABSTRACT

Polychlorinated Biphenyls (PCBs) are very stable materials of low flammability used as insulating materials in electrical capacitors and transformers, as plasticizers in waxes, in paper manufacturing and for a variety of other industrial purposes.

There are many PCB transformers and capacitors still in service throughout the United States today. The Environmental Protection Agency estimates that there are 121,000 (askarel) PCB transformers, 20 million PCB-contaminated mineral oil transformers and 2.8 million large PCB capacitors currently in use. A certain percentage of this equipment will leak, fail or rupture and spill PCB into the environment each year.[1]

Because of equipment leakage and widespread industrial dumping, PCBs have appeared as ubiquitous contaminants of soil and water. Chemical analysis for PCBs has been almost exclusively performed by gas chromatography. Other analytical techniques such as nuclear magnetic resonance (NMR) and liquid chromatography with UV detection are alternative methods for PCB analysis but can only be successfully applied where the suspected concentration level of PCBs is greater than 1000 ppm.[2]

A new instrumental method has been developed to analyze for PCB content using electrochemical methodology and a chloride-specific electrode to measure quantitatively the amount of chloride. The instrument converts the chloride concentration into a PCB equivalent amount of PCBs in an oil or soil sample and gives a direct readout in parts per million of PCBs. The preparation steps involve extracting the PCBs from the soil (not necessary for oil samples) and reacting the sample with a sodium reagent to transform the PCBs into chloride which subsequently can be quantified by the instrument. Oil samples take approximately 5 minutes to prepare and soils approximately 10 minutes. One operator can complete approximately 150 oil tests or 100 soil tests in an 8-hour day.

Although this paper will concentrate on the results of soil samples obtained from a Superfund site analyzed both electrochemically and by gas chromatography, it demonstrates the accuracy and economic advantage of employing the electrochemical procedure in analyzing both oil and soil samples.

INTRODUCTION

PCBs were first formulated in 1881. Although they were known to exist in the late 1800s, manufacturing on a commercial scale did not start until 1929. All U.S. production of PCBs was halted in 1977.

In the late 1960s, PCBs were recognized as a potential environmental problem, which was probably due to the unregulated maintenance and handling of PCB-containing equipment. Several studies have been done to identify and quantify the distribution of PCBs in the United States. The overall distribution is shown in Figure 1.

Presently in use	750 million pounds	60%
In landfills and dumps	290 million pounds	23%
Released to environment	150 million pounds	12%
Destroyed	55 million pounds	5%
Total production	1,245 million pounds	100%

Figure 1
U.S. Distribution of PCBs[4]

The wide use of PCBs was due to their nonflammable characteristics as well as their chemical inertness, heat resistance, chemical stability, low vapor pressures at atmospheric temperature and high dielectric constant. Although the use of PCBs in some applications has been banned, they still are being used in vacuum pumps and gas-transmission turbines. PCBs previously were used as plasticizers in synthetic resins, in hydraulic fluids, in adhesives, in heat transformer systems, in lubricants, in cutting oils and in many other applications.

The U.S. EPA currently recommends two PCB-specific methods of analysis: (1) the GC/MS Method 680 for quantitating PCB isomer class totals and (2) the GC/ECD Method 8080 for quantitating Aroclors. Over the past decade, the use of these instrumental methods has increased dramatically. It is the purpose of this paper to provide an example of one type of nonspecific analysis of PCBs where simple inexpensive chemical procedures can, in fact, under certain circumstances be a preferable alternative to chromatographic methods.

The two examples chosen in this paper are the analyses of PCBs in transformer oil and soil. The tests involve measurements of PCB concentrations down to a few parts per million where, as a result of extensive legislation, inaccurate results would likely evoke expensive litigation and heavy fines. The different methodology and apparatus will be described, the accuracy and precision of each method discussed and the costs of each analysis reported.

METHOD FOR THE ELECTROCHEMICAL DETERMINATION OF PCB IN OILS AND SOIL

This procedure utilizes sodium metal to remove chlorine from any PCBs present in the sample. Using a chloride-specific electrode, the concentration of chloride contained in the final aqueous extract can then be determined electrometrically. By immersing a chloride-specific electrode in the aqueous extract and measuring the EMF produced, the chloride concentration and, thus, the PCB content can be estimated. The chloride concentration is exponentially related to the electrode EMF and thus with a suitable electronic circuit design the results can be presented digitally on an appropriate meter in ppm of the selected PCBs.

This is a nonspecific method, testing for the presence of chlorine in the sample being examined. As a result, other chlorinated compounds will cause a false positive result because the analysis method reads all chlorinated compounds as PCBs. False negative results should not occur, however, because if no chlorine is present, PCBs cannot be present.

SAMPLE PREPARATION

Oil Samples

A 0.2-mL aliquot of a solution of naphthalene in diglyme is added to 5 mL of oil sample. To this mixture is added 0.4 ml of a dispersion of metallic sodium in mineral oil, and the mixture is shaken for 1 minute. A 5 mL quantity of buffer is then added to neutralize the excess sodium and to adjust the pH to 2.0 to ensure the pH of the mixture is within the operating range of the electrode. A 5-mL aliquot of the aqueous layer is then carefully decanted into a suitable vessel.

Soil Samples

A 10-g sample of soil is extracted by shaking for 1 minute with 12 mL of solvent containing 2 mL of distilled water in 10 mL of an immiscible hydrocarbon. The soil is then allowed to settle and the supernatant liquid is filtered through a column containing Florisil to remove any moisture and inorganic chloride. A 5-mL aliquot of the dry filtrate is then treated with 0.2 mL of a solution containing naphthalene in diglyme, followed by 0.4 mL of a dispersion of metallic sodium in mineral oil and shaken for 1 minute. A 5-mL aliquot of buffer solution is then added and the aqueous layer is allowed to separate. Finally, 5 mL of the aqueous layer are then decanted into a suitable vessel.

ANALYTICAL METHOD

The measuring instrument (Dexsil L2000™, Hamden, Connecticut) is fitted with temperature compensation as the output of the chloride-specific electrode varies with temperature. Initially, the temperature compensation adjustment is set to the sample/electrode temperature. The electronic measuring device is then calibrated employing a solution containing chloride equivalent to 50 ppm. The electrode is immersed in 5 mL of the calibration solution and appropriate adjustments are made to the calibration control to provide an output on the digital meter of 50 ppm of chloride.

After rinsing and drying, the chloride-specific electrode is immersed into the 5 mL sample, gently stirred for 5 seconds and allowed to stand for 30 seconds. The concentration of PCB in ppm is then read directly from the digital output meter. The dynamic range of this analytical procedure is from 5 to 2000 ppm. The precision varies with the concentration. At concentrations between 50 and 2000 ppm, the precision is +/- 10%. Between 5 and 50 ppm, the precision is approximately +/- 2 ppm.

ANALYTICAL TESTS, RESULTS AND DISCUSSION

Oil Samples

In general, PCB-specific methods are more accurate than nonspecific methods, but they also are more expensive, more lengthy to run

and less portable. The L2000™ PCB analyzer provides accurate analysis of PCB concentrations in oil by testing for the total amount of chlorine that is present in the sample.

The PCB concentration is calculated from the chloride concentration using a conversion factor based on the Aroclor present in the sample. If the specific Aroclor is not known, then the most conservative estimate results from assuming that the PCB present is Aroclor 1242. Aroclor 1242 contains the lowest percentage of chlorine of the commercially produced PCB mixtures.

The 1260 setting is used when a sample contains Aroclor 1260 but not the associated trichlorobenzene.

The Askarel setting is used for samples that contain Aroclor 1260 and associated trichlorobenzene. Askarel accounts for the majority of contaminated transformer oil samples and, therefore, this setting will usually supply the most accurate results. However, if a 1242-contaminated sample is tested on the Askarel setting, a false negative will result if the sample contains between 50 and 120 ppm.

Tables 1 and 2 show comparison results of transformer oils contaminated with 1242 and 1260 (as Askarel), respectively, analyzed by the PCB-specific GC method versus the L2000™. The GC method used to analyze the transformer oils in this study is U.S. EPA Method 600/4-81-045.

Table 1
Results of GC Analysis of PCBs (1242) in Transformer Oil vs. Results of L2000 Analysis

Standard (ppm 1242)	Results from GC Analysis (ppm 1242)		Results from L2000 Analysis (ppm 1242)	
	None Detected (< 2 ppm)		0.6	
	None Detected (< 2 ppm)		0.9	
	None Detected (< 2 ppm)		1.5	
			MEAN	1.0
			STD. DEV.	0.4
10		10.0		9.7
		10.8		9.3
		10.4		9.7
	MEAN	10.4	MEAN	9.6
	STD. DEV.	0.4	STD. DEV.	0.2
50		51.6		50.7
		52.3		46.2
		50.3		51.4
	MEAN	51.4	MEAN	49.4
	STD. DEV.	1.0	STD. DEV.	2.8
100		96.8		104.9
		95.8		95.2
		94.2		95.4
	MEAN	95.6	MEAN	98.5
	STD. DEV.	1.3	STD. DEV.	5.5
500		474.0		522.0
		482.2		492.0
		497.0		470.0
	MEAN	484.4	MEAN	494.0
	STD. DEV.	11.7	STD. DEV.	26.1

Accurate and precise results are obtained over a wide concentration range of PCBs and although false positives can cause unnecessary secondary testing, this method can be very economical when used on transformer oil, which contains few sources of chlorine other than PCBs. Used crankcase and cutting oils, however, always contain some chlorinated paraffins and almost always give false positive results with nonspecific testing. More expensive gas chromatographic analysis is required when testing for regulated levels of PCBs in these matrices.

Standard (ppm 1260)	GC Analysis Results (ppm 1260)		L2000 Analysis Results (ppm 1260)	
10		9.482		9.2
		9.241		9.5
		9.186		10.6
	MEAN	9.303	MEAN	9.8
	STD.DEV.	0.129	STD.DEV.	0.6
50		50.923		53.7
		48.409		48.6
		51.883		50.8
	MEAN	50.405	MEAN	51.0
	STD.DEV.	1.465	STD.DEV.	2.1
250		233.911		255
		232.007		262
		230.215		261
	MEAN	232.044	MEAN	259
	STD.DEV.	1.509	STD.DEV.	3.8
500		493.232		530
		486.400		519
		472.423		510
	MEAN	484.018	MEAN	520
	STD.DEV.	8.661	STD.DEV.	10.0

Soil Samples

The U.S. EPA Spill Cleanup Policy stipulates that a PCB spill, once detected, must be cleaned up within 48 hours.[3] The U.S. EPA mandates that cleanup actions are taken in this short time-frame in order to minimize the risk of human and environmental exposure to the spilled PCBs. In addition to the many PCB Superfund sites, there are many other PCB spill sites that have not made the National Priorities List that still must be cleaned up.

One of the most time-consuming steps in laboratory soil analysis is the drying time. When a soil sample is received for GC analysis by ASTM D3304, the sample is dried for 24 hours. The sample is then weighed and placed in an extractor and allowed to cycle for 8 hours. The sample must be completely dry, since the extraction solvent (usually hexane or isooctane) is immiscible with water. Extraction of a wet sample would yield a low result since the solvent cannot fully interact with the soil to extract the PCBs. Typically, 90% of soil samples received for laboratory analysis by GC require drying prior to extraction. With a 48-hour cleanup policy, 24 hours of drying time could be a substantial setback. Ideally, the content of the spilled material must be determined at once and the cleanup procedures begun immediately. The L2000™ allows the operator to respond immediately and to make a quick evaluation of the PCB concentrations at the site. At an excavation site where soil analysis is being performed, the decision can be made immediately if more soil needs to be removed or if the excavation has been carried far enough.

The results of soils obtained from a Superfund site and analyzed by GC and the L2000™ are compared in Table 3. Since gas chromatography can quantitate each Aroclor present, the GC results are presented for each Aroclor actually detected in the soil samples. The corresponding L2000™ results for that particular sample are seen on the same line. These results are listed according to each setting available to the analyst. The L2000™ does not have the capability to quantitate each Aroclor; instead, all the chloride present is interpreted according to the Aroclor setting being used. For samples contaminated with an unknown Aroclor, the prudent analyst would use the 1242 conversion to provide the most conservative estimate.

Using the L2000™ as a screening method, the samples are

evaluated according to column 4 interpreting chloride as 1242. For the ten samples analyzed, Samples 2, 3, 4 and 6 would be considered as below the Code of Federal Regulations limit of 10 ppm set by the U.S. EPA. Since this is a site remediation, the results would indicate that these areas can be considered clean and would not need further treatment. If active cleanup were underway, these samples would indicate that the excavation has gone far enough in that area.

The remaining samples indicate that there is still possible contamination above the 10 pm level. This would result in further excavation being required to reach safe levels. If active excavation is not underway, the samples can be further analyzed to determine the specific Aroclor content. Whether the samples are further analyzed, or excavation is continued based on the 1242 estimate, will depend on the cost consideration of waiting for laboratory results while paying for an idle excavation team and remediation equipment, or excavating excess material while the crew and equipment are still on-site.

From the GC analysis, it was determined that only two of the six "positives" were "false positives" in that the total chlorine makeup indicated an equivalent of PCBs above the regulatory 10 ppm limit, whereas GC analysis of those samples showed an actual level below 10 ppm.

The problem of contamination with chlorinated solvents is exemplified by Sample 1, where the L2000™ result is considerably higher than the GC results. This high reading again is an overestimation of the PCBs present, and would result in a conservative action being taken such as retesting using GC or further excavation.

To make a systematic comparison of the GC results which quantify each Aroclor separately, to the L2000™ results, an equivalent amount of a single Aroclor must be calculated from the sum of all Aroclors detected. For the results given in this paper, Aroclor 1242 was chosen as the basis for equating the L2000™ results with the GC results. The equivalent L2000™ reading, which converts the chloride concentration to PCBs using a single Aroclor conversion factor, can then be calculated. The direct conversion of ppm 1260 by GC to its equivalent in ppm 1242 is based on the percent chlorine difference of 1242, 42%, versus 1260, 60%, according to the equation:

$$\text{L2000 equivalent ppm } 1242 = (X)(60/42)$$

where

X = ppm 1260 by GC
60/42 = ratio of percentage chlorine

For example, the GC results for the first soil sample shown in Table 3 of 11.59 ppm 1242 and 2.24 ppm 1260 should theoretically read 14.79 on the L2000's 1242 setting. The value of 14.79 is attained by converting the GC 1260 value to 1242 according to the equation above, and adding it to the GC value for 1242. The actual reading on the L2000 1242 setting was 25.0 ppm, which is significantly higher than the theoretical prediction. The false high reading can probably be attributed to other chlorinated compounds being present in the soil that the GC does not detect. Nevertheless, from a regulatory point of view, a false positive is preferable. A more realistic and expected result is seen from the results for the seventh soil analysis shown in Table 3 and, once again, a theoretical concentration of 1242 can be predicted from the conversion equation. The GC result for that sample was 92.66 ppm 1242 and 15.08 ppm 1260. 15.08 ppm 1260 converts to 21.54 ppm 1242 which, when added to 92.66 ppm 1242, gives a theoretical projection of 114.2 ppm 1242 as the L2000 result. The actual 1242 result given by the L2000 was 122.7, which is within the +/- 10% accuracy level accepted for GC analysis.

Like the oil samples, soil sample concentration of PCBs are also based on the detection of chlorine; however, it is only chlorine present from an organic source that would cause a false positive, as seen in the first example above, rather than an inorganic source such as road salt or sea salt. Some possible sources of chlorine contamination are pesticides and solvents.

Table 3
Comparison of Superfund Site Soil Analyses:
Gas Chromatography vs. L2000 Readings

GC RESULTS			L2000 RESULTS (read as)		
1242	1254	1260	1242	1260	ASKAREL
11.59 ppm		2.24 ppm	25.0 ppm	17.5 ppm	10.6 ppm
... ppm		0.25 ppm	0.9 ppm	0.6 ppm	0.4 ppm
	2.64 ppm	1.78 ppm	7.9 ppm	5.5 ppm	3.3 ppm
0.33 ppm		0.20 ppm	2.8 ppm	2.1 ppm	1.4 ppm
5.00 ppm		2.53 ppm	10.6 ppm	7.5 ppm	4.6 ppm
0.77 ppm	0.80 ppm	0.35 ppm	7.5 ppm	5.3 ppm	3.2 ppm
92.66 ppm		15.08 ppm	122.7 ppm	85.8 ppm	51.7 ppm
7.18 ppm	1.54 ppm	0.08 ppm	11.5 ppm	8.1 ppm	4.9 ppm
7.87 ppm	3.25 ppm	0.30 ppm	13.0 ppm	9.2 ppm	5.6 ppm
		9.43 ppm	16.2 ppm	11.4 ppm	6.9 ppm

Table 4 shows a comparison of results from soil samples obtained from a PCB spill site.

Table 4
Comparison of PCB Spill Site Soil Analyses:
Gas Chromatography vs. L2000

GC RESULTS			L2000 RESULTS (read as)		
1242	1254	1260	1242	1260	ASKAREL
.30 ppm		6.09 ppm	10.8 ppm	7.5 ppm	4.5 ppm
.10 ppm		41.59 ppm	62.5 ppm	43.8 ppm	26.4 ppm
.97 ppm		0.40 ppm	5.7 ppm	4.0 ppm	2.4 ppm
.38 ppm		0.05 ppm	6.1 ppm	4.3 ppm	2.6 ppm
.68 ppm		6.67 ppm	14.8 ppm	10.3 ppm	6.2 ppm
		4.42 ppm	7.3 ppm	5.1 ppm	3.1 ppm
		206.0 ppm	404.0 ppm	281.0 ppm	167.5 ppm
		1699.0 ppm	>2000 ppm	1642.0 ppm	996.0 ppm

One benefit to the laboratory personnel analyzing soils is to use the L2000™ first to screen PCB content, thus allowing the GC chemist to make an accurate dilution immediately. The appropriate dilution is to 1 ppm, and one chromatographic analysis is approximately 40 minutes long. The analysis time can certainly add up with trial-and-error dilutions being made, especially if there are many samples waiting to be analyzed. Knowing the right dilution also prevents overloading the column with PCB contamination.

The L2000™ system can analyze to fewer than 5 ppm in oil and soil, can be used in the field by non-technical personnel and requires less than 10 minutes to run an analysis. These attributes make the instrument an excellent alternative to gas chromatographic analysis, especially for soil samples.

Although this new technique does not replace gas chromatography, it can significantly reduce the number of samples requiring GC analysis, and thus allow a greater amount of samples to be run at a lower cost.

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Source Identification and Characterization Using Areal and Vertical Soil Gas Sampling Techniques

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ABSTRACT

Areal and vertical soil gas sampling techniques were used to locate and characterize a 200-foot diameter carbon tetrachloride (CCl_4) release area within a 370-acre site. In 1985, a municipal well was found to be contaminated with CCl_4. A detailed site history profile was developed to help identify the source of the groundwater contamination. This profile identified several potential sources within the site boundary, but subsequent sampling yielded no conclusive data.

A shallow areal soil gas survey was conducted, which consisted of 100 samples collected at 86 sampling locations within the site. Soil gas samples were taken from a depth of 2 to 3 feet and analyzed on-site for CCl_4 by a close support laboratory. The results identified three areas for further study.

As a result, PRC devised a technique to determine vertical CCl_4 concentration in soil gas profiles. This technique consisted of driving a soil gas collection probe ahead of a hollow-stem auger and taking a gas sample. Soil gas samples were collected from eight boreholes at regular intervals throughout the unsaturated soil zone (approximately 120 feet).

The borehole soil gas data identified the presence of CCl_4 above the water table in one borehole next to a former grain storage facility. To identify the source of this contamination, PRC collected shallow to mid-level soil gas samples from three depths between 8 and 22 feet at 34 locations around the facility. The results identified a CCl_4 release area and its areal extent. Subsurface soil gas sampling in additional boreholes in the source area confirmed the location and described the vertical configuration of the soil gas plume and its relation to the water table. Sufficient in situ groundwater samples were taken from each borehole within the saturated zone to describe the CCl_4 source and to select remediation alternatives. The approach used to locate and characterize the CCl_4 source area was very efficient and cost-effective.

INTRODUCTION

To remediate contamination at Superfund sites, it is often difficult, yet critical, to pinpoint the exact location of the contaminant source. Our firm, PRC Environmental Management, has developed an approach that was efficient and cost-effective in locating and characterizing the source of contamination at a subsite of a Superfund site in Hastings, Nebraska.

As part of an extensive Superfund investigation initiated in 1984, the U.S. EPA identified six subsites that may be contributing to groundwater contamination in the city of Hastings, Nebraska. The sites found included the M-3 subsite, which is the focus of this paper. The subsite covers approximately 370 acres in the west central part of town. It contains the release area responsible for the CCl_4 contamination of a nearby municipal well (M-3) in Hastings, Nebraska, and is partially respon-

sible for the contamination of the drinking water supply for the entire town.

The State of Nebraska discovered in 1984 that well M-3 was contaminated with CCl_4; it was decommissioned in 1985. The source of contamination was not identified until intensive investigations were initiated in late 1987. The field work for the remedial investigation activities for the M-3 subsite was conducted between the fall of 1987 and the spring of 1989.

METHODOLOGY

The approach used to locate and characterize the source of contamination consisted of the following five steps:

Source Location Steps

- Conducting a historical search of property use
- Conducting a surface soil gas survey
- Drilling boreholes using multiple-phase data collection techniques
- Conducting a followup shallow to mid-level soil gas survey in the source area

Source Characterization Steps

- Drilling additional boreholes in the source area using multiple-phase data collection techniques

The ability to have immediate access to data throughout the investigation was essential. Therefore, a close support laboratory (CSL) was used on-site to keep the investigation progressing in a timely manner. Use of the CSL allowed ongoing data interpretation, which was necessary to make the decisions and implement the steps outlined above. The CSL located in the PRC field office, was equipped with a gas chromatograph. The CSL was used to analyze samples collected during the M-3 subsite remedial investigation. The U.S. EPA's Contract Laboratory Program (CLP) laboratories were used to analyze replicate portions of the samples collected as quality control checks on the CSL and to provide litigation-quality data.

The following sections discuss each of the remedial investigation steps.

Historical Records Search

U.S. EPA Region VII conducted an historical search uses of the site, which consisted of a title search and interviews with area residents. The results revealed the locations of former grain storage areas and other operations that may have been responsible for the well M-3 contamination. CCl_4 had been used extensively as a grain fumigant in the area.

Surface Soil Gas Survey

A surface soil gas survey was conducted in the areas of former grain

storage activities in an attempt to locate the source of contamination at the subsite. Since the locations of the former grain storage areas were so widespread, 100 surface soil gas samples had to be collected. The samples included duplicates and were collected from 86 locations within the subsite.

To collect the surface soil gas samples, a hand-held probe was hammered into the ground to reach the sampling interval at a depth of 1 to 3 feet below the ground surface. At the top of the probe, a sampling air line was connected to a quick-disconnect fitting. The sampling line ran from the top of the probe to a small vacuum pump. Prior to sampling at each location, the probe and line assembly were purged with the pump until the pump exhaust reached equilibrium. To determine the point of equilibrium, the exhaust from the pump was monitored with an HNu organic vapor analyzer. The purge times were approximately 12 minutes. When the purge was completed, soil gas samples were collected in Tedlar bags and sent to the CSL.

The results of the surface soil gas sampling effort were generally inconclusive. However, trace amounts of CCl_4 were detected in an area where a railroad company had once operated a solvent-generating maintenance facility. CCl_4 also was found in the vicinity of a few former grain storage areas.

Borehole Drilling

Exploratory boreholes were drilled using the "multiple-phase" approach, so named because it determines the distribution of volatile organic compound (VOC) contaminants in three phases—soil, gas and water. The borehole data were used to establish vertical profiles of the chemical and physical characteristics for each phase. In the unsaturated zone of each borehole, vertical profile data were collected for specific parameters—relative density, visual classification, unsaturated permeability, moisture and the chemicals of interest for soil and soil gas. The CSL analyzed all soil and soil gas samples for CCl_4 and other selected VOCs.

Boreholes were drilled using hollow-stem augers. Soil samples were collected with a 3-inch-diameter split spoon sampler at 5-foot intervals beginning at the surface and continuing to a depth of 120 feet (depth of the water table). Soil samples were monitored in the field with an HNu organic vapor analyzer, followed by visual classification. Portions of the samples were sent to the chemical and physical CLP laboratories for analysis. In situ soil gas samples were collected at 10-foot intervals between soil samples. A soil gas probe was driven into the undisturbed formation ahead of the auger flights. Samples were collected in the same manner as described above in the surface soil gas survey section.

Based on the results of the historical survey and the surface soil gas survey, eight locations were designated for drilling exploratory boreholes. Six of the eight boreholes failed to yield more than background levels of CCl_4. Soil gas results from the seventh borehole indicated that a nearby gas tank was leaking or had leaked in the past. CCl_4 concentrations in the range of 15 ppmv were found in samples above the water table at the eighth borehole (C-2), located in the western portion of the subsite. As a result, this portion of the subsite was chosen for more detailed study, which included a shallow to mid-level soil gas survey.

Shallow to Mid-level Soil Gas Survey

Shallow to mid-level soil gas samples were collected throughout the source area. A grid was surveyed over the entire source area and, where possible, sampling locations were evenly spaced along the grid. Thirty-four soil gas samples were collected along the surveyed grid.

The shallow to mid-level soil gas samples were collected by using a hydraulic soil gas sampling device called a Geoprobe. The Geoprobe is a van-mounted sampling unit consisting of a hydraulic press capable of pushing a 1-inch outer diameter rod, with a slotted rod, used as a screen, as deep as 40 feet below the ground surface. Samples generally were collected at intervals of between 8 to 10 feet, 14 to 16 feet and 20 to 22 feet below the ground surface. The exact sampling depths varied slightly between locations, depending on the types of soils encountered. Some soil types were too resistant for the Geoprobe, in which case samples could not be collected.

At the top of the Geoprobe rod was a sample port with an attached gas sample line. The soil gas samples were collected in basically the same manner as the surface soil gas samples and were analyzed by the CSL.

The shallow to mid-level soil gas survey identified the exact location of the suspected CCl_4 release area within the M-3 source area. Figure 1 is a plan view of the approximate boundaries of the CCl_4 soil gas plume. The highest concentrations were detected in a sample from the southeast corner of a warehouse. Generally, CCl_4 concentrations increased with depth. However, the Geoprobe soil-gas survey was intended as a screening tool to help locate the next borehole locations. The Geoprobe survey was actually used to locate the source of contamination, while the multiple-phase borehole drilling activities characterized the soil gas contamination plume.
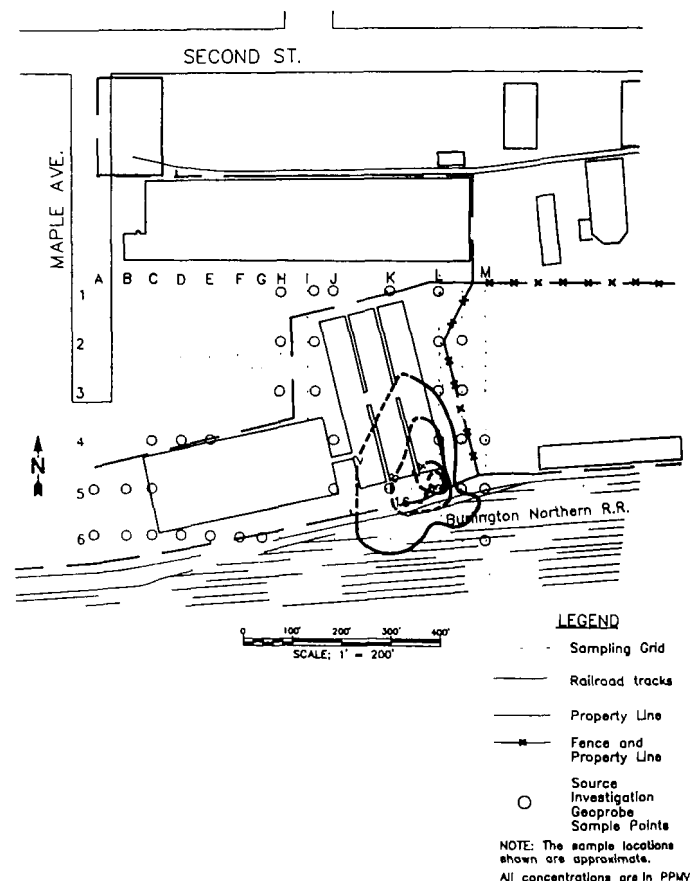
Figure 1
Carbon Tetrachloride Concentrations at
8-10' on Geoprobe Results at M-3 Subsite

Additional Borehole Drilling

Once the source of contamination was identified, three additional boreholes were drilled to characterize the source. The multiple-phase approach was used again for drilling the boreholes. These boreholes were different from the boreholes previously drilled in that they were advanced into the saturated zone. In the unsaturated zone, soil and soil gas samples were collected in the same manner previously described using the hollow-stem auger technique. In the saturated zone of each borehole, vertical profile data were collected for specific parameters—relative density, visual classification, porosity, specific yield, horizontal hydraulic conductivity and the chemicals of interest for soil and groundwater. The CSL analyzed all soil and groundwater samples for CCl_4 and other selected VOCs. In situ groundwater samples were collected at 10-foot intervals between soil samples. Groundwater samples were collected using a groundwater sampling probe that was driven into

the undisturbed formation ahead of the auger flights. A pneumatic slug test method was used to test hydraulic conductivity in the same intervals from which groundwater samples were collected.

Figure 2 depicts the CCl_4 concentrations soil gas plume in the unsaturated zone. CCl_4 soil gas concentrations ranged from 0 to greater than 1,200 ppmv. The greatest concentrations were recorded directly above the water table. Groundwater samples collected from 5 to 10 feet below the water table contained CCl_4 concentrations ranging from 33 to 49 ug/L in borehole C-9.

The dimensionless Henry's Law constant for the partitioning of CCl_4 from the gas phase to the water phase is 0.97 or, for practical purposes, unity. This finding means that a one-to-one relationship probably exists between the CCl_4 concentrations in the soil gas and the ground water in the capillary fringe and directly below the water table. The gradient of CCl_4 concentrations between the water table and the groundwater sampling zone located 5 to 10 feet below the water table is apparently very steep, as evidenced by relatively low CCl_4 concentrations in groundwater samples collected from this lower zone. Also, the data clearly indicate that soil gas contamination is responsible for groundwater contamination in the subsite area.

CONCLUSIONS

Using the above approach, PRC successfully located a source area, with an approximate diameter of 200 feet, within a 370-acre subsite. The source was located and sufficiently characterized to begin remediation activities. Based on this study, soil vapor extraction will be used to remediate the unsaturated zone. Not only will soil vapor extraction remove the contaminated soil gas, but it also will favor limited partitioning of the CCl_4 from the surface of the ground water into the gas phase above the ground water. The source area should be remediated using this approach in a relatively short period of time. More study will be needed, however, before the ground water can be remediated.
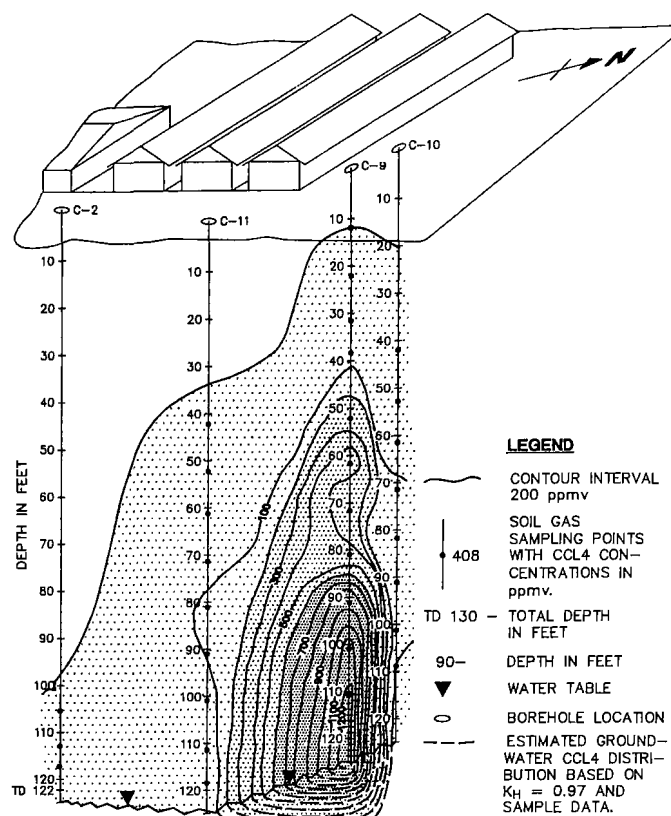
Figure 2
Vertical Distribution of CCl_4 in Borehole
Soil Gas and Groundwater

Economic Analysis of the New Toxicity Characteristic Leaching Procedure

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ABSTRACT

On Mar. 29, 1990, the U.S. EPA published in the Federal Register the final Rule of the Toxicity Characteristic Leaching Procedure (TCLP). The Implementation of this rule will bring an estimated 730 million metric tons of waste each year under the provisions of Subtitle C of RCRA. This figure is roughly 300% increase in the volume of regulated hazardous waste. The goals and merits of this ruling are examined from a neoclassical economics perspective. Does this regulation succeed as government policy to maximize the social welfare?

The history of the Extraction Procedure Toxicity Characteristic (EPTC) which proceeded the TCLP is considered. Each procedure uses a similar logic to determine the regulatory concentration.

The U.S. EPA, although required by Congress to change the EPTC, had considerable leeway in creating the new regulation. The intent of the TCLP is to reduce human health risks and environmental damage. Given these criteria, the TCLP rule should be very successful. When the costs of the rule to industry are considered, however, the rule may be too expensive. Higher allowable regulatory concentrations provide very nearly the same benefits but at substantially reduced costs. In economic terms, the marginal cost of the rule exceeds its marginal benefits.

As with any economic analysis, this one suffers from a lack of sound data. Measurements of economic costs are relatively easy to compute, but measurements of benefits are notoriously difficult.

INTRODUCTION

In 1976 Congress passed the Resource Conservation and Recovery Act.[2] RCRA contains provisions which affect the disposal of nearly all municipal and industrial material waste produced in this country. This act created two broad categories of waste: hazardous and nonhazardous waste. The disposal requirements of hazardous waste are governed by Subtitle C of RCRA. As might be expected, the disposal requirements for hazardous waste are more stringent and more expensive than those for nonhazardous wastes.

RCRA uses two methods for classifying waste. One method is based on the industrial process which created the waste. The U.S. EPA has performed numerous studies of different industries and of different industrial processes. These studies have identified wastes that are considered to be hazardous. The U.S. EPA then promulgates a regulation which brings all of the waste produced by a particular industrial process under the realm of Subtitle C. This process works well for industry which prefers easy determinations of regulatory applicability. A process either is or is not regulated and the waste either is or is not hazardous.

The time and expense of these industrial process studies combined with the sheer number of industrial processes necessitated a second method of classifying waste. This method is based on four characteristics: ignitability, corrosivity, reactivity and toxicity. Each of these characteristics is determined by a laboratory test and compared to a regulatory criteror. The Mar. 29, 1990 Federal Register[1] changes the protocol of the laboratory test and the criteria used for determining the toxicity characteristic. This new rule becomes effective Sept. 25, 1990 for large facilities and Mar. 29, 1991 for small facilities. (A small quantity generator is defined as one producing less then 1000 kg/mo.)

Mismanagement Scenario

TCLP will replace the old toxicity characteristic Extraction Procedure Toxicity Characteristic.[6] Before elaborating on the critical differences between the these procedures, it is important to understand the logic behind the toxicity characteristic. A specific mismanagement scenario which assumes the disposal of wastes in an unlined municipal landfill creates a mechanism for human exposure via groundwater contamination.[1,5,6] As water migrates downward through the landfill, it contacts the waste. Some constituents of the waste become mobile, traveling downward with the water until they reach groundwater, then traveling laterally in the subsurface aquifer. Once in the aquifer the waste may become a contaminant in a downgradient drinking water well. Human exposure occurs and the potential for toxic response exists.

The U.S. EPA set out to model the toxic risk resulting from improperly disposed waste. The model assumes a toxicity threshold for human exposure. The toxicity threshold is the concentration of a contaminant below which humans show no toxic response. This may be considered the maximum safe exposure level over the lifetime of a human, referred to as chronic toxicity reference level (CTRL).[1,5,6] The CTRLs are based on the maximum concentration limits (MCLs) promulgated as part of the National Interim Primary Drinking Water Standards (NIPDWS) when available. When these do not exist for specific compounds in question, oral reference doses (RfDs) and risk-specific doses (RSDs) for carcinogenic and noncarcinogenic compounds, respectively, are used. These are based on published and generally accepted standards.

From the landfill to human exposure dilution of the contaminant is assumed to occur.[1,5] A dilution and attenuation factor (DAF) can be determined by modeling the groundwater flow through the hydraulic media. To determine the maximum contaminant level safe for disposal in an unlined landfill, the CTRL is multiplied by the DAF. This product determines the regulatory levels:

$$DAF \times CTRL = Regulatory\ Concentration \qquad (1)$$

Both the TCLP and the EPTC are extraction procedures designed to mimic the possible conditions resulting in the leaching of toxic compounds into the groundwater. The waste extract is then analyzed and compared to the regulatory levels.

EPTC vs. TCLP

The original EPTC contains criteria for 14 compounds; eight metals and six organic compounds.[5] Only 14 compounds were regulated due to the lack of widely accepted data for determining the CTRLs for other compounds. A DAF of 100 was applied as a "best guess" for the time. Accurate groundwater modeling data were unavailable.

From its first use in the early 1980s, it was felt that the EPTC underestimated the leaching of organic compounds due to technical inadequacies in the procedure[1]. Critics of the EPTC also pointed out that testing should be conducted for a larger list of compounds.

In 1984 as part of the HSWA Congress mandated that The U.S. EPA make changes to address these concerns(Sections 3001 g-h,2). In the June 13, 1986 *Federal Register*, The U.S. EPA proposed the TCLP with 38 new compounds to be regulated.[5] The TCLP overcomes the technical shortcomings of the older extraction procedure and regulates a variety of new organic compounds.

Before a proposed regulation is put into effect, however, it goes through a period of comment and study. When the regulatory agency is satisfied that the rule has been studied, explained and commented on to the extent that is productive, it is published in its final form in the *Federal Register*.

In March of 1989, nearly 3 yrs. after the rule had first been proposed and nearly 5 yrs. after Congress had mandated that the U.S. EPA make changes, the TCLP rule had not been finalized. On Mar. 8, 1989, the Environmental Defense Fund(EDF) brought a citizens action suit against the U.S. EPA for failing to meet a number of mandates including the TCLP that had been set forth in the HSWA.[7] On Feb. 21, 1990, a federal judge ruled in favor of the EDF and ordered the U.S. EPA to release the new rule.[8]

The Mar. 29, 1990 TCLP will regulate 25 additional organic compounds. Thirteen compounds originally proposed in 1986 will not be regulated. The 14 compounds regulated under the EPTC will continue to be regulated at the same maximum concentrations. Some of the CTRLs for the 25 new compounds have been changed from the 1986 proposal based on changes in accepted toxicity threshold.[1] A DAF of 100 is used to calculate the maximum concentration levels of all of the regulated compounds.

REGULATORY OPTIONS

All major rule makings require the U.S. EPA to prepare a Regulatory Impact Analysis (RIA).[6] The RIA considers five regulatory options: the baseline (i.e., no TCLP rule) and DAF options of 500, 250, 100 and 33. These options are listed in order of increasing regulation. The base line represents the situation before the implementation of the TCLP. The regulatory concentrations are proportional to the DAF. Lower DAFs result in lower maximum concentrations or increased levels of regulation. The RIA provides estimated data for each of these options, and it is from this document that many of the cost/benefit figures come.

GOALS/BENEFITS

The benefits to be achieved from this rule are both reduced financial cost and reduced human health risk.[6] The financial benefits can be divided into two separate categories; reduced resource damage and reduced future cleanup costs. Resource damage is defined as the cost to replace or provide an alternate supply of a resource that has been lost due to pollution. In this case the resource is the groundwater, and if it becomes polluted an alternate supply will need to be provided.

Under CERCLA, out-of-control hazardous waste contamination must be cleaned up.[9] The funds for clean up come largely from taxpayer dollars. Clean up cost is a measure in dollar value of the expenditures required to clean up groundwater to meet cleanup targets. The TCLP rule will reduce the likelihood of the formation of future Superfund sites requiring cleanup under CERCLA.

Human health risk is calculated in 2 ways: for the most exposed individual(MEI) and for the population. The risk for the MEI is the health risk for that person who receives water from the closest downgradient well from the contamination source.[1,10] If no downgradient well exists, then no MEI risk is computed. Population risk is also calculated for landfills with down gradient wells. Population risk is based on the number of people affected by the contamination plume. Both the MEI risk and the population risk are calculated for carcinogenic and noncarcinogenic compounds.

Table 1 summarizes both the financial and health benefits. It is a compilation of all the major affected industries and all of the waste that they produce. Note that all of the noncarcinogenic exposure above the threshold reference dose is eliminated for all of the regulatory options. In a similar manner, all of the resource cleanup costs are eliminated for all options. Resource damage and the number of cancer cases both decrease with increasing levels of regulation, but DAF 500 removes more than half of the risk or damage.

Table 1
Summary of Regulatory Benefits[1]

Benefit Measure (units)	Base-line Risk	Benefit For Regulatory Option[2]			
		DAF33	DAF100	DAF250	DAF 500
Cancer cases over 70 years (number of cases)	5.6	5.6	5.5	5.5	5.2
Facilities with cancer risk >10E-5 (number of facilities)	790	790	780	730	460
People exposed to non-carcinogenic compound>RfD (number of people)	320	320	320	320	320
Resource Damage (billions of dollars)	3.8	3.8	3.8	3.6	2.4
Cleanup Costs (billions of dollars)	15	15	15	15	15

1   Table adapted from TC RIA exibit 5-6

2.   All regulatory options are reported as reduction from baseline risk (i.e. Benefit)

COSTS

The TCLP, because it represents an increase in the level of industrial regulation, will force more sophisticated and expensive waste management practices. The RIA makes two types of cost predictions: social costs and costs to industry or compliance costs. Social costs are a measure of the goods and services lost to society due to the increase in regulation. Industry, however is more concerned with the compliance costs. What are the additional revenue requirements to maintain the same profitability? Industry uses compliance costs to make economic decisions. The RIA defines social cost as the total cost minus transfer payments. The RIA gives the example of a Subtitle C landfill owner/operator who charges $200 per unit of waste for disposal. If it only costs the owner/operator $105 to dispose of the waste, then $200 is the total or compliance cost, $105 is the social cost and $95 is a transfer payment from the generator of the waste to the landfill owner/operator.

The RIA makes cost predictions by examining each industry. First base line management practices are identified along with waste streams that are likely to be affected by the TCLP. Alternative practices for the disposal of these wastes are considered along with the costs of these options. Industry is assumed to choose the most cost-effective solution. Based on the cheapest alternative for industry, social costs and

Table 2
Summary of Total Annual Costs[1]

	Regulatory Options			
	33	100	250	500
Large Facilities				
Annual Cost (millions)	320	220	89	68
Facilities Incurring Cost	1900-2600	1100-1800	870-1300	700-1100
Small Facilities				
Annual Cost (millions)	35	28	25	13
Facilities Incurring Cost	15,000-16,000	14,000-16,000	13,000-15,000	13,000-15,000
Total Cost to Industry (millions)	350	250	110	82
Total Social Cost (millions)	270	190	67	52

1.   Table adapted from TC RIA exibit 3-3 and 3-4

compliance costs are estimated. Table 2 summarizes these costs. From DAF=250 to DAF=100, social costs nearly triple and compliance costs more than double.

IMPACTS

The effect of this rule on industry is varied. There is a disproportionate burden placed on different industries and waste stream types.

A vast majority of the affected waste (over 99%) by volume for all of the regulatory options considered is wastewater managed in surface impoundments.[4,6] Based on the least expensive alternative, most of this wastewater will be managed in tanks which are exempt from Subtitle C requirements. This conversion from impoundments to tanks is relatively inexpensive. By comparison nonwastewater costs account for more than 95% of the total compliance cost. Table 3 provides wastewater and nonwastewater costs for 12 different industries.

CONCLUSIONS

When government policy is considered from a neoclassical economics perspective, the test of effective policy comes from a comparison of the marginal benefits of the general social welfare to the marginal costs that are a result of the policy.[11] If the marginal costs exceed the marginal benefits, then our economic system is existing in a state of over regulation. If the marginal costs are less then the marginal benefits, then society would benefit from a greater degree of regulation. The question of whether this type of standard is the most efficient regulatory framework economically is a topic to itself, although I will conclude with a few remarks on this issue.

This kind of analysis can be used for regulation designed to control and minimize pollution. Large amounts of uncontrolled hazardous waste entering the environment cause; exposure of people to dangerous chemicals, increased cancer risk and destruction of vital resources which may need to be replaced or cleaned up at great expense. The RIA estimates that the average Superfund cleanup costs $15 million. All of which implies a reduction in the social welfare.

If, however, regulations are made too restrictive, then industry in this country will be paying a disproportionately large share of the costs for hazardous waste disposal.[11] People may lose their jobs, needed products may become unavailable or more expensive and people's standard of living may decrease. Once again, the social welfare is not maximized.

The test of effectiveness of the new TCLP is simply a matter of measuring the benefits to society resulting from more protective waste classification compared to the costs that society will bear resulting from greater expenses for waste disposal. The RIA prepared by the U.S. EPA provides a great deal of information regarding the expected costs and benefits to society. From this I have extracted what information I could about the marginal costs and benefits of this rule. The Methods section which follows describes how the marginal cost and benefit data were derived. Following the methods section is an Analysis and Discussion of the data generated.

Methods

Marginal benefit and marginal cost are nowhere presented for the TCLP rule. The RIA does, however, provide four increments in regulation. Average marginal cost or benefit between each of the regulatory options is calculated. For example, the total annual social costs of the rule at DAFs of 100 and 250 are $190 million and $67 million dollars respectively.[6] The difference is $123 million annually. The average marginal social cost (MSC) is the quotient of $123 million and the change in DAF of 150.

$$\text{Average Marginal Cost} = \frac{\text{change in cost}}{\text{change in DAF}} = \frac{190-67}{250-100} \quad (2)$$

$$= .82 \ (\$million/unit \ DAF)$$

When making a comparison of the MSC and the average marginal resource damage benefit (MRB),(the value of resources that would have been destroyed if the regulation were not implemented), present value terms are used because the resource damage benefit presented in the RIA and in Table 1 presents the data as total resource damage avoided, not in terms of an annual figure. Table 4 computes the present value of all of the future costs of the rule discounted at 3% and at 10%. The

Table 3
Costs to Industry Split by Wastewaters and Non-wastewaters[1,2]

Industry	DAF 33			DAF 100			DAF 250			DAF 500		
	WW	NWW	T	WW	NWW	T	WW	NWW	T	WW	NWW	T
Textile Manufacturing	800	14,000	15,000	230	7,600	7,800	20	2,400	2,500	2.4	0	2.4
Sawmill, Planning Mill and Finishing	.82	0	.82	.82	0	.82.	.82	0	.82.	.78	0	.78
Pulp and Paper Mill	360	84,000	85,000	35	42,000	42,000	0	2,900	2,900	0	530	530
Plastics Materials and Resins	310	5,300	5,600	240	5,100	5,300	130	3,000	3,100	110	2,300	2,400
Synthetic Rubber	200	8,300	8,400	190	8,100	8,300	190	8,100	8,300	180	8,100	8,200
Synthetic Fibers	350	22,000	22,000	350	22,000	22,000	350	22,000	22,000	340	22,000	22,000
Pharmaceuticals	330	17,000	17,000	270	14,000	14,000	250	11,000	11,000	220	10,200	10,400
Organic Chemicals	730	25,000	25,000	600	20,000	21,000	530	18,000	18,000	502	14,000	14,000
Petroleum Refining	4,000	130,000	140,000	4,000	95,000	99,000	4,000	13,000	17,000	3,800	5,400	9,200
Miscellaneous Petroleum and Coal Products	0	7,900	7,900	0	5,300	5,300	0	2,700	2,700	0	2,000	2,000
Petroleum Pipelines	59	3,200	3,300	60	2,700	2,800	58	2,600	2,700	60	1,200	1,200
Wholesale Petroleum Marketing	1,000	29,000	30,000	1,000	24,000	25,000	1,000	23,000	24,000	1,000	11,000	12,000
Total	8,200	350,000	350,000	7,100	250,000	250,000	6,600	110,000	110,000	6,300	76,000	82,000

WW - Wastewaters   NWW - Non-Wastewaters   T Total
1 Table adapted from TC RIA exhibit 3-5 through 3-8.
2 All costs are listed in thousands of dollars.

discount rate used by the U.S. EPA in the RIA is 3% and the 10% value is given for comparison.

Table 4
Present Values of Costs

	33	100	250	500
Present Value of All Social Costs to Infinity Discounted at 3%	9.0	6.3	2.2	1.7
Present Value of All Social Costs to Infinity Discounted at 10%	2.7	1.9	.67	.52
Present Value of All Social Costs to 20 years[1]	5.2	3.7	1.6	1.2

1   These figures are taken from the RIA Exhibit ES-5

If C is the annual cost and r is the discount rate, then the discounted value of all of the future cost is given by the formula:[11]

$$\text{Discounted Value} = \frac{C}{r} \qquad (3)$$

Table 5 presents the marginal cost and benefits as calculated. Marginal human health risk reductions are calculated in a manner similar to the MSC and the MRB, except that it must be done in annual risk reduction rather than total present day value since I know of no accepted way to discount future human lives. The marginal cleanup cost reduction is not even considered because, as calculated by the U.S. EPA, the cleanup cost benefit is nearly constant across all of the options.

Table 5
Marginal Costs and Benefits

	33 to 100	100 to 250	250 to 500	500 to Baseline
Average Marginal Social Cost (Summed to Infinity, Present Value)[1]	39.8	27.5	2.0	3.4
Average Marginal Social Cost (Summed to 20 years, Present Value, $billions)	22.4	14	1.6	2.4
Average Marginal Resource Benifit ($billions)	0	1.3	4.8	4.8
Average Marginal Cancer Risk Reduction	.1	0	.3	5.2
Average Marginal Social Cost (Annual, $millions)	1.19	.82	.06	.11

All marginal units are (units of benifit/Change DAF)

Using the marginal values generated in Table 5, curves can be generated as shown in Figures 1 and 2. Based on the "Mean Value Theorem," all that we can really say about the relevance of the average marginal values calculated is that they are equal to the actual marginal cost/benefit value at least one point. The mean value theorem says that the average rate of change along a curve whose slope is continuous along the interval, equals the slope of the curve at least one point.[12] Throughout the rest of the discussion the average marginal cost/benefit will be used synonymously with the marginal cost/benefit, although mathematically the two are quite different.

Analysis and Discussion

If all of the costs and benefits are represented accurately, then neoclassical economics tells us that the ideal level of regulation, that which maximizes the social welfare, should be where the marginal costs to society equal the marginal benefits.[11] At this point, if the level of regulation were increased, then the costs to society of the regulation would be greater than the benefits of greater protection from hazardous wastes. Conversely, if the level of regulation were reduced, then the increased damages caused by the less protective disposal requirements would be greater than the money saved from less regulation. This point of equal marginal cost and benefit is an ideal point; the best compromise between pollution and environment.
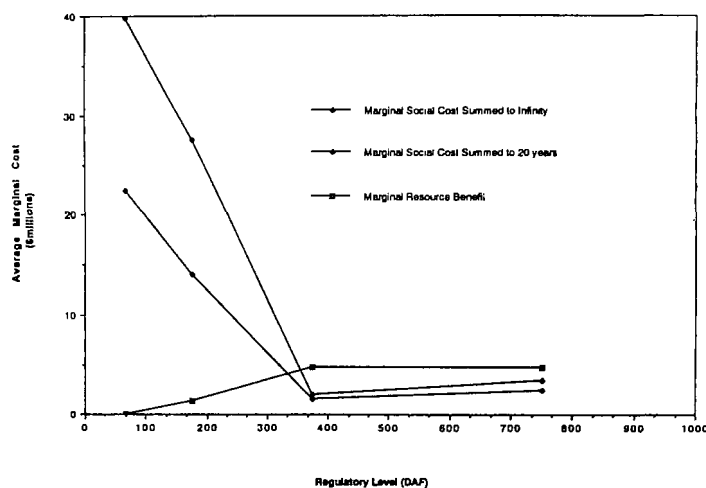
Figure 1
Marginal Cost vs. DAF
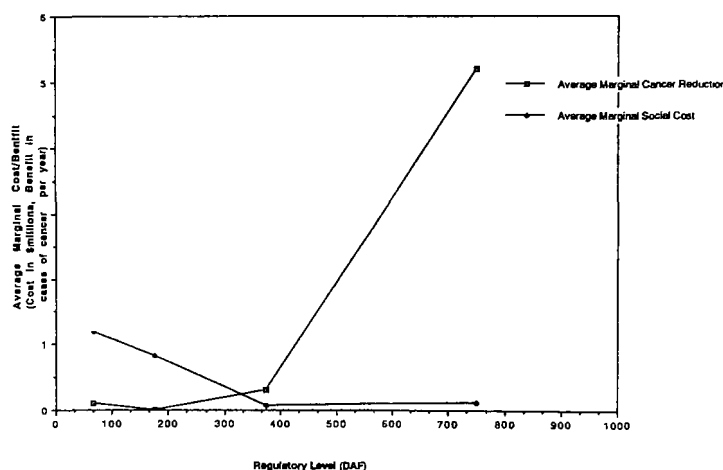
Figure 2
Marginal Cancer Reduction and Marginal Annual Cost

Table 6
Cost Effectiveness of Regulatory Options Based on Present Values[1]

	33	100	250	500
MEI Cancer Risk Reduction per Million Dollars (Reduction in the Number of Facilities Exceeding 10⁻⁵ divided by present value compliance cost	.15	.21	.46	.38
Population Cancer Risk Reduction per Million Dollars (Reduction in Present Value No. of Cases Divided By Present Value Social Cost	.001	.002	.003	.004
Reduction in Resource Damage per Million Dollars (Reduction in Present Value Resource Damage Divided by Present Value Compliance Cost, Millions of Dollars)	.73	1.0	2.3	2.0

1   Table adapted from the RIA Exhibit ES-5

From the curves generated and shown in Figures 1 and 2. It would seem that a DAF of approximately 300-400 would be ideal. The DAF used in the actual regulation is 100. The RIA makes some attempt to show what the most cost effective levels of regulation are. These are shown in Table 6. The results shown here indicate that DAF 250 is the most efficient for two out of three benefit criteria and DAF 500 is the most cost effective for the third criteria listed.

Before coming to the firm conclusion that the TCLP rule as it stands represents over regulation a number of considerations need to be made. First we must consider the validity of the data that EPA has presented. By their own admission the data often represents a worse case scenario when presenting costs.[6] There are still many questions about what

wastes will need to be handled as hazardous. Many waste streams have not been tested by this new protocol.

Given the uncertainty and the drastic cost of environmental cleanups it may make sense to regulate in an apparently sub-optimal way. If the RIA has not anticipated some of the benefits to society then our comparison may no longer be valid. Only ground water damage is considered in this RIA. Hazardous waste discharge to surface waters and other land areas cause large amounts of environmental damage that is not accounted for. Economic analysis often place a low monetary value on land that is undeveloped because value is based on market value. Some intrinsic value of the land may not be accurately represented in the analysis.

There are other sources of environmental damage like volatile organic compound release into the air from such things as wastewater impoundments are a form of air pollution. Quantitative data is unavailable for this pollution source. Lastly, in the past several years, most notable since the Love Canal site became infamous for the effects of hazardous waste, public sentiment has been very much in favor of tighter restrictions of the production and disposal of hazardous waste. This has been the great impetus for much of the legislation that has gone through Congress during the last 10 yrs. and seems to indicate that people are willing to pay for a cleaner environment. Preservation value is a more important concern then it has been in the past.

One of the interesting conclusions to come out of this type of analysis is that there is an ideal level of pollution. No pollution is not an option if we wish to live in a modern society. Conversely, a completely laissez faire system allows too much pollution. At the beginning of this paper, I spoke of compliance costs versus social costs. In a completely unregulated system there are no compliance costs. Waste may be disposed of at no cost to industry although perhaps at great cost to society. The task of regulators is to attach a cost to the disposal of waste (i.e., compliance cost) that balances the damage caused to society while allowing market forces to distribute the burden in the most equitable manner. One of the important conclusions to come from neoclassical economic analysis is that the free market will create the most efficient and beneficial distribution of resources provided that there are not significant externalities. An externality is a cost to society that is not reflected in the compliance costs of industry. Many types of pollution are externalities. Regulators should be trying to internalize the cost of pollution. When pollution costs industry money, then steps are taken to reduce the amount of pollution. This may mean, however, that some businesses or industries will no longer be profitable or competitive,

particularly if regulated businesses are forced to compete with unregulated businesses. This is often the case when United States manufacturers compete with those from less developed and less regulated nations.

The TCLP rule described in this paper is part of the regulatory framework established by RCRA under subtitle C. [2,13] Until now, I have considered this change as compared to the EPTC rule being phased out. Let me point out several interesting features of the subtitle C regulations. No facility or plant is prohibited from producing hazardous waste. Disposal costs are not directly regulated, they are market driven. Thus, market forces will allow firms to set their marginal costs of waste disposal equal to their marginal benefits from producing the waste. The most efficient outcome should result provided the costs of producing the wastes have been adequately internalized.

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Long-Term Environmental Monitoring at Hanford, Washington

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ABSTRACT

Environmental monitoring has been an ongoing activity on the U.S. Department of Energy's Hanford Site in southeastern Washington for over 45 years. The objectives of this monitoring program are to detect and assess potential impacts of site operations (nuclear and nonnuclear) on air, surface and groundwater, foodstuffs, fish, wildlife, soils and vegetation. Data from monitoring efforts are used to calculate the overall radiological dose to humans working on-site or residing in nearby communities.

In 1988, measured Hanford Site perimeter concentrations of airborne radionuclides were below applicable guidelines. Tritium and nitrate continued to be the most widespread constituents in on-site groundwater. Concentrations of radionuclides and nonradiological water quality in the Columbia River were in compliance with applicable standards. Foodstuffs irrigated with river water downstream of the Site showed levels of radionuclides that were similar to those found in foodstuffs from control areas. Low levels of ^{137}Cs and ^{90}Sr in some on-site wildlife samples and concentrations of radionuclides found in soils and vegetation from on-site and off-site locations were typical of those attributable to worldwide fallout. The calculated dose potentially received by a maximally exposed individual (i.e., based on hypothetical, worst-case assumptions for all routes of exposure) in 1988 (0.08 mrem/yr) was similar to those calculated for the years 1985-1987.

In addition to monitoring radioactivity in fish and wildlife, population numbers of key species are determined. Chinook salmon (*Oncorhynchus tshawytscha*) spawning in the Columbia River at Hanford have increased in recent years with a concomitant increase in winter roosting activity of bald eagles (*Haliaeetus leucocephalus*). An elk (*Cervus elaphus*) herd, established by immigration in 1972, is increasing. The Hanford site also serves as a refuge for Canada geese (*Branta canadensis*), great blue heron (*Ardea herodias*), and various plants and other animals, e.g., mule deer (*Odocoileus hemionus*) and coyote (*Canis latrans*).

INTRODUCTION

The U.S. Department of Energy's (DOE) Hanford Site occupies a land area of approximately 1,450 km² (560 mi²) in semi-arid southeastern Washington (Figure 1). The Columbia River flows through the site and forms part of its eastern boundary. Flow of the Columbia River is regulated daily according to electric power demands. Although the river was once closed to public access, public use for recreational and barge traffic is again practical. The southwestern portion of the site includes the southern terminus of the Rattlesnake Hills with elevations exceeding 1000 m. Both unconfined and confined aquifers lie beneath the site.
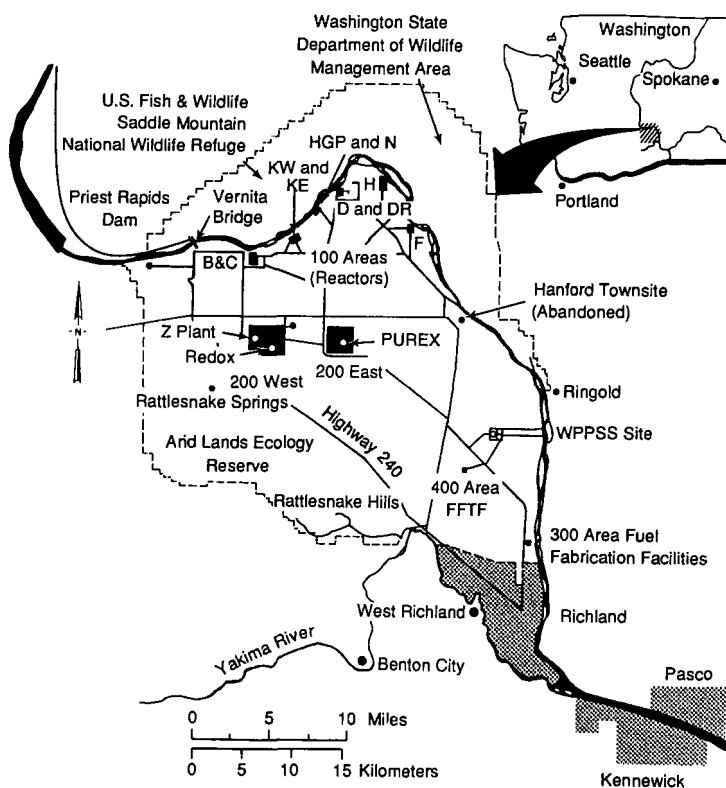
Figure 1
The Hanford Site

Nuclear and nonnuclear industrial and research activities have been conducted at Hanford since 1943. The most environmentally significant activities have involved the production of nuclear materials and the chemical processing and waste management associated with the major product, plutonium. By-product wastes have included gamma-, beta-, and alpha-emitting radionuclides and various nonradioactive chemicals in gaseous, liquid and solid forms.

There are currently four major DOE operations areas on the Hanford Site (Fig. 1). The 100 Areas located along the Columbia River include the dual-purpose N Reactor that produced plutonium for national defense and steam for the Hanford Generating Project (HGP), operated by the Washington Public Power Supply System (WPPSS) and eight, now

deactivated single-purpose, plutonium production reactors. The plutonium uranium extraction (PUREX) plant (reactor fuel reprocessing), plutonium finishing plant (Z Plant) and waste-disposal facilities are located in the 200 Areas on a plateau (elevation 229 m) approximately 11.3 km west of the Columbia River. The 300 Area, located just north of Richland, Washington, contains the uranium fuel manufacturing facilities in support of N Reactor and research and development laboratories. The Fast Flux Test Facility (FFTF) which has operated intermittently since 1981 to test new fuels and materials for future breeder reactor technology is located in the 400 Area. Nongovernment facilities within Hanford Site boundaries include HGP, the WPPSS nuclear plant (WNP) sites, WNP-1, WNP-2 and WNP-4, including one commercial reactor (WNP-2) that achieved full operation status in the fall of 1984 and a commercial low-level radioactive-waste burial site near the 200 Areas, operated by U.S. Ecology. The Advanced Nuclear Fuels Corp. (formerly Exxon) fuel fabrication facility is immediately adjacent to, but not located on, Hanford Site property.

Environmental monitoring at Hanford has been ongoing for 45 years. The program is conducted to assess potential impacts to individuals and populations that may be exposed to radionuclides, ionizing radiation and hazardous chemicals. Environmental monitoring currently includes air, surface and groundwater, fish, wildlife, soil, vegetation and foodstuffs (fruits, vegetables and milk). Fish and wildlife are monitored for radioactivity and to determine the population status of key species.

RADIOLOGICAL MONITORING

Air

Potential airborne transport of stack releases containing radionuclides from Hanford facilities offers a direct pathway for human exposure. Thus, air is sampled continuously for airborne particulates and analyzed for radionuclides at 50 locations on-site, at the site perimeter and in nearby and distant communities.[1] At selected locations, gases and vapors are also collected and analyzed. Many of the longer-lived radionuclides released at Hanford are also present in atmospheric fallout that resulted from nuclear weapons testing in the 1950s and 1960s or from nuclear accidents that occurred elsewhere.

In May and June of 1986, air samples collected on-site as well as those from distant locations showed increases in several long- and short-lived radionuclides (e.g., ^{137}Cs, ^{131}I, ^{103}Ru) that resulted from the April 1986 reactor accident at Chernobyl in western Russia. However, even then, no sample exceeded 0.17% of the applicable DOE derived concentration guide (DCG) for areas permanently occupied by the public.[2]

Groundwater

The shallow unconfined (water-table) aquifer has been affected by wastewater disposal practices at Hanford more than the deeper, confined aquifers. Discharge of water from various industrial processes has created ground-water mounds near each of the major wastewater disposal facilities in the 200, 100 and 300 Areas (Fig. 1). Discharge to groundwater in the 200 Areas may contribute ten times more water annually to the unconfined aquifer than natural input from precipitation and irrigation.[3] These groundwater mounds have altered local flow patterns in the aquifer, which are generally from west to east.

Groundwater, primarily from the unconfined aquifer, is currently sampled from 551 wells and analyzed for radionuclides.[1] Tritium (^{3}H) occurs at relatively high levels in the unconfined aquifer, is one of the most mobile radionuclides and thus reflects the extent of groundwater contamination from on-site operations. Many liquid wastes discharged to the ground at Hanford have contained^{3}H. The PUREX facility is currently the main source for ^{3}H-containing wastes.[4] Tritium from releases prior to 1983 that passed downward through the vadose (unsaturated) zone to the unconfined aquifer continues to move with groundwater flow toward the Columbia River. Tritium concentrations in Hanford groundwater range from less than 300 pCi/L to over 2,000,000 pCi/L near or within the 200 Areas.[1,2,5]

Groundwater from the unconfined aquifer enters the river through subsurface flow and springs that emanate from the riverbank.

McCormack and Carlile[6] identified 115 springs along a 41-mile stretch of river. Tritium concentrations in wells near the springs ranged from 19,000 to 250,000 pCi/L and averaged 176,000 pCi/L in 1985.[7] Although the distribution of ^{3}H and other radionuclide concentrations in springs generally reflected those in nearby groundwater wells, the magnitude was generally less in springs due to mixing of surface and groundwater. Tritium concentrations in the river were generally less than those in springs. Tritium concentrations in springs were less than 4% of the DOE DCG (2,000,000 pCi/L). Tritium concentrations in the river were less than 0.5% of the DCG and less than half the regulatory limit for drinking water (20,000 pCi/L).[8] From 1983 to 1988, annual average ^{3}H concentrations in the river (<200 pCi/L) were at least a factor of 100 below the drinking water limit.[1] It is noteworthy that ^{3}H also occurs naturally in the Columbia River upstream from Hanford. From 1983 to 1988, annual average ^{3}H concentrations in the river, upstream at Priest Rapid Dams, ranged from 70 to 100 pCi/L.

Surface Water

Columbia River water is used for drinking at downstream cities, for crop irrigation and for recreational activities (fishing, hunting, boating, waterskiing and swimming). Thus, it constitutes the primary environmental pathway to people for radioactivity in liquid effluents. Radionuclides can be delivered to human foodstuffs through crops irrigated with river water and cow's milk through irrigated alfalfa and other cattle forage. Although radionuclides associated with Hanford operations, worldwide fallout and natural phenomena continue to be found in small but measurable quantities in the Columbia River, concentrations are below Washington State and U.S. EPA drinking water standards.

Deep sediments in downstream reservoirs still contain low concentrations of some long-lived radionuclides.[9-13] Trace amounts of ^{239}Pu, ^{60}Co, ^{137}Cs and ^{152}Eu persist in sediments accumulated above the first downstream dam (McNary). In 1977, approximately 20 to 25% of the total plutonium inventory ($^{239, 240, 241}$Pu) in Lake Wallula sediments, 100 km downstream, was believed to originate from the 1944 through 1971 releases at Hanford.[13] However, only ^{239} Pu was believed to actually reflect earlier reactor operations. Further, this ^{239}Pu was derived from ^{239}Np (produced by neutron capture in natural uranium followed by decay to ^{239}Np), an abundant isotope in Columbia River water. Thus, plutonium may not have been released to the river from reactor operations.

Fish and Wildlife

Fish are collected at various locations along the Columbia River, and boneless fillets are analyzed for ^{60}Co, ^{90}Sr and ^{137}Cs. Carcasses are analyzed to estimate ^{90}Sr in bone. Following shutdown of the last single-purpose, once-through cooling reactor and installation of improved liquid effluent control systems at N Reactor, short-lived radionuclides, including the biologically important ^{32}P and ^{65}Zn, essentially disappeared from the river[14] through radioactive decay. Radionuclide concentrations in fish collected from the Hanford Reach of the Columbia River are similar to those in fish from upstream locations.

Deer (*Odocoileus* sp.), ring-necked pheasants (*Phasianus colchicus*), mallard ducks (*Anas platyrhynchus*), Nuttall cottontail rabbits (*Sylvilagus nuttallii*) and black-tailed jack rabbits (*Lepus californicus*) are collected and tissues are analyzed for ^{60}Co and ^{137}Cs (muscle), $^{239, 240}$Pu (liver) and ^{90}Sr (bone). The doses that could be received by consuming wildlife at the maximum radionuclide concentrations measured between 1985 and 1988 were below applicable DOE standards.[1,2,5,7]

Soil and Vegetation

Airborne radionuclides are eventually deposited on vegetation or soil. Samples of surface soil and rangeland vegetation (sagebrush) are currently collected at 15 on-site and 23 site perimeter and off-site locations.[1] Samples are collected from nonagricultural, undisturbed sites so that natural deposition and buildup processes are represented. Sampling and analyses in 1985 through 1988 showed no radionuclide buildup off-site that could be attributed to Hanford operations.[1,2,5,7]

Foodstuffs

The most direct way for deposited radionuclides to enter the food-chain is through consumption of leafy vegetables. Samples of alfalfa and several foodstuffs, including milk, vegetables, fruit, beef, chickens, eggs and wheat, are collected from several locations, primarily down-wind (i.e., south and east) of the site.[1] Samples are also collected from upwind and somewhat distant locations to provide information on radiation levels attributable to worldwide fallout. Foodstuffs from the River-view Area (across the river and southeast) are irrigated with Columbia River water withdrawn downstream of the site. Although low levels of ³H, ⁹⁰Sr, ¹²⁹I and ¹³⁷Cs have been found in some foodstuffs, concentrations in samples collected near Hanford are similar to those in samples collected away from the site.

Penetrating Radiation

Penetrating radiation (primarily gamma-rays) is measured in the Hanford environs with thermoluminescent dosimeters to estimate dose rates from external radiation sources. Radiation surveys are routinely conducted at numerous on-site locations including roads, railroads and retired waste-disposal sites located outside of operating areas. On-site and off-site measurements and survey results from 1985 to 1988 were similar and comparable to past years. Dose rates near some operating facilities were only slightly higher than natural background rates.

Overall Impact from Hanford Operations

Beginning in 1974, the evaluation of radiation doses has included assessment of the maximum external dose rate at a location accessible to the general public, doses to a hypothetical maximally exposed individual and doses to the population within 80 km of the site. The calculated 50-year whole-body cumulative dose received by the maximally exposed individual ranged from 0.5 to 3 mrem during the years 1981 through 1986.[2] The maximally exposed individual is a hypothetical person who receives the maximum calculated radiation dose when worst case assumptions are used concerning location, inhalation of radioactive emissions, consumption of contaminated food and water and direct exposure to contaminants. Expressed as effective dose equivalents, the calculated dose received by a hypothetical maximally exposed individual was 0.05 to 0.1 mrem annually from 1985 through 1988. The average per capita effective dose for 1985 through 1988, based on the human population of 340,000 living within 80 km of the site, was 0.01 to 0.03 mrem annually.[1,2,5,7] Based on these assessments, potential radiation doses to the public from Hanford operations have been consistently below applicable standards and substantially less than doses from other routinely encountered sources of radiation, such as natural terrestrial and cosmic background radiation, medical treatment and x-rays, natural internal body radioactivity, worldwide fallout and consumer products (Fig. 2).

	Dose (mrem/yr)
U.S. Average Radon Dose	200
Natural External Background, Denver CO	140
Average Washington State External Background	88
Measured (TLD) Hanford Area External Background	78
U.S. Average Natural External Background	60
Average Per Capita U.S. Medical Dose	53
Average U.S. Internal Dose from Natural Radioactivity	40
Consumer Product Radiation (TV, Smoke Detector, etc.)	10
Global Weapons Fallout	<1
Average Per Capita Dose (Internal and External) from 1988 Hanford Operations	0.01

Figure 2
Annual Radiation Doses from Various Sources

CHEMICAL MONITORING

Air Quality

Nitrogen oxides (NO_x) are routinely released on-site from fossil-fueled steam and chemical processing facilities, most notably the PUREX plant. Nitrogen dioxide is currently sampled at seven on-site locations by the Hanford Environmental Health Foundation (HEHF). Nitrogen dioxide concentrations measured between 1984 and 1988 were well below federal (U.S. EPA) and local (Washington State) ambient air quality standards.[1,2,5,7]

Groundwater

In 1988, samples from 328 groundwater wells were collected and analyzed for chemical constituents. In addition, on-site drinking water sources (not public) were sampled and analyzed by HEHF for water quality. Detected constituents included several metals, anions, coliform bacteria, radionuclides and total organic carbon. Many of these constituents are expected in natural groundwater. Chromium, cyanide, fluoride and carbon tetrachloride were found in wells not used for drinking water near operating areas.

Columbia River

Nonradioactive waste water is discharged at seven locations along the Hanford reach of the Columbia River. Discharges consist of backwash from water intake screens, cooling water, water storage tank overflow, a building drain and fish laboratory wastewater. Effluents from each outfall are monitored by the operating contractors. The Columbia River also is monitored by the United States Geological Survey, upstream and downstream of the site, to verify compliance with Class A[18] water quality requirements.

Numerous studies have evaluated and resolved the potential environmental issues associated with water intake and thermal discharge structures on the Columbia River at Hanford. For example, retrofitting of the HGP water intake and a newer design for the intake used at WNP-2 have ensured safe downstream migration of juvenile chinook salmon.[19-22] Other studies have concluded that thermal discharges from N reactor and HGP to the Columbia River were biologically insignificant.[23,24]

HANFORD FLORA AND FAUNA

Most of the Hanford Site consists of undeveloped land that supports stands of native vegetation and a few exotic species (e.g., cheatgrass, *Bromus tectorum*; Russian thistle, *Salsola kali*; and tumble mustard, *Sisymbrium altissimum*) is free from agricultural practices and has been essentially free from livestock grazing and hunting for 45 years. Thus, the site serves as a refuge for migratory waterfowl, elk (*Cervus elaphus*), mule deer (*Odocoileus hemionus*), coyote (*Canis latrans*) and other plants and animals.[25] Restricted land use has favored native wildlife species that frequent riverine habitats, for example, mule deer, great basin Canada goose (*Branta canadensis*) and great blue heron (*Ardea herodias*).

The Columbia River at Hanford supports up to 48 species of fish[26] and serves as a migration route for upriver runs of chinook (*Oncorhynchus tshawytscha*), coho (*O. kisutch*) and sockeye (*O. nerka*) salmon and steelhead trout (*O. mykiss*, formerly *Salmo gairdneri*). The Hanford Reach supports the last remaining mainstem spawning habitat for fall chinook salmon. Steelhead trout also spawn in the Hanford Reach. The salmon population is maintained by a combination of natural spawning, artificial propagation and regulated commercial and sport harvest of returning adults.

Based on redd (nest) counts from the air, fall chinook salmon spawning in the Hanford Reach of the mainstem Columbia River has increased dramatically since 1980 (Fig. 3). Recent observations by divers[28] showed salmon redds at depths below those visible by boat or aircraft and suggests that salmon spawning in the Hanford Reach may be even greater than previously estimated.) The increase in salmon spawning has attracted increasing numbers of wintering bald eagles (*Haliaeetus leucocephalus*).
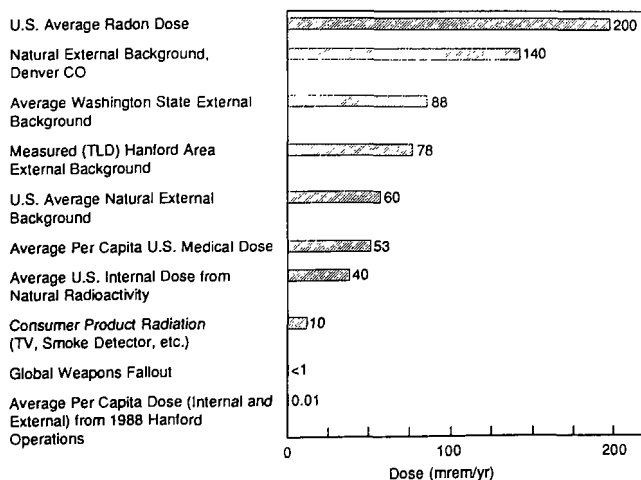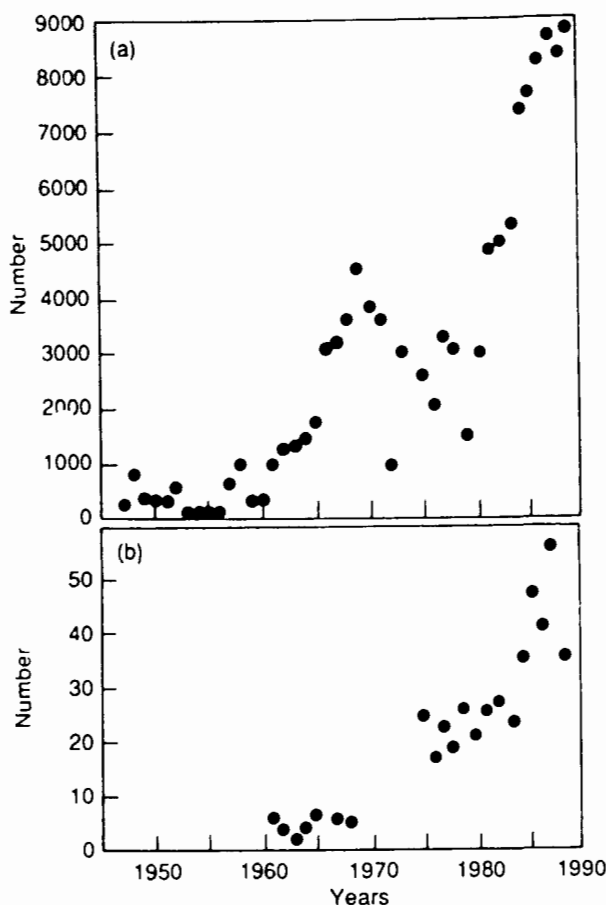
Figure 3
Numbers of (a) salmon redds (nests) and
(b) wintering bald eagles at Hanford

tions on the local environs, on-site workers and the off-site public. Monitoring for radiological emissions at Hanford has been ongoing for 45 years and includes air, surface and groundwater, fish, wildlife, soil, vegetation and foodstuffs. Measured and calculated radiation doses to the public have been consistently below applicable regulatory limits. The Hanford Site now serves as a refuge for key fish and wildlife species.
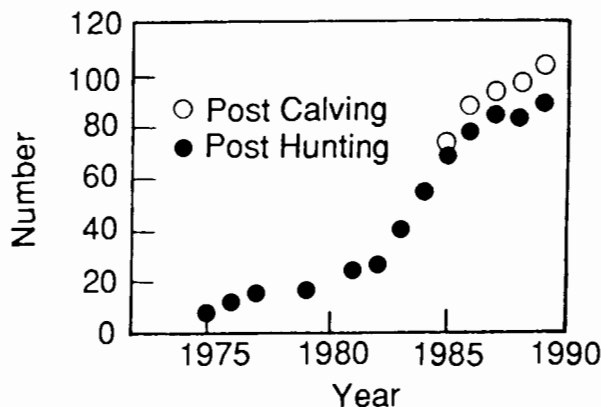
Figure 4
Numbers of Elk at Hanford After Calving
in Spring and Off-site Hunting in Fall

The sparsely vegetated islands in the Columbia River have historically been used as nesting habitat for great basin Canada goose.[29,30] From the mid-1950s to the mid-1970s the number of goose nests declined from a high of 250-300 to approximately 100 annually. From the late 1970s to the present, the number of nests has increased and appears to have stabilized at approximately 150-200. Initially, closure of the Hanford Reach was beneficial to the geese by providing freedom from human intrusion. However, the coyote, a natural goose predator, also benefitted and is believed to be the major cause of the decline in numbers of goose nests into the mid-1970s.

Initially there were no nesting great blue heron on the Hanford Site. However, there are now four active colonies consisting of approximately 35-40 or more birds each and herons are present year-round.[25] Elk first arrived on the Hanford Site in 1972.[31] From a small founding population, the herd size grew to approximately 80 animals in 1987 (Figure 4). The rapid increase in elk is attributed to the lack of predation or human disturbance during calving, absence of on-site hunting and the lack of competition from sheep and cattle for available forage. For the last four years, off-site hunting has limited further population increases by removing approximately 15 to 20 animals annually from the herd.

The mule deer population at Hanford is estimated at several hundred animals and appears stable even in the absence of on-site hunting. Coyote predation on fawns is believed to be an important factor that maintains the stable deer population.[32]

CONCLUSIONS

The Pacific Northwest Laboratory (PNL) conducts an environmental monitoring program to assess potential effects of Hanford Opera-

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Applications and Comparison of Soil Gas, Flux Chamber and Ambient Air Sampling Results to Support Risk Assessment at a Hazardous Waste Site

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ABSTRACT

Soil gas sampling, ambient air sampling and emission isolation flux chamber sampling are techniques used to evaluate organic vapor distributions at hazardous waste sites. This paper presents comparative results of tests on all three sampling methods used during characterization of a hazardous waste site. The site at which the monitoring took place is a residential housing tract constructed on abandoned pits and trenches containing heavy hydrocarbon and sulfuric acid sludge wastes. The waste material periodically seeps to the surface, posing a potential acute dermal, ingestion and inhalation threat. Various air sampling tasks were implemented to evaluate the acute and chronic health threats posed by airborne vapors and provide data to support a risk assessment.

Soil gas sampling was used to delineate the horizontal extent of the buried waste. Ambient air sampling using Tedlar bags and Tenax tubes was performed to determine if a release to the breathing zone was occurring. Results were not conclusive, but indicated that soil vapor concentrations were below Permissible Exposure Limits; ambient sampling results were ambiguous due to the detection of relatively high background concentrations of contaminants of concern.

A sampling strategy was employed during the remedial investigation, combining ambient sampling at the breathing zone with Tedlar bags and soil-air interface sampling with a co-located emission isolation flux chamber. Sampling stations were on and adjacent to emergent waste seeps. Indoor ambient sampling was conducted at the same time for comparative analyses. Data obtained were more conclusive; consistent detections were obtained from co-located bag and flux chamber samples, allowing for calculation of vapor flux rates. Benzene, toluene and xylene isomers were detected above California Department of Health Services Applied Action Levels. Relative contributions of contaminants from waste seeps compared with the soil column were defined, demonstrating the emergent seeps to be the source of potentially harmful concentrations. Taken together, the data indicate that vapor emissions from emergent waste seeps pose the greatest potential health threat.

Results obtained are critical for a risk assessment, which is essential for completing a feasibility study and remedial action plan for the site. Field activities, advantages and disadvantages of the sampling methods and applications to future remedial planning are discussed.

INTRODUCTION

This report describes analytical data obtained by various techniques for collecting soil gas and air samples. Samples were collected during a series of site evaluation projects conducted at a hazardous waste site in southern California. Four sampling techniques were employed:

- Soil gas sampling with subsurface probes
- Ambient air sampling with sorbent tubes
- Ambient air sampling with Tedlar bags

- Soil gas sampling at the soil-air interface with an emission isolation flux chamber (flux chamber).

Comparative results and applications to risk assessment are discussed. The experience gained from these studies is useful for developing sampling/analytical strategies for remedial investigations and risk assessment projects.

Site Description

Westminster Tract No. 2633 is located in the city of Westminster in northern Orange County, approximately 35 miles south of downtown Los Angeles, CA (Fig. 1). The site is in a residential neighborhood surrounded by industrial and commercial areas. The surface of the tract is either paved, vegetated or occupied by buildings (Fig. 2). Isolated areas of vegetation appear to be stressed or neglected.

Prior to development, portions of the site were used for disposal of refinery wastes and drilling muds. The waste material is primarily polycyclic aromatic hydrocarbons (PAHs) and sulfuric acid sludge. The waste has a distinct odor, attributable to sulfur compounds and mercaptans. Waste is less dense than surrounding soil matrix and becomes plastic and mobile at ambient temperatures greater than 80 °F. During warm weather, waste migrates upward in tabular veins and necks, emerging and spreading at the surface. These surface seeps present a potential acute health threat due to organic vapors generated and direct contact with the acidic waste. The buried waste also presents a potential chronic health threat due to emissions of organic vapors through the soil column.

In the late 1950s, the site was purchased by a real estate company for residential development. During the construction of Tract No. 2633 in the late 1950s and early 1960s, tar pits were discovered. The Regional Water Pollution Control Board (now the Regional Water Quality Control Board) stipulated that waste could be left on-site if it were isolated from groundwater, but warned that problems might result if the waste remained in place. Waste was to be redisposed in trenches and covered with concrete. No evidence of a concrete cap has ever been found in the course of field investigations; the waste may have reacted with and dissolved any concrete, or the cap was never placed.

Homeowners have reported problems with differential settling of foundations and fences, difficulty growing gardens, odors and waste seeps in yards, swimming pools and, in one case, under the living room carpet (the waste had migrated through the concrete foundation). Homes at the site do not have basements or extensive crawl spaces.

The original disposal areas were identified through analysis of historical aerial photographs. Five separate areas were identified, with a total surface area of approximately 68,972 ft² (1.58 acres). The present extent of waste has been determined through an intensive drilling investigation; sample locations are depicted in Figure 2. Both the original

Figure 1
Regional Site Map; Westminster Tract No. 2633
Westminster, California
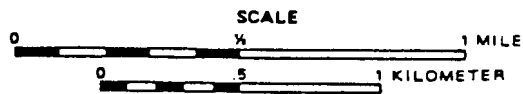
pits and the redisposal trenches are potential sources of organic vapors.

Figure 2 shows the locations of the streets, parcels and approximate locations of the trenches. No other waste disposal areas are known to exist, based on site investigation work, historical reports and historical aerial photographs. Waste material may be present beneath some houses in the tract, but investigations to date have not evaluated the subsurface beneath homes.
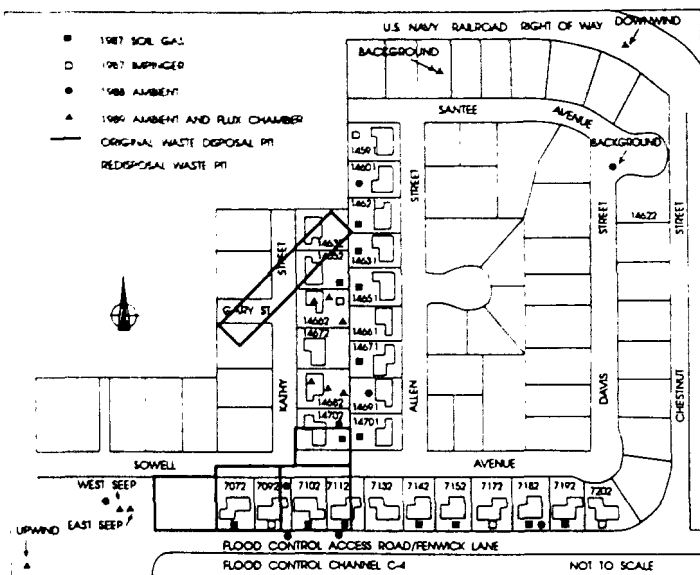
Figure 2
Westminster Site Location Map; Air Sampling Locations

Site Investigations

Several investigations of potential environmental and health problems at the site were performed by local, state and federal agencies, as well as independent parties. The key investigations and their principal objectives discussed in this report are:

- The preliminary site investigation conducted by E & E under contract to DOHS in 1987, was designed to evaluate the need for further investigation and possible remedial action[1]
- The Listing Site Inspection (LSI) performed by the U.S. EPA Region IX field investigation team (FIT) in 1988 was designed to develop a Hazard Ranking System score for potential inclusion on the NPL[2]
- The Phase I remedial investigation (RI) conducted by E & E under contract to DOHS in 1989 was designed to determine the extent of contamination and provide data for a feasibility study and risk assessment[3]

Project tasks have included:

- Review of historical data from regulatory agencies
- Aerial photographic analyses
- Geophysical surveys
- Surface soil, water and waste sampling
- Subsurface soil and groundwater sampling
- Real-time air monitoring during drilling and sampling activities with Hnu, OVA, H₂S monitors, SO₂ monitors, dust meters)
- Soil gas sampling
- Ambient air sampling with Tedlar bags and Tenax tubes
- Flux chamber sampling

Since 1987, DOHS has also implemented annual excavation and removal of waste seeps to prevent exposure to residents. This annual removal project has served as an interim remedial measure until the RI/FS is completed and full-scale remediation proceeds. The California Department of Health Services (DOHS) currently is preparing a risk assessment for purposes of completing the FS. The site eventually may be proposed for NPL listing.

AIR INVESTIGATIONS

E & E/DOHS—1987

The DOHS tasked E & E to conduct a site investigation to describe the source and extent of contamination at the site and identify any potential migration pathways.[1]

Soil gas sampling was conducted at 20 sample locations (Fig. 2) to identify the types of volatile contaminants present and the extent of their possible release. Samples were collected by driving perforated pipe to a depth of 5 feet, then retracting the pipe a few inches; samples were then collected in Tedlar bags.

Four groups of compounds were analyzed: halogenated organics, aromatics, aliphatics and hydrogen sulfide (H₂S). Analytical results are presented in Table 1. H₂S was tentatively identified in four of the Tedlar bag samples. Independent real-time monitoring with H₂S-specific devices during soil sampling suggested no H₂S was present in the free atmosphere. Therefore, additional samples were collected with zinc acetate impingers to confirm the H₂S detections. H₂S was not detected in the impinger samples, leading to the conclusion that previous H₂S detections were false positives caused by a reaction with the Tedlar bag material.

The survey was unsuccessful in defining the boundaries of the redisposal trenches because soil gas was detected in all locations sampled. Real-time air monitoring in two residential homes revealed OVA readings slightly above the background level, but the concentrations were not considered significant. Sulfur dioxide and hydrogen sulfide were not detected in the survey.

Table 1
Summary of SCR Soil Gas Results, Westminster Tract #2633, 1987

Compound	Maximum Concentration (ppm)	ACGIH TLV (1) (ppm)	10% of ACGIH TLV
Halogenated Organics:			
Carbon Tetrachloride	0.011	5	0.5
Chloroform	0.0042	10	1
1,2-Dichloroethane	0.012	10	1
1,2-Dichloroethylene	0.027	200	20
Dichloromethane	0.014	50	5
Perchloroethylene	0.004	50	5
1,1,1-Trichloroethane	0.02	350	35
Trichloroethylene	11	50	5
1,1,2-Trichloro-1,2,2-Triflouroethane	0.042	1000	100
Aromatics:			
Benzene	0.34	1.0	0.1
Ethylbenzene	0.3	100	10
Toluene	1.8	100	10
Xylenes (mixed)	0.68	100	10
Aliphatic Carbons:			
One to Four Carbons	6.8	800*	80
Five Carbons	0.8	600**	60
Six Carbons	0.42	50;500**	5;50
Seven Carbons	1.6	400+	40
Eight Carbons	1.4	300	30
Hydrogen Sulfide:			
Tedlar Bag	128	10	1
Impinger	ND	10	1

* TLV for Butane. Other C1-C4 compounds to be simple asphyxiants without a TLV.
** TLV for n-Pentane.
* TLV of 50 ppm for n-Hexane; TLV of 500 for other isomers.
+ TLV for n-Heptane.
++ TLV for n-Octane. (1) Limits for Benzene changed in 1989 from 10.0 to 1.0

U.S. EPA-FIT—1988

During March and April 1988, the U.S. EPA Field Investigation Team (FIT) collected air, surface water, groundwater, soil and soil/waste and sediment samples. The purpose of this investigation was to collect data necessary to support a Hazard Ranking System (HRS) score for poten-

tial NPL listing.[2] Target compounds for the air samples were essentially the same as for the soil gas survey.

Air samples were collected from the breathing zone (4-6 ft above ground surface). Two rounds of sampling were conducted, using sorbent tubes and Tedlar bags in Round 1 and sorbent tubes only in Round 2. Because of the previous false detections of H_2S with Tedlar bags, sorbent tubes were utilized to provide analytical redundancy. Bag samples were collected by using a negative pressure/passive inflation technique, similar to that described in *Air Resources Board Procedure for Atmospheric Tedlar Bag Sampling, Appendix A, Method 201*. Tube samples were collected by drawing air through a Tenax tube connected with Tygon tubing to a personal air sampling pump.

Air sampling locations are shown in Figure 2. The sample locations were selected to discriminate between air contamination arising from the on-site waste and that coming from an industrial area south of the site.

Analytical results for the tube samples are presented in Table 2. The Tedlar bag samples were judged to be inconclusive due to contamination of field blank samples; the cause of this problem has not been diagnosed. Although valid analytical results were obtained from the Tenax tube samples, the results still did not conclusively demonstrate the release of vapors into the atmosphere from the wastes. Background and upwind samples detected levels of contaminants comparable to those detected at on-site sample stations.

Table 2
U.S. EPA - FIT Air Sampling Results (ppb)

Round 1 Compound	14601 Allen St.	14622 Davis St. BG	14702 Kathy St.	7182 Sowell Ave.	MW-3 BG
Benzene	15 UJ	10 UJ	40 UJ	15 UJ	20 J
Ethylbenzene	ND	ND	ND	ND	ND
Xylene (M/P)	ND	ND	ND	5 UJ	15 J
Xylene (0)	ND	ND	ND	ND	ND
Methylbenzene	ND	ND	ND	ND	10 J
PCE	40 UJ	ND	ND	20 UJ	20 J

Round 2 Compound	14622 Davis St. BG	14691 Allen St.	7092 Sowell Ave.	MW-3 BG	Parking Lot Golden West St. BG
Benzene	8J	5 UJ	10 UJ	15 J	10 J
Ethylbenzene	ND	1 UJ	ND	5 J	1 J
Xylene (M/P)	ND	5 UJ	5 UJ	2 J	10 J
Xylene (0)	ND	ND	1 UJ	3 J	2 J
Methylbenzene	5J	5 UJ	5 UJ	5 J	10 J
PCE	5J	10 UJ	5 UJ	5 J	5 J

Notes:

ND=Not detected. BG=Background. J=Estimate. UJ=Not detected above the value listed

Analysis by: Paul H. Johnson, FIT E & E May 3, 1988 (Source: EPA-Field Investigation Team, 1988)

E & E/DOHS RI—1989

The original RI/FS workplan proposed ambient air sampling utilizing absorbent tubes (Tenax or charcoal) and impingers. Based on inconclusive results from U.S. EPA-FIT air sampling, DOHS requested consideration of other alternatives to this approach be considered.[3]

DOHS proposed an air sampling program different from that proposed in the RI/FS workplan. The revised program comprised indoor air sampling, ambient air sampling (breathing zone), flux chamber sampling, real-time air monitoring (following protocols established in the Health and Safety plan), review of historical meteorological conditions and collection of meteorological data with an on-site meteorological monitoring and data collection station (the "met station").

Sampling with Tedlar bags and air sampling at the soil surface using a flux chamber were the preferred alternatives for obtaining data to be applied to a quantitative risk assessment. Bag samples were collected by negative pressure/passive inflation (California Air Resources Board, Method 201). The flux chamber device is designed to collect air at the soil/air interface and hold the sample in a Tedlar bag until analyzed; the procedure is discussed in more detail below. A diagram of the flux chamber device is shown in Figure 3.
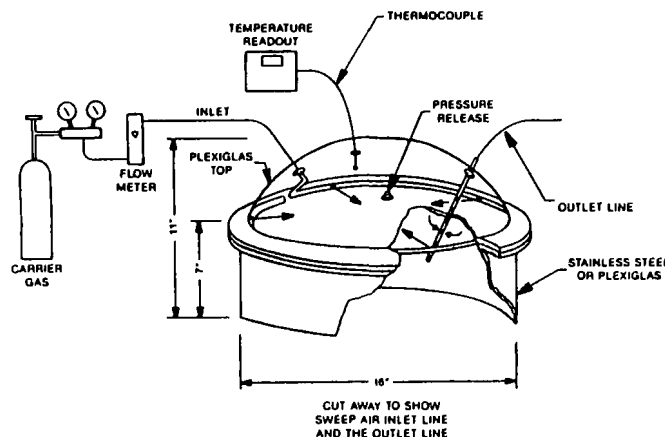
Figure 3
A Cutaway Diagram of the Emission Isolation Flux Chamber

A review of 1987 and 1988 sampling data resulted in a revised list of target compounds. The contaminants of concern are mainly volatile organic compounds: benzene, toluene, xylene isomers (ortho/meta/para), ethylbenzene, cyclopentane, cyclohexane, methylcyclohexane and tetrahydrothiophene. All air samples (indoor, flux chamber and ambient air; described below) were analyzed for these compounds.

Thirty samples were collected during two rounds of sampling, which included ambient indoor and outdoor air samples (Tedlar bag) and outdoor flux chamber sampling. The on-site sampling stations (indoors and backyards at 14662 and 14682 Kathy Street) were specified due to the past or current presence of waste seeps at these homes. Seeps had recently been removed from the 14662 Kathy Street yard; two seeps were present in the 14682 Kathy Street yard. An additional sampling station on Santee Avenue was used as a control (background) for the flux chamber measurements. The upwind and downwind locations were selected based on historical prevailing wind conditions (generally from the southwest). Air sampling stations (indoor, flux chamber and ambient air) are shown in Figure 2.

Air sampling results obtained in the RI are presented in Table 3. Calculated emission rates from the flux chamber sampling are presented in Table 4.

Table 3
Flux Chamber and Ambient Air Sampling Results, July 1989
Rounds 1 and 2 (ppb)

Compound	14662 Kathy				14662 Kathy/Tedlar Bag			
	Indoor (Bag)	Flux #1 Blank	Flux #2 Grass	Flux #3 Mound	Upwind	Indoor	Backyard	Duplicate
Benzene	26	< 2	< 2	< 2	18	16	33	37
Ethylbenzene	20	< 2	< 2	< 2	6.6	3	79	62
Toluene	19	3.7	< 2	5.6	21	49	35	50
Xylene (M/P)	110	< 10	< 10	< 10	89	150	410	380
Xylene (0)	40	< 5	< 5	< 5	33	< 5	130	200
Cyclopentane	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Cyclohexane	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Methylcyclohexane	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Compound	14682 Kathy/Flux Chamber				7151 Santee/Flux Chamber	
	Flux #4 Blank	Flux #5 Ground	Flux #6 Seep	Flux #7 Seep	Flux #8 Blank	Flux #9 Grass
Benzene	< 2	< 2	3700	4000	< 2	< 2
Ethylbenzene	< 3	< 3	280	330	< 3	< 3
Toluene	11	11	8700	8200	< 2	< 2
Xylene (M/P)	< 10	< 10	3700	3600	< 10	< 10
Xylene (0)	8.1	< 5	890	440	< 5	< 5
Cyclopentane	< 20	< 20	1300	1400	< 20	< 20
Cyclohexane	< 5	< 5	410	340	< 5	14
Methylcyclohexane	< 5	< 5	600	390	< 5	< 5

Compound	Day 1				Day 2				Day 3			
	Upwind	West Seep	East Seep	Downwind	Upwind	West Seep	East Seep	Downwind	Upwind	West Seep	East Seep	Downwind
Benzene	4.2	3.2	4.0	3.8	2.5	2.1	2.2	2.0	< 2	< 2	< 2	< 2

Table 4
Calculated Emission Rates
(ug/min. • m²)

Compound	Flux #6	Flux #7	Relative Percent Difference
Benzene	354	393	10.44
Toluene	1009	719	33.56
Xylene (M/P)	494	481	2.67
Xylene (O)	119	59	67.42
Ethylbenzene	37	44	17.28
Cyclopentane	115	124	7.53
Cyclohexane	43	36	17.72
Methylcyclohexane	74	48	42.67

Indoor Air Monitoring and Sampling

Indoor real-time air monitoring and ambient air sampling were conducted at the two homes to determine if VOCs were present at hazardous levels and to compare these results with flux chamber and ambient air samples collected in the backyards. Two types of in-home monitoring were performed at the residences: real-time monitoring with portable field screening instruments (OVA, Hnu and SO₂ monitor) and ambient air sampling with Tedlar bags, using the same procedure as for outdoor ambient air sampling.

Prior to monitoring and sampling, a preliminary survey was initiated to document the floorplan of the house and to evaluate the potential emission sources for volatile organic compounds. The survey identified the following sources in each home that could contribute to in-home air contaminants: gas wall heaters, gas stoves and gas hot water heaters; solvents and miscellaneous chemicals in garages; and cleaning fluids below baths and kitchen sinks. The floorplans of the two homes were nearly identical.

The results suggest that the presence of these compounds may be due to in-home sources mentioned above or may be the result of outdoor air which has filtered into the houses. The BTEX compounds in indoor air samples could come from automobile exhaust emissions on nearby roads and freeways and from other industrial sources.

Flux Chamber Sampling

A flux chamber was used to determine the rates of emission for several volatile compounds from the backyards of three homes at the site (the Kathy Street residences and a background residence on Santee Avenue on the northern side of the site). The flux chamber offers several advantages over other ambient air monitoring methods for detecting and measuring emissions. Operating procedures are described in *Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber User's Guide* which has been used by the U.S. EPA⁶. The flux chamber allows direct measurement of emissions from the ground surface or waste material. It was determined that flux chamber would provide the most reliable source of data to be used in a risk assessment.

Samples were collected from five separate stations: the designated background location on Santee Avenue, one lawn area where no seeps were present (14662 Kathy Street), one location where seeps had been removed earlier (14662 Kathy Street), one location on bare ground adjacent to a seep (14682 Kathy Street) and one location on top of a

seep (14682 Kathy Street). A duplicate sample was collected from over the large seep at 14682 Kathy Street. The duplicate was obtained by splicing a "tee" fitting onto the sample line inside the chamber containing a pair of Tedlar bags, allowing the simultaneous collection of duplicate samples.

Samples were collected by connecting a Tedlar bag to the sampling line from the flux chamber and filling the bag by the negative pressure/passive inflation method. Prior to sample collection, the flux chamber was purged using ultra high purity nitrogen. System blanks were collected after purging by placing a glass plate between the flux chamber and bare ground and following the normal collection procedure. The purge and sampling cycle was then repeated with the glass plate removed. Ambient temperatures (inside and outside the flux chamber) were monitored during sample collection. Exit gas concentrations were measured using a Hnu; use of the Hnu was discontinued due to a battery problem. Background and system blank samples provided QA/QC checks.

The flowrate into the flux chamber was set at 4 L/min. The residence time in the chamber was 7.5 minutes. Sampling started after purging the flux chamber for a minimum of four residence times (30 minutes or greater). The flowrate into the Tedlar bag from the flux chamber was 1.2 L/min with a sampling period of 8 minutes. Multiple point calibration on the flux chamber sampling train was performed prior to field sampling. Single point calibration was performed in the field prior to and following daily sampling events.

Flux Chamber Sampling Results

The analytical results for the flux chamber samples are presented in Table 3. Table 4 summarizes the emission rates for each chemical of interest for flux chamber Samples 6 and 7, which were calculated using Equation 2-1 from the *User's Guide:*

$$E_i = Y_i Q/A \tag{1}$$

where: E_i = emission rate of component i (mass/area-time)
Y_i = concentration of component i in the N₂ flowing from the chamber (mass/volume)
Q = flow rate of N₂ into the chamber (volume/time)
A = surface area enclosed by the chamber (0.130 m²)

The laboratory results reported concentrations for each chemical species of interest in ppb by volume. In order to perform the necessary emission rate calculation, ppb by volume must be converted into μg/L using the following equation:

$$\mu g/L = [ppb] (4.09 \times 10^{-2} (\mu g \; mol)/(g \; m^3)) (Mwt) (m3/1000 \; L) \tag{2}$$

No emission rates for tetrahydrothiophene were calculated since it was not found above detection limits in any of the samples. The two duplicate samples (6 and 7) collected over the waste seep at 14682 Kathy Street were the only samples with emissions of the high concentration. Toluene was detected in four of the samples, while o-xylene and cyclohexane were each found in one sample. The detection of toluene in two of the three system blanks (flux Samples 1 and 4) and o-xylene in Sample 4 are anomalous. These findings could possibly be from laboratory contamination or incomplete purging of the flux chamber system. The system blank collected at 7151 Santee Avenue did not contain any contaminant above detection limits, nor did flux Sample 2 which was collected over grass immediately after the system blank at 14622 Kathy Street.

The results of this sampling effort indicate that small amounts of certain volatile compounds may be released through lawn or dirt areas into the backyard atmosphere. But these releases are negligible compared with the amount of volatile compounds released from waste material which has seeped to the surface.

Ambient Air (Outdoor) Sampling with Tedlar Bags

Ambient air samples were collected from the breathing zone at locations near the flux chamber sample stations in the backyard at 14682 Kathy Street and in upwind and downwind locations chosen in accor-

dance with the prevailing wind direction (Fig. 2). Flux chamber samples were collected from the backyard at 14662 Kathy Street, as discussed above; no waste seeps were emergent in this yard during the July 1989 sampling and therefore no ambient air samples were collected at that location.

Two rounds of ambient air sampling with bags were conducted: Round 1 in July 1989 (concurrent with flux chamber sampling) and Round 2 in August 1989. A malfunction with the met station had occurred during Round 1 sampling; therefore, an additional round of samples was collected concurrent with operation of a new met station.

The same ambient air sampling procedures were used, but Round 2 samples were collected using lower flow rates and at different on-site locations. (Seeps at the 14682 Kathy Street residence had been removed; fresh seeps had appeared in a vacant lot at the southwest corner of the site). Therefore, field and duplicate samples also were collected during Round 2.

In Round 2, a laboratory blank and daily trip blanks were analyzed for QA/QC purposes. The laboratory blanks were prepared using new Tedlar bags. Trip blanks were prepared by the laboratory on a daily basis and carried to and from the field to determine if cross-contamination occurred during transport. No contaminants of concern were detected in any of the blank samples above the method detection limits. The analytical results are presented in Table 3.

Round 1 Results

The results obtained from the outdoor ambient samples are consistent with those of the flux chamber samples for BTEX compounds, but are lower in concentration. Cyclopentane, cyclohexane, methylcyclohexane and tetrahydrothiophene were not measured above the method detection limits in the Round I ambient air samples.

At the 14682 Kathy Street location, BTEX compounds were detected in both field and duplicate samples, as well as the upwind station. (The sampling pump at the downwind station was stolen approximately 20 minutes after initiation of sampling; therefore no results were obtained).

The analytical results from the flux chamber and outdoor ambient air samples suggest that the observed airborne contamination originates primarily from seeps. This conclusion is supported by comparison of the results of the indoor sampling versus the flux chamber samples collected over the waste seeps. Indoor and off-site sources, such as gas heaters and automobile exhaust, are other possible contributors. The variations in concentrations detected probably are due in part to the differing nature of the sampling devices: the flux chamber captures vapors at the soil/air interface, while the ambient samples are subject to dilution by mixing, diffusion or dispersion during transport from the seep to the sample intake.

Round 2 Results

The analytical results of the Round 2 samples were less definitive than Round 1. In general, concentrations at field stations were comparable to upwind and downwind locations.

Quantified concentrations were lower than for Round 1 sampling. This finding may be an artifact of the lower flow rates used for sample collection. A lower flow rate allows for longer sample collection time, but also allows for dispersion and diffusion to take place at a faster rate relative to the sample collection rate. Other factors could have contributed to lower concentrations, notably the smaller size of seeps over which samples were collected. Also, the seep locations on the southwest side of the site (vacant lot) were exposed to the wind to a greater degree than those seeps investigated in Round 1 (located in walled back yards).

Round 2 samples did confirm the prior detections of benzene, toluene, ethylbenzene, cyclopentane and cyclohexane. Cyclopentane was not confirmed by the duplicate field station. Cyclohexane was detected in only the downwind sample at 9 ppb on the final day of sampling. While cyclohexane was detected in flux chamber samples collected over seeps in Round I, it is possible that the Round 2 detection could have originated from an off-site source. Methylcyclohexane was detected only in one sample at 14 ppb, at the upwind station. This compound was also detected in flux chamber samples collected over seeps in Round 1;

however, the Round 2 detection suggests an additional off-site source.

Results from the Round 2 sampling are not as definitive as Round 1. Round 2 sample results suggest that off-site sources are contributing to the observed airborne contamination. The generally lower concentrations detected suggest that source concentrations were lower, or that more dilution in the free atmosphere was taking place. The seeps at 14682 Kathy Street had been removed between Rounds 1 and 2 and the seeps in the vacant lot were much smaller than those at 14682 Kathy Street. Also, the seep stations in the vacant lot were not shielded from the wind as much as samples in Round 1, allowing for greater dilution in the atmosphere between the seep surface and the intake line.

A summary of all soil gas and air sampling data is presented in Table 5. This table compares the common compounds detected in the investigations with established DOHS Applied Action Levels.

Table 5
Comparison of Detections by Different Methods (ppb)

Compound	Flux Chamber	Tedlar Bag	Tenax Tube	Soil Gas	DOHS Applied Action Level
Benzene	4000	37	40	340	1.0
Ethylbenzene	330	79	5	300	32.3
Toluene	8700	50	nd	1800	53.3
Xylene (M/P)	3700	410	15	680	23.1
Xylene (O)	890	200	3	na	--
Cyclopentane	1400	200	nd	nd	--
Aliphatic/C5	na	na	nd	800	--
Cyclohexane	410	9	nd	nd	--
Aliphatic/C6	na	na	nd	420	--
Methylcyclohexane	600	14	nd	nd	--
Tetrachloroethylene	na	na	40	4	--
Methylbenzene	na	na	10	nd	--

Notes:
(1) Flux Chamber detections are all from seep at 14682 Kathy Street
(2) Tedlar bag samples -- cyclopentane not confirmed by duplicate; cyclohexane detected at downwind station only; methylcyclohexane detected at upwind station
(3) Tenax Tubes -- ethylbenzene and xylene detections at station just upwind of known Waste area
(4) Soil Gas originally reported in ppm; aliphatic C5 and C6 shown for qualitative comparison with cyclopentane and cyclohexane
(5) Maximum detections recorded in various surveys
(6) na = not analyzed
(7) nd   not detected

APPLICATIONS TO RISK ASSESSMENT

Three different categories of risk evaluation may be used during hazardous waste site investigation and remedial planning. Qualitative risk assessment answers the question of whether a site is sufficiently contaminated to warrant further investigation (e.g., do preliminary data indicate potential health/environmental threats). Semiquantitative risk assessment compares relative risk of a site as determined by a standardized model (e.g., the Hazard Ranking System/HRS). Quantitative risk assessment is a more intensive evaluation for establishing site-specific cleanup standards; a variety of approaches may be used. For the Westminster site evaluation, all three levels of assessment were applied.

Qualitative Assessment

During the 1987 investigation, soil gas data were compared to ACGIH Threshold Limit values (TLV) for preliminary evaluation. To be conservative, 10% of the TLV value was established as the level of concern. Contaminants detected by the soil gas survey during the SI were all well below this action level at that time.

Preliminary data indicated that residents were not endangered due to soil vapors. However, the recommended TLV for benzene was revised downward in 1989 to 10% of the prior value. Therefore, under the current permissible exposure limit (PEL) criteria, potential exposure to benzene is a concern warranting further evaluation in the risk assessment. In retrospect, the soil gas data were acceptable for a preliminary qualitative assessment. However, these data are deceptive because at the time of the 1987 site investigation the potential health threat posed by soil vapors could not be conclusively determined. The preliminary conclusion was that the soil vapor was not a major cause for concern.

For qualitative assessment, any of the air sampling and monitoring methods discussed herein could be applied.

Semi-Quantitative Assessment

The HRS utilized in the Superfund program is a commonly used method of semiquantitative risk assessment. The original HRS requires that exposure to receptors via the air pathway be verified by sampling data which demonstrate that an airborne release is occurring or has occurred. The revised draft HRS allows potential air releases to be a component of the total score. (The revised draft HRS has not been implemented yet for NPL listings).

The LSI (U.S. EPA-FIT) was conducted to determine if the Westminster site could be eligible for inclusion on the NPL. The low HRS score (less than the 28.5 required to propose for inclusion on the NPL) was due to the lack of a demonstrated release of hazardous materials to the atmosphere or drinking water aquifers beneath the site.[2] Tenax tube sampling data obtained by U.S. EPA-FIT did not pass the rigorous QA/QC criteria for NPL listing.

Ambient air sampling data obtained during the RI could be applied to either version of HRS. Rescoring the Westminster site could be performed using these more recent air sampling data.

Under the original HRS, soil gas data were unacceptable for air pathway scoring, but could be applied to the revised HRS to show potential air releases. Ambient sampling data of the breathing zone with sorbent tubes or Tedlar bags are applicable to either version of the HRS. Flux chamber sampling would not be acceptable under the original HRS as it does not sample the breathing zone, but it is applicable to revised HRS as it shows release to the free atmosphere.

Quantitative Risk Assessment

Quantitative risk assessments are necessary to establish cleanup standards and select remedial action alternatives. A complete risk assessment includes an exposure assessment, which requires analytical or numerical modeling based on field sampling data.

The combined flux chamber and ambient sampling with Tedlar bags provided the critical quantitative data necessary to proceed with the risk assessment. The flux chamber samples provided the data to calculate emission rates at the soil-air interface which, in turn, are used for downwind exposure modeling. Results from ambient air sampling at co-located stations provide the information to evaluate the effects of diffusion and dispersion during airborne transport.

The risk assessment for the Westminster site currently is being conducted by DOHS.

CONCLUSIONS

Soil gas sampling is acceptable for preliminary site investigations, but in this case was inconclusive and did not provide usable data for risk assessment. Concentrations detected suggested that there was no cause for concern with the exception of benzene because of the recent change in TLV.

Ambient air sampling with Tenax tubes was inconclusive in this case, due to high background concentrations detected. Tenax analyses are inherently more difficult to interpret due to more complicated analytical methods (e.g., desorption, runs with standards, etc). If only one or two target compounds are to be monitored, Tenax may be a preferred method. Also, theoretical detection limits are lower with adsorbent tubes since the detection limit is proportional to the volume of air passing through the tube.

Ambient air sampling with Tedlar bags is probably more reliable due to simpler analytical procedures (vapor in the bag is essentially run directly to GC). The method may be prone to false detections; hydrogen sulfide in particular was deemed to result in erroneous measurements on the soil gas program.

Flux chamber sampling is an elegant combination of the soil gas and ambient air methods; bags or sorbent tubes can be used for sample collection and retention. Flux chamber data allow one to calculate actual emission rates at the soil-air interface. If only one method can be used, this technique should be strongly considered.

The combination of flux chamber and co-located ambient sampling with Tedlar bags proved to be the most conclusive approach. Emission rates were calculated for flux chamber data; ambient sampling data confirmed that key compounds of concern were migrating into the breathing zone. This combined method approach provided critical data for the risk assessment necessary to continue with regulatory action on the site.

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Development of Innovative Penetrometer Systems for the Detection and Delineation of Contaminated Groundwater and Soil

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ABSTRACT

Modern penetrometers typically employed in foundation investigations provide the basis for a rapid, economical system for investigating hazardous waste sites. The major changes needed to produce a useful tool for waste site work include: development of hardware that can be easily decontaminated, development of a grouting system that can seal the holes that are produced by the penetrometer, production of sensor and sampler systems for detecting the presence of contaminants of interest and integration of the components into a site characterization system. This paper discusses the progress that has been made in developing such a penetrometer system.

INTRODUCTION

Cone penetrometers were originally designed to assess soil strength properties for railroad grades and unpaved roadways. Typical penetrometer equipment consists of a standard instrumented rod (35 mm in diameter) tipped with a 60° cone. The rod is driven into the soil using hydraulic rams at a standard rate of 2 cm/sec. The reaction force for the rams usually is provided by earth anchors or a large mass (such as a 20-ton truck). The penetrometer equipment generally is mounted on skids if earth anchors are used or on a heavy-duty truck equipped with all-wheel drive if a reaction mass is used (Fig. 1).

Soil strength is determined by measuring the resistance developed on the cone tip and on a fixed area of the rod behind the tip (referred to as the sleeve). The tip resistance and sleeve friction vary with the grain size of the soil and the degree of compaction or cementation. The cone resistance and sleeve friction measurements when combined can be used to determine the type of soil penetrated as the rod is advanced.[1,5]

In addition to its role in determining the strength properties and character of the soil under a site, the penetrometer is now being recognized as a simple, rapid method of introducing a variety of sensors and samplers into the soil. The penetrometer generally can be used to push to a depth of up to 50m in normally compacted soil. Penetrometers are becoming increasingly popular for use in hazardous waste site (HWS) investigations because they combine speed and versatility with a degree of safety that is not available in conventional drill-and-sample operations.[3] The purpose of this paper is to show how the basic penetrometer can be combined with sensors to produce a site characterization system for use in investigating toxic and hazardous waste sites.

SOIL CHARACTERIZATION

Penetrometers have become very popular as a method of investigating soil conditions, and the basis for a soil contamination investigation system is present in a modern penetrometer unit. The soil strength measurement systems have been linked to a computer and to real-time data displays so that soil characteristics can be displayed for the operator as the penetrometer rod advances. For example, in a typical foundation investigation, the operator can watch the real-time display of the tip resistance and sleeve friction as the penetrometer moves through the soil. Computer programs have been developed that work out the type of soil encountered from the strength properties measured by the rod and cone and display the probable soil type directly.

Figure 1

A penetrometer unit in operation in the field. The expanded cupola on top of the enclosure allows the rods to extend through the roof. During a push, the unit is supported on jacks as shown to use the entire weight of the truck for reaction.

HAZARDOUS WASTE SITE INVESTIGATIONS

HWS investigations can build on the basic soil investigation capabilities of the penetrometer equipment. In conventional foundation work there typically was no requirement for sealing the penetrometer holes produced during operation. On an HWS, a grouting system must be used to seal the holes as a guarantee that the penetrometer holes will not prolvide conduits for the movement of toxic material on the investigation site. Conventional grouting systems used for servicing well drilling operations

can be adapted for use with penetrometers. Some penetrometers are now equipped with grouting systems that pump grout through the push rod to seal the hole as the rod is withdrawn.

The penetrometer operations usually are run from inside a heated and air-conditioned, truck-mounted enclosure. The truck body makes a useful shelter for the computer equipment needed to make a fully-integrated HWS characterization system. The enclosure can be divided into separate areas equipped with controlled and filtered ventilation systems to house the "clean" computer area and the "dirty" rod-handling area. A decontamination system can be provided for cleaning the rods and the "dirty" part of the enclosure containing the hydraulic rams and rod handling and sampling equipment (Fig. 2).

The major adaptation to a penetrometer system involved in HWS work relate to sensors and samplers furnished with the penetrometer. The sensors and samplers must be suited to the type and level of contaminant being considered.

Figure 2
Interior of the rod-handling compartment in a truck equipped for HWS investigations. Note the walls and floor are surfaced with stainless steel. The unit is equipped with floor drains and a waste-containment tank so that the area can be decontaminated.

PENETROMETER SENSORS/SAMPLERS

Penetrometers developed for foundation investigations have instrumentation designed to measure soil strength and soil pore pressure. Sensors are now available for measurement of electrical conductivity of soil, natural radioactivity and soil optical properties (fluorescence and reflectance).

The electrical conductivity sensor usually takes the form of a series of metal bands separated by ceramic or epoxy insulators mounted on the penetrometer rod. The unit is analogous to an electric logging sonde, but with close contact to the soil and short electrode array, conductivity changes in the soil can be located to within a few centimeters. Conductivity sensors have been successfully used in locating closed evaporation ponds and in delineating the plume of contaminated (high conductivity) water associated with abandoned landfills.[3,4]

The cone developed for detecting radioactivity is analogous to the well logging tools used for measuring natural gamma activity. A miniaturized downhole scintillation counter can locate both natural radioactivity (such as that associated with weathered organic shales) and manmade radioactivity from mine tailings or other radioactive wastes.

The optical sensor for the cone penetrometer is a new device that uses a visible or ultraviolet light source (lamp or laser) shining through a sapphire window in the penetrometer tube wall. The return signal from the soil is collected by a fiber optic element that passes the signal to analytical equipment at the surface. The optical cone has been used primarily in the fluorescence mode to locate and track fluorescent tracer dyes and waste oil and fuel in natural soils and hydraulic fill materials. The unit has potential applications as a colorimeter for locating geologic units or contaminated soils with distinctive spectral characteristics. The optical cone uses an 8-mm diameter window and can technically locate the position of a soil color or fluorescence interface within 1 cm.

Soil and water samplers suitable for use in HWS investigations are available for incorporation into a penetrometer-based system. The samplers typically are of all-stainless steel construction and are designed to be disassembled for thorough cleaning between uses.

INTEGRATING DEVELOPMENTS TO FORM A SYSTEM

Pulling together a coherent picture of the conditions in the subsurface at a HWS requires simultaneous data acquisition and data evaluation. The sensors provide unprocessed responses that require refinement and interpretation before they can be displayed in a meaningful way. For example, the operator must know the depth of the rod reading when all of the sensors are positioned at different places on the penetrometer rod. The soil strength is measured on the bottom 50 cm of rod, the optical and electrical sensors are positioned 25 cm above this point. The operator must see all of the information produced for a common depth with all of the various calibration and standardization factors applied to the data.

Figure 3 shows the level of complexity involved in the data transfer for a penetrometer unit that is measuring the optical response and the soil strength properties (soil type) simultaneously. The system shown uses two 386-level personal computers (386 PCs) and a separate optical multichannel analyzer computer (OMA computer) to handle data acquisition and display. The three computers are linked with a token ring network inside the truck so that each machine can communicate with the other two. This system can measure optical properties and strength properties of the soil and maintain a record of the exact depth of the rod tip (through the string pot amp) and the geographic position of the truck on-site (survey equipment). The truck-mounted computers also can pass data to a large graphics computer for presentation level displays.

CONCLUSIONS

The existing penetrometer systems used in foundation investigations provide the platform for a new and sophisticated HWS characterization system that combines the speed and versatility of the penetrometer for data collection and sampling, with the ability of modern computer equipment to log data and produce a

synthesis of the data for operator interpretation. This approach allows the penetrometer crew to obtain immediate information in the field on the soil type being penetrated and an index of the level of contaminant present in the soil unit. Site investigations can now become interactive exercises where the direction of the characterization effort can be altered to take advantage of the information collected in each penetration. Soil and groundwater samples can now be obtained as a confirmation of the information obtained from sensors.

Monitoring wells can be placed late in the HWS investigation program in positions that penetrometer sensor and sampler data indicate are critical for long-term monitoring. It also is possible to consider using the penetrometer to implant well points to serve as monitoring wells where a full well installation cannot be justified.
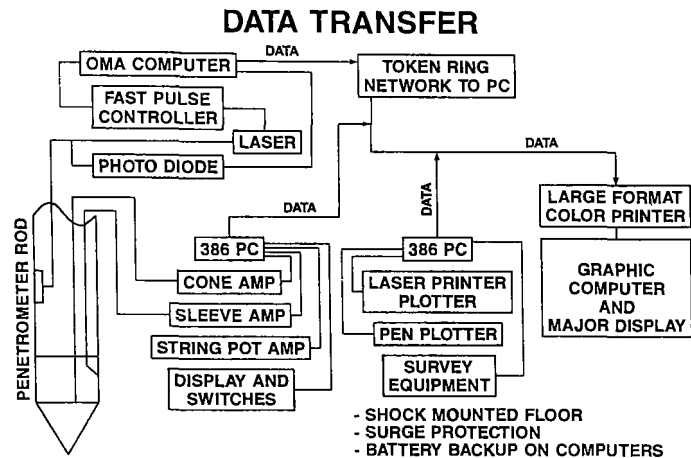
DATA TRANSFER

Figure 3
Schematic showing the data transfer involved in penetrometer measurements of soil strength and optical properties. The terms are explained in the text discussion.

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Slug Testing in Highly Permeable Aquifers Using a Pneumatic Method

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ABSTRACT

Highly permeable, unconsolidated deposits with horizontal hydraulic conductivities in the 10^{-3} to 10^{-1} cm/sec range often are encountered during environmental site characterization studies. Standard slug tests are ineffective in such formations, since a large and nearly instantaneous decrease in the well water level is required for a rising head test and an instantaneous increase in the water level is required for a falling head test. PRC Environmental Management, Inc. developed a quick and cost-effective pneumatic slug test method to lower or raise the static water level in such wells. Viable data can then be recorded when the water level is allowed to return to equilibrium. The method is very flexible and has been successfully used in 2-inch wells with a shallow (10-foot) water table and in 4-inch wells with a deep (125-foot) water table. Unlike other methods, it has the added advantage that both rising and falling head tests can be performed with a single, four component equipment setup.

The pneumatic slug test method requires four components: (1) a pneumatic well head assembly capable of providing an air-tight seal with a pressure/vacuum port, a quick release pressure valve and the capacity to accommodate a transducer cable and water level indicator tapes; (2) an oil-less air compressor capable of supplying positive and negative pressure; (3) a high-speed data logger interfaced with a pressure transducer; and (4) two electronic water level indicators. Statistical analysis of replicate rising and falling head tests in the same well showed that a high level of precision is attained using the pneumatic slug test method in highly permeable formations that were previously unsuited to slug test methods.

INTRODUCTION

Recent advances in slug testing, using a pneumatic technique, have increased the range and application of measuring hydraulic conductivity. Hydraulic conductivity has long been successfully determined in single wells by introducing or removing water or solid slugs.[1-4,7] These methods, coupled with water level measurement devices such as electrical water level indicators or percussion sounding instruments, can accurately determine hydraulic conductivities in the range of 8×10^{-4} cm/sec to 1×10^{-3} cm/sec.

The advent of data logging devices used in conjunction with pressure transducers allows successful slug testing in aquifers with hydraulic conductivities in the range of 1×10^{-2} cm/sec. However, these methods typically cannot be applied in aquifers with hydraulic conductivities greater than 1×10^{-2} cm/sec. In these instances, water levels rapidly reach equilibrium before the entire slug is added or removed. The initial change in water level is neither instantaneous nor of great enough magnitude to adequately monitor the recovery period. The use of solid slugs also makes it difficult to measure water levels, since the slug can

jar and offset the pressure transducer suspended inside the well. This problem particularly occurs in small diameter wells. At sites where wells are to be sampled for environmental parameters, traditional slug test methods have on additional limitation because the addition of potentially contaminated solid slugs or clean water can bias subsequent sampling results.

The pneumatic method for conducting slug tests overcomes all of these limitations. This method involves either injecting air into a sealed well to lower the water level[5] or applying a partial vacuum to a sealed well to raise the water level.[6] PRC has developed a pneumatic slug test method capable of conducting both rising and falling head tests with essentially the same equipment setup. This method is very versatile and has been used at sites with distinctly different geology and well construction. It has been used successfully in 2-inch I.D. wells, where depth to water was only 10 feet, and in 4-inch I.D. wells, where depth to water was 125 feet.

EQUIPMENT

The equipment needed to conduct pneumatic slug tests includes the well head assembly, two electronic water level indicators, a pressure transducer coupled with a high speed data logger, an oil-less air compressor capable of supplying both positive and negative pressure and a stop watch.

The principal component of this system is the well head assembly. This assembly, shown in Figure 1, consists of three major parts: (1) a rubber sleeve connector, (2) a quick release pressure valve, (3) and the pneumatic well cap assembly. The entire assembly is connected to the well head by means of the rubber sleeve connector. The sleeve is fitted around the riser pipe and a short section of pipe (of the same diameter) and sealed with hose clamps. A T-type pipe connector is attached to the top of the short pipe section.

The quick release pressure valve assembly and the pneumatic well cap assembly are in turn attached to the T-connector, as shown in Figure 1. The quick release pressure valve assembly consists of a ball-type valve attached to a short section of pipe. The pipe and valve must be equal to or greater in diameter than the well riser pipe. The pneumatic well cap assembly is shown in greater detail in Figure 2. This assembly fits into and rests on top of a short section of pipe. The assembly is constructed of two steel plates, separated by a 1- or 2-inch thick disk of foam rubber. The lower plate must be slightly smaller in diameter than the connector pipe it fits into. A quick release hose fitting is attached to the upper plate and passes through the foam rubber gasket and lower plate. The pressure or vacuum hose attaches to this fitting. The upper and lower plates are slotted to accommodate the transducer and water level indicator lines. An airtight seal is created by tightening the three bolts. This raises the lower plate, which in turn compresses the foam rubber gasket to make the seal.
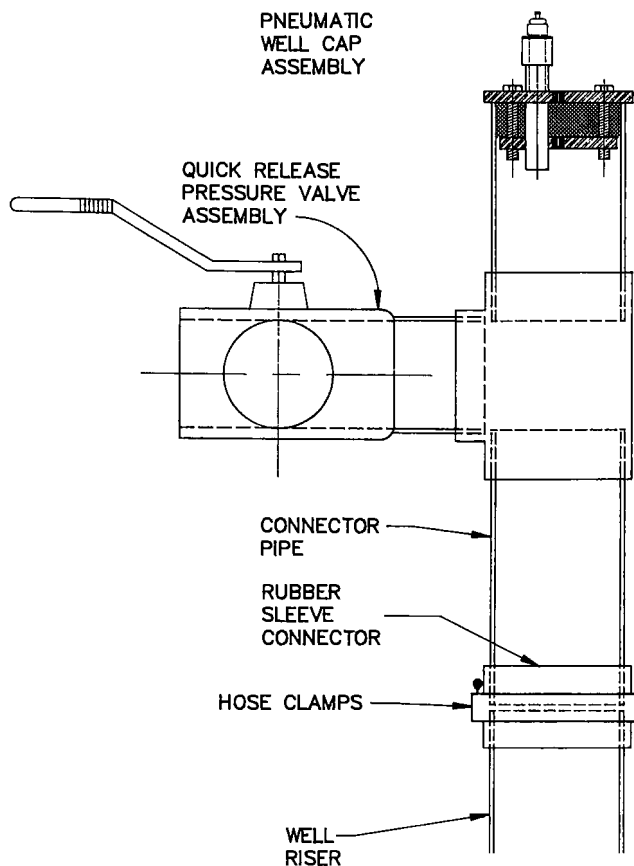
Figure 1
Pneumatic Well Head Assembly
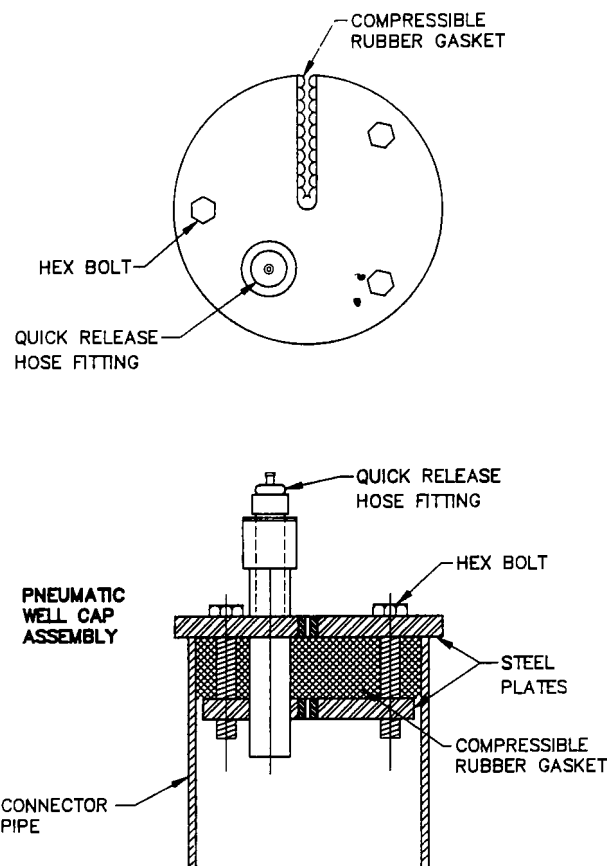
Figure 2
Pneumatic Well Cap Assembly

METHODOLOGY

Specific site information, such as the depth to water and well construction details, must be known before conducting pneumatic slug tests. As in all slug test procedures, the top of the well screen must lie well below static water level. Before the rising head test can be conducted, the height of the water column above the top of the well screen must be determined to ensure that air is not injected into the aquifer in the course of lowering the water level in the well.

A pretest should be conducted prior to performing rising or falling head tests. The pretest is conducted in much the same manner as the actual test, except that the transducer and data logger are not activated. The equipment setup for conducting a falling head pretest and actual test is shown in Figure 3. The two water level indicators and the pressure transducer are lowered into the well through the pneumatic well cap assembly and set at the proper depths. The pressure transducer is typically set in the well screen. One water level indicator probe is set 1 inch above static water level; the other is set 10 feet above static water level.

With both water level indicators turned on and the quick release pressure valve closed, the vacuum line is attached to the quick release hose fitting on the pneumatic well cap assembly, causing the water level in the well to rise. At the instant the upper water level indicator sounds, the quick release pressure valve is opened. A stop watch records the time required for the water level to return to equilibrium (shown by the lower water level indicator). This time interval should be at least three seconds, which is the minimum elapsed time necessary to collect accurate data for the standard hydraulic conductivity calculations. If the initial 10-foot water level rise recovers to equilibrium before three seconds, the upper water level indicator should be raised in increments of 5 feet until the 3-second limit is reached. Experience with this equipment has shown that water levels can be raised or lowered 25 feet in 4-inch I.D. wells with little effort.

To conduct pretests for rising head tests, the water level indicators are set approximately 1 inch and 10 feet below static water level (Fig. 4). The quick release pressure valve is closed and the pressure line is attached to the quick release hose fitting on the pneumatic well cap assembly, causing the water level in the well to fall. The quick release pressure valve is opened and the stop watch is activated simultaneously when the lower water level indicator stops sounding. The time required for the water level to return to equilibrium (shown by the upper water level indicator) is recorded. The lower water level indicator is lowered in five foot increments until the three second recovery limit is reached.

The water level recovery times noted during the pretests are also useful for estimating the test duration. This pretest process prevents the unnecessary monitoring of the water level recovery after well conditions have returned to equilibrium.

For the actual falling head and rising head tests, the initial depression or elevation of the water level in the well is performed as in the pretests. When the water levels reach the predetermined elevation, the quick release pressure valve is slightly opened and closed to maintain the water level in the well (as indicated by the water level indicator) at that elevation. This is done for 5 to 10 seconds so that the aquifer can return to equilibrium (an assumption for hydraulic conductivity calculations) before the recovery phase. The actual test is then initiated by simultaneously opening the quick release pressure valve and starting the data logger. The rate of recovery, as well as the initial head displacement, will be recorded automatically by the data logger.

It is important to stress that the quick release pressure valve opening must be equal to or greater in diameter than the riser pipe. This relative sizing is required if air pressure inside the well is to return to atmospheric pressure instantly. Smaller diameter openings prohibit the instantaneous return to atmospheric pressure. In the case of a rising

head test, an inordinately small pressure release opening causes the well to recover under pressures greater than 1 atm, thereby leading to erroneously slow recovery rates. The same result is true in the case of the falling head test, where a partial vacuum above the water column will decrease the rate at which the water column falls back to static water level. Both conditions will lead to erroneously low estimates of hydraulic conductivity.

Figure 5 demonstrates the importance of the valve diameter. In the figure, replicate rising head tests are plotted with the Hvorslev method.[4] The log of the head ratio is plotted on the vertical axis and the recovery time is plotted on the horizontal axis.

Test A is the plot for a test using the quick release pressure value assembly shown in Figure 1. When the air pressure inside the well returns instantly to atmospheric conditions, as in the case of Test A, the plot is a straight line. If an apparatus that restricts the flow of air into or out of the well is used, as shown in Test B, water levels in the well fluctuate radically until air pressures reach atmospheric conditions (at point R). After this point, water levels recover at the same rate observed in Test A, as indicated by the parallel slopes. However, the basic time lag T_o, defined by Hvorslev as the time at which the log of the head ratio = -0.43, is erroneously high in Test B. If this high T_o value is used in the Hvorslev equation for partially penetrating wells, the resulting hydraulic conductivity will be too low. The Hvorslev equation is shown below:

$$K_h = \frac{d^2 \ln (2 \, mL/D)}{8 \, LT_o} \qquad (1)$$

where:

K_h = horizontal hydraulic conductivity
d = diameter of riser pipe

m = transformation ratio
L = length of well screen
D = diameter of well screen
T_o = basic time lag

The error described above will be accentuated as the depth to static water level increases, since greater volumes of air must escape or enter the well before equilibrium is reached.

ANALYSIS

The pneumatic slug test method has been successfully tested at two Superfund sites with very different hydrogeology and monitoring well types. At the first site, in northern Michigan, monitoring wells are constructed of 2-inch I.D. PVC riser and screen. The aquifer consists of very clean, well-sorted, fine to medium-grained quartz sand. The static water level in this aquifer is approximately 10 feet below ground surface. At the second site, in central Nebraska, monitoring wells are constructed of 4-inch I.D. stainless steel riser and screen. This aquifer is composed primarily of poorly sorted sands and gravels with some silt. The static water level in this aquifer is approximately 125 feet below ground surface.

PRC conducted six replicate rising and six replicate falling head tests on a single well at each site using the pneumatic method. The precision of the method was measured by: (1) the reproducibility of the results within each set of six tests and (2) the reproducibility of the results between the rising and falling head tests conducted at each well. The data for each test were plotted using the Hvorslev method. The slopes of the linear portion of the curves were determined using linear regression analysis. The average slope and the upper and lower 95 percent confidence limits were determined for each of the four sets of replicates. This information is summarized in Table 1.
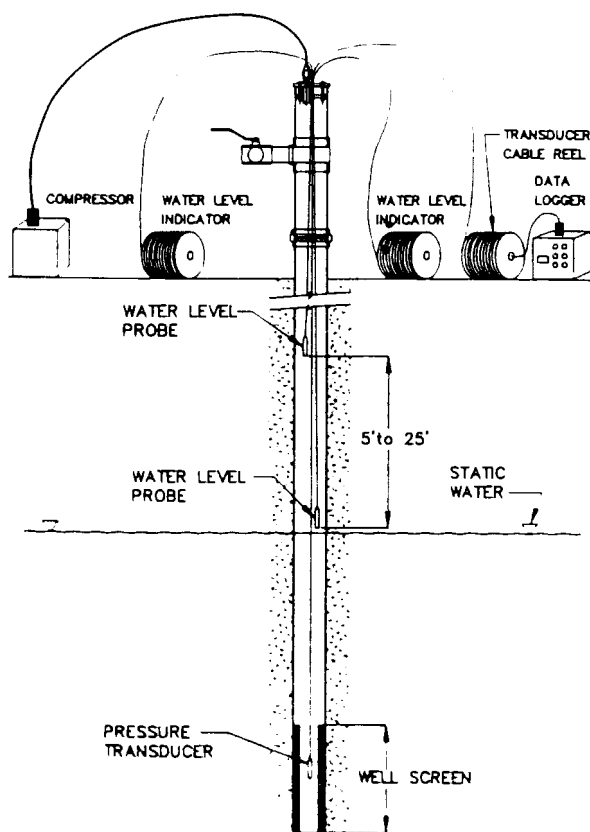
Figure 3
Equipment Setup for Conducting the
Falling Head Set
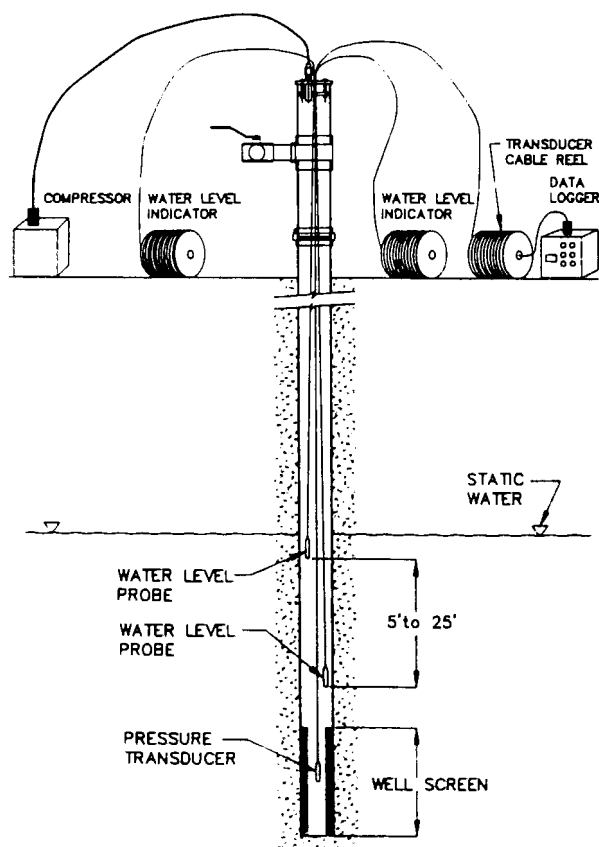
Figure 4
Equipment Setup for Conducting
the Rising Head Test
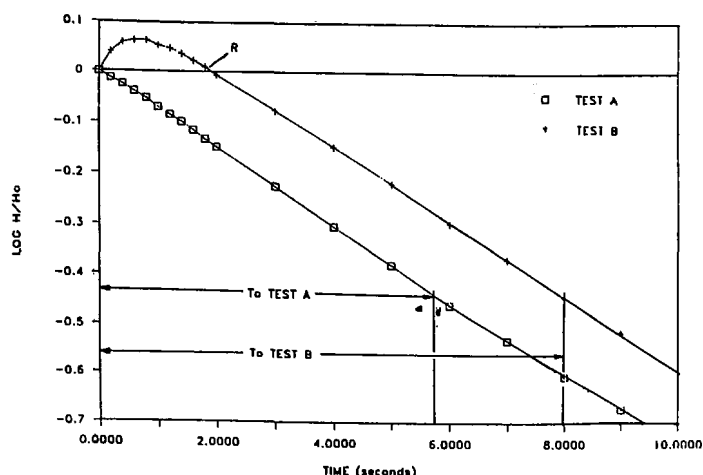
Figure 5
Replicate Rising Head Tests Showing Effect
of Inadequate Pressure Release Valve Diameter

Table 1
Statistical Comparison of Test Results

		Mean	95% LCL	95% UCL
Nebraska Site				
Rising Head	Slope	-7.857	-8.185	-7.530
	K_h	7.68×10^{-3} cm/sec	7.32×10^{-3} cm/sec	7.98×10^{-3} cm/sec
Falling Head	Slope	-8.962	-9.169	-8.751
	K_h	8.74×10^{-3} cm/sec	8.53×10^{-3} cm/sec	8.94×10^{-3} cm/sec
Michigan Site				
Rising Head	Slope	-7.753	-8.412	-7.058
	K_h	1.06×10^{-2} cm/sec	9.60×10^{-3} cm/sec	1.15×10^{-2} cm/sec
Falling Head	Slope	-7.906	-8.545	-7.267
	K_h	1.08×10^{-2} cm/sec	9.90×10^{-3} cm/sec	1.16×10^{-2} cm/sec

Hvorslev's equation was rearranged to use the slope of the plot, rather than a single point, to calculate hydraulic conductivity:

$$K_h = \frac{d_2 \ln (2 \; mL/D)}{8 \; L} \quad x \;_l n \quad \frac{(H/Ho)_1}{(H/Ho)_2} \qquad (2)$$
$$\frac{}{T_2 - T_1}$$

The far right side of the equation is the slope of the linear portion of the plotted data. The absolute value of the slope, as determined by linear regression analysis, replaces the T_o (basic time lag) portion of Hvorslev's equation.

Replicate testing has shown the pneumatic method to be very precise. In Michigan, hydraulic conductivity as measured by the rising head test in the test well fell between 9.60×10^{-3} and 1.15×10^{-2} cm/sec 95

percent of the time. The falling head test results fell between 9.90×10^{-3} to 1.16×10^{-2} cm/sec 95 percent of the time.

In Nebraska, hydraulic conductivity was measured in rising head tests at between 7.32×10^{-3} and 7.98×10^{-3} cm/sec 95 percent of the time. The falling head test results fell between 8.53×10^{-3} and 8.94×10^{-3} cm/sec 95 percent of the time.

The Michigan testing showed that hydraulic conductivities calculated using the rising and falling head tests were statistically equal based upon replicate testing results. In the Nebraska testing, however, the hydraulic conductivities were statistically different for the two tests.

One possible explanation for this difference is the precision of new technology in the form of high-speed data loggers and an easy-to-use, convenient method for conducting the testing. Although the average hydraulic conductivity resulting from the rising head test (7.68×10^{-3} cm/sec) during the Nebraska testing is statistically different from the falling head test (8.74×10^{-3} cm/sec), the use of one value over the other would not significantly affect the outcomes of relationships in which hydraulic conductivity values are commonly used. More testing will be done to study the difference in results.

The Michigan and Nebraska testing were conducted in formations with medium conductivities—in the range of the upper 10^{-3} cm/sec to the lower 10^{-2} cm/sec. This range is toward the upper limit of the other slug testing methods. The authors feel that the pneumatic slug test method could easily measure hydraulic conductivity in formations where the hydraulic conductivity is several orders of magnitude higher.

CONCLUSION

The pneumatic slug method for conducting rising and falling head tests is a cost-effective and versatile procedure for determining hydraulic conductivities in highly permeable formations with hydraulic conductivities greater than 10^{-2} cm/sec. Replicate testing indicates that a high level of precision can be achieved with the pneumatic slug test method. Unlike other pneumatic methods, its flexibility allows both rising and falling head tests to be performed with the same equipment setup. Unlike traditional methods, it allows a maximum initial change in water levels, so that well recovery rates can be adequately monitored. Similarly, it allows the recovery period to begin instantaneously, a procedure that is very difficult to achieve with the traditional methods. The pneumatic method also avoids the introduction into the well of potentially contaminated solid slugs or clean water slugs, which may bias subsequent sampling results.

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Using Hydraulic Probe Sampling in Shallow Aquifers for Groundwater Contaminant Plume and Source Location

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ABSTRACT

PRC Environmental Management, Inc., developed a technique to conduct preliminary groundwater contaminant plume and source location surveys using a hydraulic probe sampler in shallow aquifers (water table less than 30 feet). The technique was used to conduct an areal site survey at a Michigan Superfund site to define a contaminant plume and identify the sources of that contamination.

Periodic sampling of residential wells had detected gasoline-derived contaminants in groundwater from many of those wells. Rather than relying on the usual approach of drilling boreholes and installing monitoring wells, PRC used a hydraulic probe sampler and a close support laboratory (CSL) to determine the areal extent of the groundwater contaminant plume and identify the contaminant sources. The collected data were used to design a borehole drilling program to define the vertical extent of contamination and install monitoring wells in the optimum locations.

Soil gas sampling techniques were modified to accommodate the collection of groundwater. The hydraulic probe sampler was used to collect in situ groundwater samples at depths ranging from 9 to 20 feet at 69 locations. The 1-inch outer diameter hollow probe was hydraulically driven to 2 feet below the water table, as determined using an electronic water level indicator. Groundwater samples were then taken, using a peristaltic pump and transported directly to the on-site CSL for analysis. Groundwater levels were recorded and locations were surveyed. All the field work was completed in 5 days. Data analysis required another 5 days.

Using these data, PRC was able to develop a preliminary potentiometric surface map, determine the groundwater flow direction, determine the areal configuration of the groundwater contaminant plume and identify two contaminant sources. A cost-effective borehole drilling program then was designed to establish the vertical extent of contamination and to install a groundwater monitoring system. By using the preliminary survey technique, PRC reduced data collection time from as long as 12 weeks to only 2 weeks, which resulted in significantly lower costs for the remedial investigation.

INTRODUCTION

During the summer of 1989, a remedial investigation (RI) was conducted at a Michigan Superfund site. The site was centered in the commercial portion of a small residential town in northeast Michigan. Previous investigations and site background information suggested that possible sources of chlorinated solvents and petroleum hydrocarbons existed at the site. The goals of the RI were to define the areal extent of groundwater contamination and to identify contaminant sources.

Rather than use the conventional approach of strictly drilling boreholes, a technique was used to conduct a preliminary groundwater plume and source location survey. This technique consisted of using a hydraulic probe sampler to collect groundwater samples in a fast and, therefore, cost-effective manner. It was essential to have a close support laboratory (CSL) on-site during this groundwater survey to provide short turn around time for the sample results.

INVESTIGATION METHOD

The groundwater plume and source location survey was conducted by first establishing a grid system for sampling. A local licensed surveyor laid out a 200-foot grid within the preliminarily designated site boundaries. As samples were collected from grid locations and analyzed by the CSL for target compounds of concern, the generated data dictated in which direction to stray from the grid and in which area to concentrate sampling efforts. Figure 1 shows the locations where the in situ groundwater samples were collected.

The sampling procedures used were tailored to the conditions at this particular site. The local geology consists of approximately 30 feet of consolidated sand overlying a silty clay aquitard unit. The water table was encountered at depths ranging from approximately 15 feet to the southwest to only a few feet to the northeast (Fig. 2). The sampling equipment included a van with the capability to hydraulically push the sampling probes, 3-foot sections of threaded 1-inch outer diameter (OD) stainless steel rod, rigid 0.375-inch PVC tubing, a peristaltic pump and sample containers.

Sampling was conducted by pushing the probes to the desired depth of 2 feet below the water table. The depth to the water table was established by using an electronic water level indicator. The water level sensor was lowered inside the probe after the probe was pushed to the expected depth of the water table. When the water table was located, the depth of the probe tip was adjusted so that the tip was 2 feet below the water table before sampling was initiated. The probe tip was retractable so that when the rod was pulled back, the tip remained in place and a void space was created for groundwater to enter the rod. Rigid 0.375-inch PVC tubing was inserted into the rod to the bottom of the hole and cut above grade. The tubing was connected to a peristaltic pump. The system was purged and a sample was collected and promptly transported to the CSL. PVC tubing was discarded after sampling and the stainless steel rods were steam cleaned prior to reuse. The peristaltic pump was flushed with clean water between each sample. When field monitoring detected the presence of organic vapors, the tubing in the peristaltic pump was replaced as well.

The total time required to drive the rod, collect the sample and remove the rod usually was no more than 30 minutes. The limiting factor for this procedure was the rate at which the CSL could analyze the groundwater samples. More samples could be collected during a given day than could be analyzed the same day.

Figure 1
Hydraulic Probe Sampling Locations

Figure 2
Groundwater Contour Map
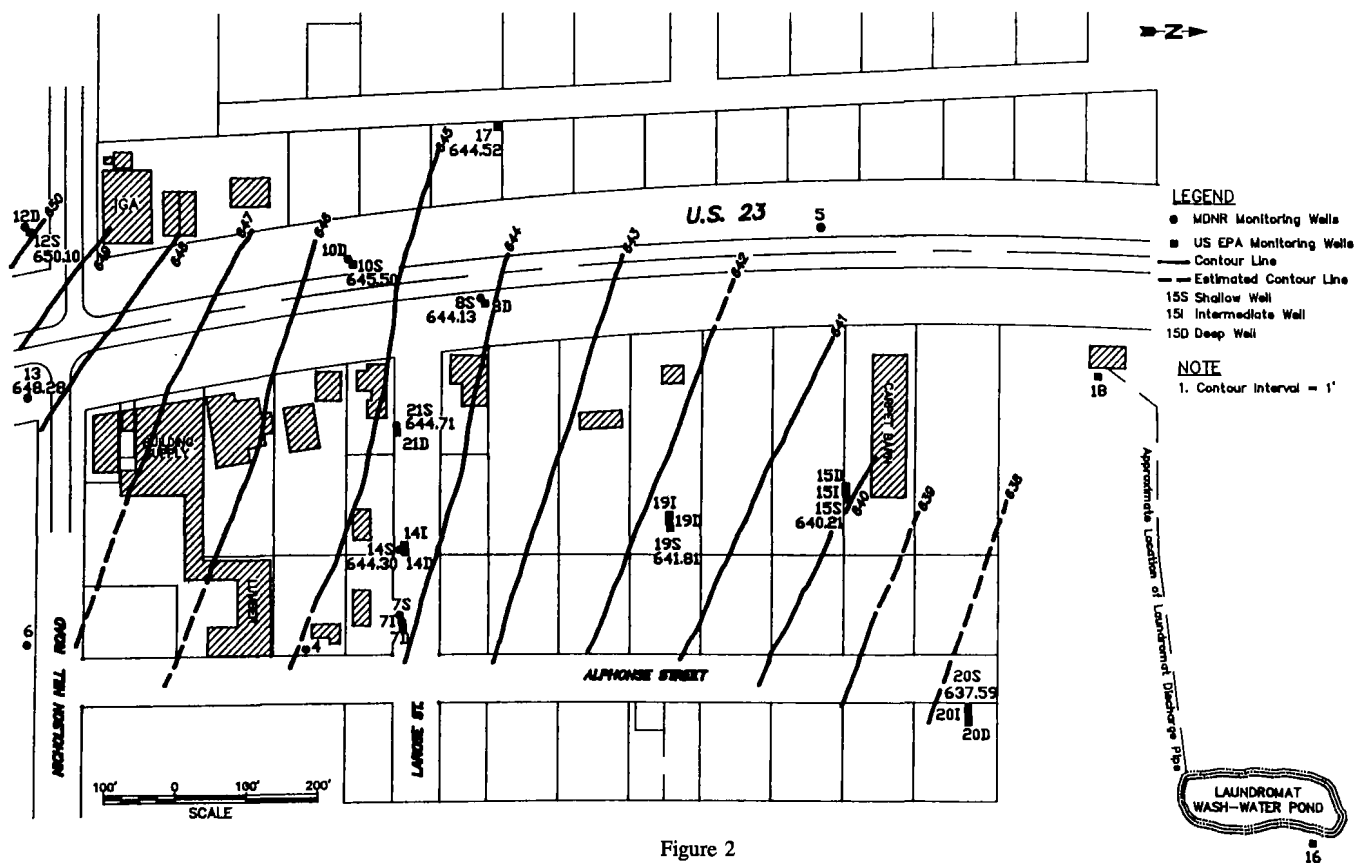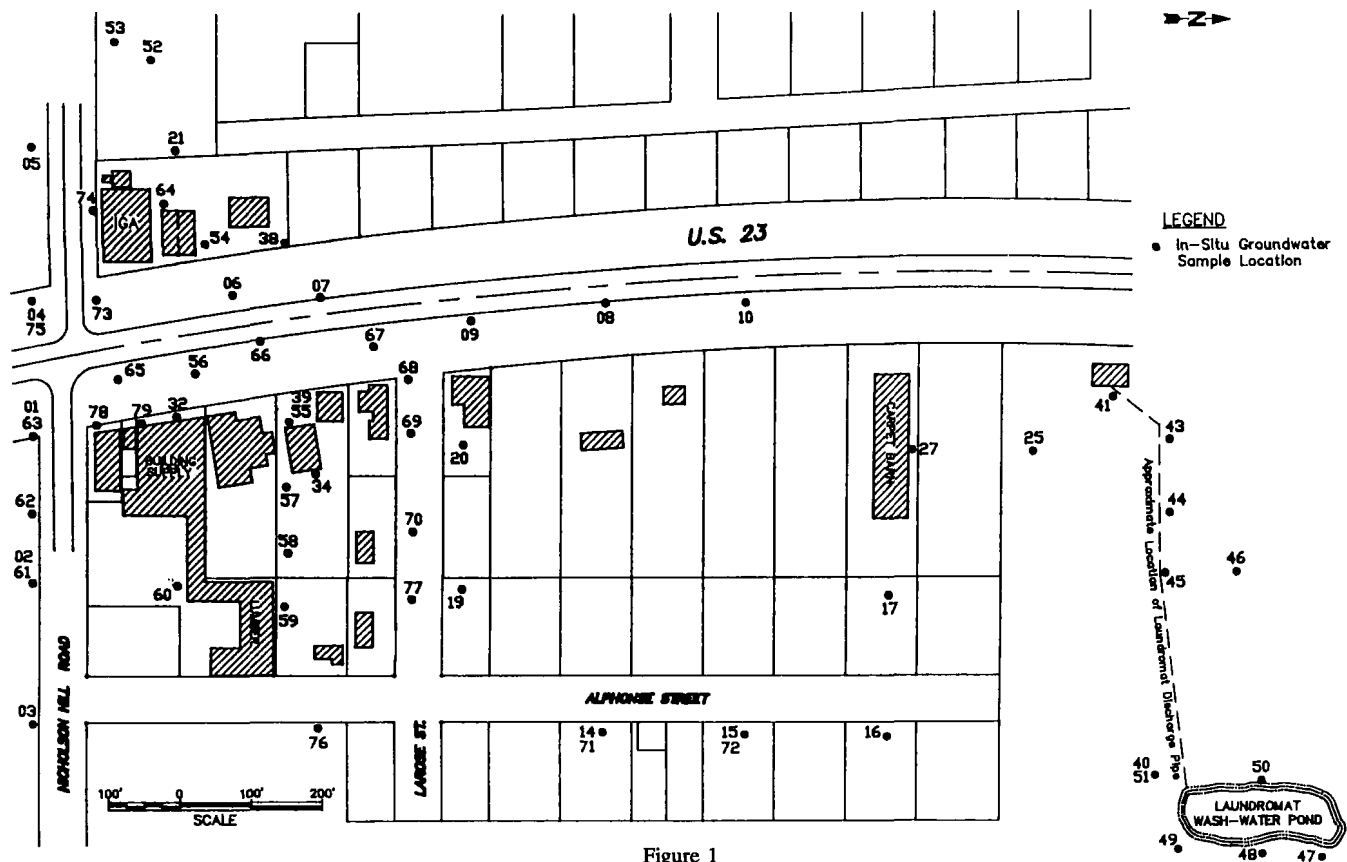
In addition to obtaining in situ groundwater samples, this method also can be used to collect preliminary groundwater elevation data. In loose soils or sands, a water-level indicator can be inserted inside the stainless steel rod to obtain a water-level measurement, as described above. This technique is best suited for loose soils where collapse of the hole is likely. In a more cohesive soil environment, the rod can be removed and a 1-inch PVC temporary piezometer can be inserted into the void space. Either one of these techniques can be used to measure groundwater levels to get an indication of the flow direction. Each temporary piezometer (probe or PVC) location is surveyed to establish the horizontal coordinates as well as the surface elevation. The piezometer stickup is measured at the same time as the water levels. After all locations are surveyed, the elevations of the groundwater levels are determined.

In less than 2 weeks, 69 locations were sampled at depths ranging from approximately 9 to 20 feet. Quality control samples were collected as part of the survey. Duplicate samples were collected at the frequency of one duplicate for every 10 samples. Equipment blanks were collected at the same frequency to verify the effectiveness of the decontamination procedures.

RESULTS

Groundwater samples usually were analyzed by the CSL usually within 24-hours. The samples were analyzed for target volatile organic compounds. These target compounds included benzene, toluene, ethylbenzene, m,p and o-xylenes, tetrachloroethene and 1-2-dichloroethane. Analytical results for the groundwater samples are presented in Table 1.

Historical records indicated that several underground gasoline tanks were in operation in the area at one time. The three other areas containing elevated BETX concentrations correlate with former locations of underground gasoline tanks. The two areas near the intersection of U.S. Highway 23 and Nicholson Hill Road match two separate former tank locations and represent residual contamination from inactive sources. The third area southwest of the intersection of LaRose and Alphonse Streets is at a location where tanks had been removed and replaced with new operating tanks. The BETX detected here seems to be due to residual contamination rather than from an active source. It is much more localized than either of the active source pumps.

Trace levels of BETX contaminants were detected farther downgradient near the laundromat. The primary constituent detected was benzene, the most mobile of these compounds.

Target compounds such as 1,2-dichloroethane and tetrachloroethene were analyzed to determine the extent of contamination from chlorinated solvents. Tetrachloroethene was detected at only five locations and 1,2-dichloroethane was detected at only four locations. The highest concentration of tetrachloroethene was detected at sample location 54 (7.7 μg/L), while the highest concentration of 1,2-dichloroethane was detected at sample location 57 (41 μg/L). All other locations where these compounds were detected contain only trace levels (less than 3 μg/L).

DISCUSSION

A groundwater survey using the hydraulic probe sampling technique can be compared with other more common groundwater sampling techniques such as borehole drilling and monitoring well installation when used in shallow aquifers. Although the hydraulic probe survey most likely will not completely replace all drilling activities in a groundwater investigation, it can significantly reduce the amount of drilling and, ultimately, reduce the cost.

The information obtained from the groundwater survey served as the basis for the borehole drilling program. Boreholes were drilled at sample locations 39, 54, 55, 57 and 65 to define the vertical extent of contamination. As expected, locations 39, 54, 55 contained the highest levels of contaminants.

A monitoring well system was established to verify preliminary data and to provide permanent sampling locations for long-term monitoring (Fig. 4). Only 5-foot screen lengths were used, so many of the well locations were nested. Upgradient well locations south of Nicholson Hill Road provided background groundwater data. Monitoring wells 21, 19 and 15 were placed downgradient of one active source and wells 8 and 10 were located downgradient of the other active source. Wells 4, 7, 14 and 20 were located to monitor the eastern fringe, and wells 5 and 17 were located to monitor the western fringe. Monitoring wells 16 and 18 were located to monitor groundwater near the laundromat and its washwater pond where chlorinated solvents were suspected.

CONCLUSION

The hydraulic probe groundwater sampling technique can be an effective part of a site investigation in areas having shallow aquifers. This technique, combined with the use of a close support laboratory, provides preliminary groundwater data with short turn-around time. The quick return of sample results enables the sampling team to make decisions and draw conclusions at an expedited pace. Nearly 70 locations were sampled along with QA/QC samples and the resulting sampling data were analyzed in less than 2 weeks. The hydraulic probe van is much smaller than a drill rig, making it easier to maneuver into areas where a drill rig might not be practical. It also requires less overhead clearance from trees and utilities.

A clear picture of the areal extent of contamination was obtained by using the survey. Boreholes were drilled to define the vertical extent of contamination and monitoring wells were installed to provide a long-term monitoring system. All drilling activities were based on information generated by the groundwater survey. Because this method is relatively inexpensive compared with borehole drilling and well installation, it provides a cost-effective way to decrease the amount of drilling time and, ultimately, reduce the cost of the investigation.

Table 1
Contaminant Concentrations Detected in
In situ Groundwater Samples

Sample Location	Benzene	1 1 DCA	Toluene	Tetra chloroethene	Ethylbenzene	O-Xylene	M,P-Xylene
01	ND	ND	ND	ND	ND	ND	0 9
02	ND	ND	1 8	ND	ND	ND	ND
03	ND	ND	ND	1 11	1 5	ND	ND
07	16 7	ND	480	1 0	96 4	301	550
09	ND	6.8	ND	ND	ND	ND	ND
33	ND	ND	16	ND	18	69	72
34	ND	ND	1 1	ND	1 5	ND	ND
38	ND	ND	17	ND	2 0	ND	ND
39	2,390	ND	29,200	ND	27,000	38,700	100,000
40	3 7	ND	ND	ND	ND	ND	ND
41	ND	ND	ND	1 7	ND	ND	ND
43	3 7	1 1	1 1	ND	ND	ND	ND
44	3 6	ND	ND	ND	ND	ND	ND
45	3 6	ND	ND	ND	ND	ND	ND
46	2 6	ND	ND	ND	ND	ND	ND
47	ND	ND	1 9	ND	ND	ND	ND
48	ND	ND	3 3	ND	ND	ND	ND
51	ND	ND	ND	ND	ND	1 6	ND
52	ND	ND	ND	ND	ND	3 7	ND
53	ND	ND	ND	ND	ND	1 6	ND
54	6,000	ND	4,900	7 7	1,100	4,100	14,000
55	670	ND	30,000	ND	3,300	13,000	13,000
56	1 4	ND	13	ND	1 4	6 6	3 7
57	3 5	41	10	ND	1 8	8 3	4 5
58	ND	ND	27	ND	640	5,100	6,600
59	3 6	ND	ND	ND	ND	ND	1 3
60	6 5	ND	1 6	ND	ND	ND	ND
61	3 7	ND	1 3	ND	ND	ND	ND
62	1 5	ND	0 8	ND	ND	ND	ND
63	0 7	3 9	3 3	3 3	3 3	ND	3 3
64	ND	ND	0 7	ND	ND	ND	ND
66	1 3	ND	ND	ND	ND	ND	ND
67	ND	ND	0 6	ND	ND	ND	ND
68	1 5	ND	0 9	ND	ND	ND	ND
69	2 040	ND	1 640	ND	301	68 3	567
70	1 6	ND	0 6	ND	ND	ND	ND
71	1 7	ND	ND	ND	ND	ND	ND
72	13 6	ND	130	ND	33 7	134	64 3

Notes

Only locations with target compounds detected are presented in this table

M,p xylenes were analyzed but not detected in in situ ground-water samples

The detection limit for in situ ground water analyses is 0.5 ppb

ppb = parts per billion

ND = Not Detected

Sample locations containing levels of petroleum hydrocarbons were detected in five areas (Fig. 3). The concentrations are presented as a sum of benzene, ethylbenzene, toluene and m, p and o-xylenes (BETX) in μg/L. The two areas with the highest BETX concentrations were traced to operating underground gasoline tanks. One plume is originating from underground tanks west of U.S. Highway 23. Another plume is originating from underground tanks east of U.S. Highway 23. Sample locations along U.S. Highway 23 contain only trace levels of contaminants between the two plumes.

Figure 3
Plume Configuration Based on Hydraulic Probe Results

Figure 4
Monitoring Well Locations

The Origin and Physical Properties of Bentonite and Its Usage in the Groundwater Monitoring Industry

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ABSTRACT

Bentonite consists of mainly the clay mineral montmorillonite and is found worldwide, mostly in the deposits of the Cretaceous age. Nearly all the commercial bentonite deposits were produced by the devitrification of tuff or volcanic ash. Bentonite is known for its physico-chemical properties that include shrink-swell, cation exchange capacities, thixotropy and fluid-loss reducing properties.

Bentonite clays have been traditionally used in the oil well drilling industry since the early 1930s. The oil industry has used chemical additives with drilling mud despite concern about possible chemical reactions with aquifer waters. As recently as the 1970s, bentonite clays have also been used in the groundwater monitoring industry. Unlike the oil industry, however, the material used in well construction or borehole completion is closely scrutinized and chemically analyzed for purity. Material used in groundwater monitoring must be chemically inert and not alter the ambient quality of monitored groundwaters.

There is much confusion about historic oil field terminologies of bentonites and their applications to the groundwater monitoring industry. Recent advances in the production of bentonite-based materials have further convoluted the problem. This paper describes various properties that must be considered in evaluating when to use a drilling mud, slurry, bentonite seal, cement-bentonite grout and high-solid bentonite grout. It also provides environmental definitions for these categories.

INTRODUCTION

In the 1880s, William Taylor identified an unusual high-swelling clayey material in the vicinity of Rock Creek, Wyoming, and he called this material "taylorite." In 1898, W.C. Knight renamed this clay-like, sticky material with soapy properties "bentonite" because of its occurrence in the Fort Benton shale unit of Cretaceous age.[1] Various unique physical properties of bentonite made it commercially valuable. The bentonite-producing industry rapidly developed in Wyoming and additional bentonite deposits were soon discovered in Arizona, California, Mississippi and Texas and in England, Germany, Japan and the Soviet Union. The first serious effort at bentonite production occurred in the United States in Wyoming in about 1920. Production outside the United States developed in the late 1920s.[2]

The *Glossary of Geology*[3] describes bentonite as a soft, plastic, porous, light-colored rock composed essentially of clay minerals from the montmorillonite (smectite) group and colloidal silica. It is produced by devitrification and accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash. It often contains accessory crystal grains that were originally phenocrysts in the parent rock. Its color ranges from white to light green and light blue when fresh and becomes light cream with exposure, gradually changing to yellow, red or brown. The rock is greasy and soaplike to the touch

(without a gritty feeling) and absorbs large quantities of water, which increases its volume about eight times.

Bentonite is used in ceramics, foundry molding sands, engineering projects, the petroleum industry and in the manufacturing of a variety of miscellaneous products ranging from adhesives to soaps. Which physico-chemical property of bentonite is utilized depends on the purpose of the job. The use of bentonite in the groundwater industry is relatively new and has basically evolved from the petroleum industry. In the first part of this paper, the geology, mineralogy and the origin of bentonite are described. In the second part, monitoring well construction, the use of bentonite, its physico-chemical properties and its transition from the oil industry to environmental usage are discussed.

GENERAL GEOLOGICAL FEATURES OF BENTONITES

According to Grim and Guven,[2] bentonites are most commonly associated with beds that are marine in origin. The associated beds may also be nonmarine in origin, such as freshwater limestones, carbonaceous shale or beds of coal.[2] A few bentonites are reported to be fossiliferous.

Most bentonites are grey, bluish grey, light yellow or green in color. Individual beds of bentonite may be laminated or massive. Because of its expansion when wet and contraction while drying, bentonite outcrops frequently have a "popcorn" appearance. Weathering of an outcrop tends to increase the colloidal properties. Bentonite layers vary in thickness from less than 1 inch to more than 20 feet. Often, the thicker beds seem to be composites of several layers.

Bentonite deposits range in age from Upper Paleozoic to Recent. World-wide, most bentonites occur in the formations of the Cretaceous age. Bentonites are found on every continent. A list of countries and regions where bentonite deposits are known to occur is presented in Table 1. (The reader can refer to Grim and Guven for further details).[2]

Table 1
Countries/Regions Where Bentonite Deposits Occur

1	The United States of America	
	Black Hills Region	Rocky Mountain and California areas
	Gulf Coast Area	Other areas (Illinois, Missouri, Delaware, Georgia, and Alaska)
2	Western Hemisphere (excluding those in the United States)	
	Argentina	Brazil
	Canada	Colombia
	Cuba	Equador
	Jamaica	Mexico
	Peru	Puerto Rico
	Uruguay	
3	Africa	
	Algeria and Morocco	Namibia

Egypt	Sudan Republic
Kenya and Tanganyika	Union of South Africa
Mozambique	

4. European and eastern Mediterranean countries

Austria	Bulgaria
Cyprus	Czechoslovakia
England	Denmark
Faroe Islands (Denmark)	Federal Republic of Germany
France	Greece
Hungary	Israel
Italy	Poland
Portugal	Rumania
Spain and	Switzerland
Spanish Morocco	Yugoslavia
Turkey	

5. Soviet Union, Asia, and the Southwest Pacific

Australia	Burma
China	India
Indonesia	Iran
Iraq	Japan
Korea	New Zealand
Pakistan	Phillipines
U.S.S.R.	

The so-called metabentonites are reported in many formations of Paleozoic age. In general, these materials are composed of illite-smectite mixed-layer minerals, so that the material does not have the physical properties of a bentonite. These have been looked upon essentially as altered volcanic ash to which potassium has been added later, giving rise to the illite component with the loss of bentonite properties.

In terms of physicochemistry, there are two types of bentonites: sodium and calcium, the most commonly occurring exchangeable cations. The amount of interlayer water absorbed varies according to the type of bentonite, the nature of interlayer cations and the physical conditions. Calcium bentonites usually take up two layers of water molecules in each space, while the amount taken up by sodium compounds is variable and shows a greater swelling capacity.[6,8]

In the United States, the northern (Black Hills-Wyoming area) and the southern (Mississippi-Texas area) bentonites are marked by sodium and calcium varieties, respectively. The former shows a greater degree of swelling and is more desireable for drilling fluids, grouts and sealants. This bimodal compositional pattern is not well-defined in the literature. Three possible explanations exist: (1) the seawaters in which the ash/tuff was deposited and later yielded bentonite were enriched in sodium and calcium that are now reflected in their respective bentonite compositions; (2) the chemical composition of the original ash/tuff was different, which influenced the sodium/calcium contents of the resulting bentonites; and (3) groundwater that percolated downwards carried dissolved calcium. The leaching replacement of some exchangeable sodium by calcium rapidly re-equilibrated under low-grade burial metamorphic conditions, thereby giving rise to the calcium-rich bentonites. A combination of all three of these conditions could also have been operative in bringing about this regional variation in bentonite chemistry.

MINERALOGICAL FEATURES OF BENTONITE

The smectite group of clay minerals forms the major component in bentonite, which has exceptionally high water-absorbing and cation exchange capabilities. This group includes montmorillonite, beidellite, notronite, hectorite, saponite and sauconite. Commonly, bentonite is a mixture of the montmorillonite-beidellite series. The general chemical formula for this group is $(\frac{1}{2} Ca, Na)_{0.7} (Al, Mg, Fe)_4 [(Si, Al)_8 O_{20}]$ $(OH)_4 \cdot nH_2O$ where the composition of montmorillonite is $(Na)_{0.7}$ $(Al_{3.3} Mg_{0.7}) Si_8 O_{20} (OH)_4 \cdot nH_2O$ and that of beidellite is Al_4 $(Si_{7.34} Al_{0.66}) O_{20} (OH)_4 \cdot nH_2O$. They are all "swelling" clays in that they can contain water or organic liquids between their structural layers and all show marked cation exchange properties.[4,5]

The crystal structure of smectites consists of superimposed layers, each of which contains a plane of Al ions sandwiched between two inward-pointing sheets of linked SiO_4 tetrahedra.[6] Therefore, the two silica sheets and one alumina sheet are also called a 2:1 mineral (Fig. 1). The octahedral sheet is between the two inward-pointing sheets of silica tetrahedron sheets, with the tips of the tetrahedrons combining with the hydroxyls of the octahedral sheet to form a single layer (Fig. 2).

The thickness of each 2:1 layer is approximately 0.96 nm. Because the bonding by van der Waal's forces between the tops of the silica sheet is weak and there is a net negative charge deficiency in the octahedral sheet, water and exchangeable ions can enter and separate the layers.[7]
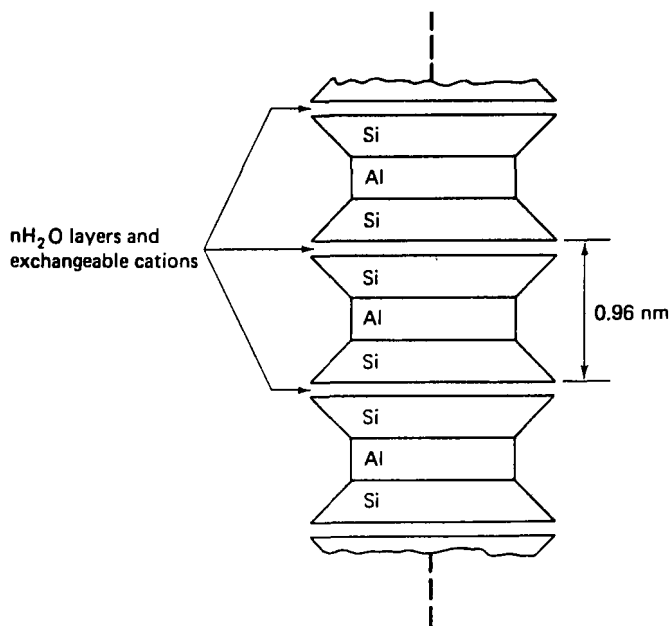
Figure 1
Schematic diagram of the structure of montmorillonite[9]
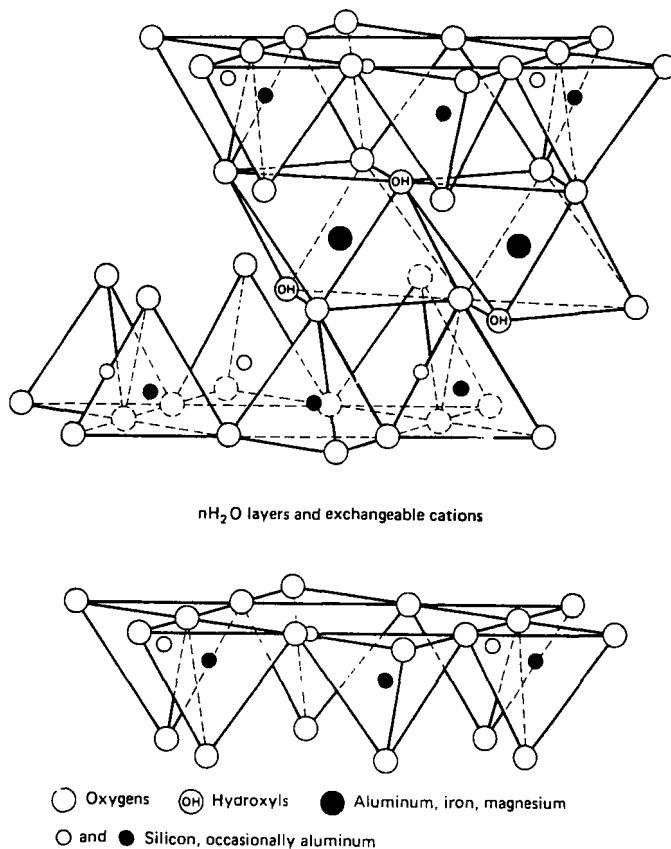
Figure 2
Atomic structure of montmorillonite[10]

As seen under the microscope, smectites occur in fine-grained aggregates that may be dendritic, lamellar or spherulitic. Refractive indices increase with loss of interlayer water. In general, optical methods alone are not reliable for the identification of smectites, and it is usually necessary to observe other properties, such as differential thermal analysis curves, dehydration curves, x-ray powder patterns, electron microscopy and atomic absorption spectroscopy. Free silica minerals, such as cristobalite and tridymite, are important components of some bentonites. Quartz, feldspars, kaolinite, mica, illite, gypsum, calcite and accessories (heavy minerals) are the minor components in bentonites. Zeolites are rare. Zircon, magnetite, apatite, magnesite and pyroxenes also have been reported.[2]

GEOLOGIC ORIGIN OF BENTONITES

The origins of all documented bentonites fall into four categories: (1) hydrothermal alteration, in which hot aqueous solutions of magmatic origin generate a zonal distribution of alteration products, including clay minerals; (2) deuteric alteration in which changes take place in an igneous rock through the reaction of the vapors and gases included within the igneous mass; (3) miscellaneous origins that include weathering and groundwater reaction; and (4) in situ alteration of volcanic ash/tuff. This last category is the most common origin of commercial bentonite deposits and is described in more detail in the next section.

In the in situ process, devitrification of ash is the basic alteration process accompanied by hydration and crystallization of smectite around multiple nuclei. Also, some beds underlying bentonite horizons have been found silicified, indicating a downward migration of silica. With a few exceptions, the devitrification process is generally believed to have taken place underwater and not by superficial weathering. The ash/tuff-to-smectite alteration process probably occurred at the same time as the accumulation of the igneous material and after the formation of smectite, very little further alteration took place. Oxygen-isotope work carried out by Henderson et al.[11] has shown that smectite was formed at approximately 25° C.

The geologic process is established by the presence of microscopic shards and other relict volcanic structures, the character of nonclay minerals and, less commonly, the transitions to associated units of ash or tuff. This transitional contact, in conjunction with high concentrations of clay minerals and the absence of detrital minerals, shows that the alteration took place in situ. The wide range of associated sedimentary rocks indicates that the environments in which the alteration took place also varied widely. These environments range from shallow marine and fresh water to desert conditions. Most bentonites have formed from volcanic ash of dacitic to rhyolitic composition.

USE OF BENTONITE IN THE PETROLEUM INDUSTRY

Bentonite clay is the primary material used in mud rotary drilling, which is a preferred oil well drilling method due to its ability to complete the most feet of hole per hour in a wide range of geologic formations. The goal of oil well drilling is to complete an oil producing well as cost-effectively as possible. A comparison of the efficiency of drilling methods (cable tool, mud-rotary and air hammer) for different geologic formations is given in Figure 3. In the past, little concern was given to the environmental effects of drilling fluids and other materials used during well completion. Much of the current drilling technology and terminology used in today's environmental investigations was developed in the oil industry.

A typical mud rotary system is shown in Figure 4. Bentonite clay and water are used as the primary drilling fluid in the system.

Bentonite clays have been widely used in the oil well industry as a drilling mud since the early 1900s. The unique chemical composition and physical properties inherent to bentonite make it an ideal natural drilling fluid. When mixed properly with fresh water, a bentonite slurry will maintain borehole integrity, reduce fluid loss, reduce bit wear and suspend and lift cuttings from the borehole. Additives can be mixed with the slurry to enhance drilling fluid performance. A list of typical oil well drilling additives is given in Table 2. However, some of these additives can cause an impact on groundwater quality and are known to have adverse toxicological effects.
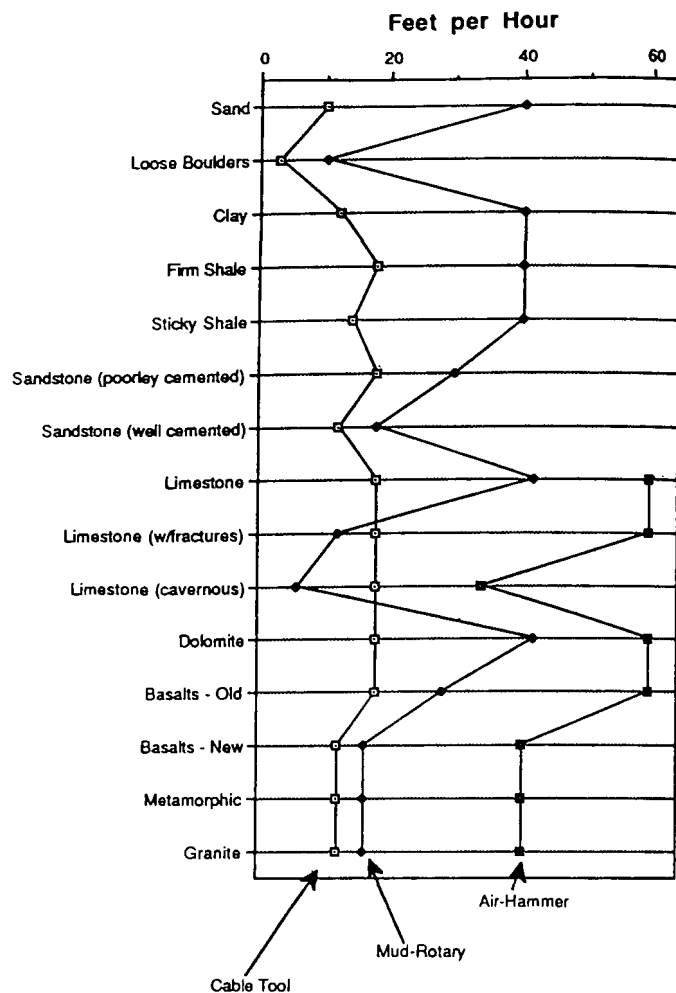
Figure 3
Diagram showing average drill performance versus lithology.
Values are approximations based on
reported values and authors' experience
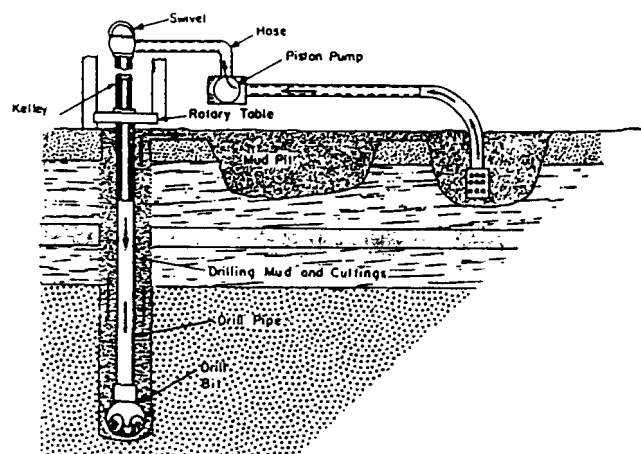
Figure 4
In a mud rotary system the drilling fluid (or water)
is pumped through the swivel and down through the kelley
which is turned by the rotary table.
The mud then flows down through the drill pipe, out
through the bit and back up the hole carrying cuttings which
settle out of the mud in the first section(s) of the mud pit.
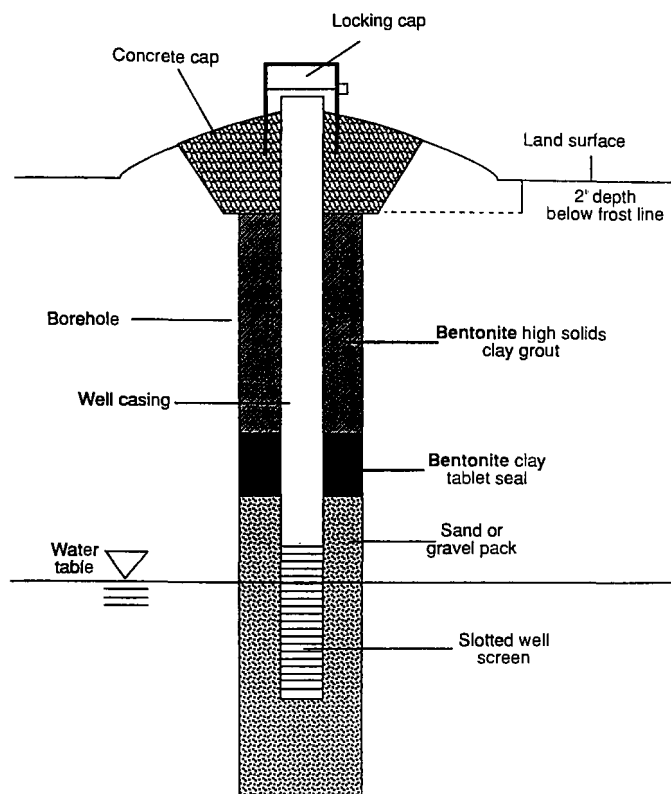
Figure 6
Use of bentonite clay products in a typical monitoring well

TERMINOLOGY

The American Petroleum Institute developed specifications and terminology for the methods and materials (including bentonite drilling fluids) used for oil well drilling. Much of this technology has been applied to the environmental industry. However, the terminology has not been updated or modified to reflect changes in applications. The following terms pertain to bentonite and are defined for accurate understanding.

- **Slurry** - A generic term that describes any suspension of bentonite clay and water.
- **Drilling Fluid** - A circulating fluid used in rotary drilling to perform various functions required in the drilling operation. The dry material (typically sodium bentonite) must be free of additives or ingredients that will adversely impact groundwater quality.
- **High Solids Clay Grout** - A mixture of sodium and calcium bentonite clays that, when mixed with fresh water, will form a slurry with a minimum 20 percent solids and a minimum mud weight of 9.5 lbs/gal. The material will remain pumpable during placement and, when set, will have a minimum permeability value of 1 x 10^{-7} cm/sec.

Table 3
Physical Properties Versus Applications of Bentonite

	High solids clay grout		Drilling fluid	
Montmorillonite Content	X	85% - 90%	X	85% - 90%
Fluid Loss Control	O		X	<15 ml. maximum
Barrel Yield	O		X	90 - 200 bbl yield
Gel Strength	O		X	PV/YP maximum of 3
Permeability	X	1 x 10^{-7} to 1 x 10^{-8} cm/sec	O	
Solids Content	X	20% - 30% solids	O	2% - 6% solids
Mud Weight	X	9.5 - 10.0 lbs./gal.	X	8.7 - 9.2 lbs./gal.
Viscosity	O		X	> 30 cps. @ 600 rpm Fann

To fully understand the difference between a bentonite drilling fluid and a bentonite high solids grout, the properties that are specific to each mixture must be understood. The properties and values significant to drilling fluids and high solids clay grout are presented in Table 3. Definitions for properties specific to the different applications of bentonite are provided below.

- **Montmorillonite Content** - Refers to the chemical purity or the percent of active ingredients in the clay. This property is presented in percent of montmorillonite. The remaining portion of materials present is usually comprised of feldspar or silica sand.
- **Fluid Loss** - Refers to the relative amount of fluid lost (filtrate) through permeable formations or membranes when the drilling fluid is subjected to a pressure differential. This property is very important to a drilling fluid and is of less importance to a grout. Drilling fluids are designed to maintain borehole integrity by maintaining a wall cake of bentonite on the borehole so that hydrostatic pressure can be maintained.
- **Barrel Yield** - A term used to define the quality of a clay by describing the number of barrels of a given viscosity (centipoise) slurry that can be made from one ton of the clay. Bentonite clays are classified as high yield (200 bbl) or low yield (90 bbl) clays. Yield is an important factor when choosing a drilling fluid.
- **Gel Strength** - The ability or the measure of the ability of a colloid to form gels. Gel strength is a pressure unit usually reported in lb/100 ft^2. It is a measure of the same inter-particle forces of a fluid as determined by the yield point, but gel strength is measured under static conditions, yield point under dynamic conditions.
- **Thixotropy** - The ability of fluid to develop gel strength with time. It is a property that causes a build up of a rigid or semirigid gel structure if allowed to stand at rest and can be returned to a fluid state by mechanical agitation. This change is reversible.
- **Plastic Viscosity (PV)** - A measure of the internal resistance to fluid flow attributable to the amount, type and size of solids present in a given fluid. It is expressed as the number of dynes/cm^2 of tangential shearing force in excess of the Bingham yield value that will induce a unit rate of shear. This value, expressed in centipoises, is proportional to the slope of the consistency curve determined in the region of laminar flow for materials obeying Bingham's Law of Plastic Flow. When using the direct-indicating viscometer, the plastic viscosity is found by subtracting the 300-rpm reading from the 600-rpm reading.
- **Yield Point (YP)** - The yield point (also called yield value) is the resistance to initial flow, or the stress required to start fluid movement. This resistance is due to electrical charges located on or near the surfaces of the particles. The values of the yield point and thixotropy are measurements of the same fluid properties under dynamic and static states, respectively. The Bingham yield value, reported in lb/100 ft^2, is determined by the direct-indicating viscometer by subtracting the plastic viscosity from the 300-rpm reading.
- **Permeability (Hydraulic Conductivity)** - A coefficient of proportionality describing the rate at which water can move through a permeable medium.[14] The density and kinematic viscosity of the water must be considered in determining the hydraulic conductivity. Typically it is expressed in cm/sec, ft/day or gal/day/ft^2.
- **Solids Content** - The total amount of solids in a drilling fluid as determined by an evaporation process that includes determination of both the dissolved and the suspended or undissolved solids. The suspended-solids content may be a combination of high and low specific gravity solids and native or commercial solids. Examples of dissolved solids are the soluble salts or sodium, calcium and magnesium. Suspended solids make up the wall cake; dissolved solids remain in the filtrate. The total suspended and dissolved solids contents are commonly expressed as percent by volume.

Percent solids in a mixture can be calculated using the following formula:

$$\frac{\text{Weight of material (lb)}}{\text{Weight of material (lb)} + \text{weight of water (lb)}} \times 100 = \% \text{ solids} \qquad (1)$$

Application	Composition	Trade Name
Alkalinity or pH Control	Calcium Chloride Potassium hydrate Sodium hydroxide Hydrated lime Organic-silicate comp.	Caustic Potash Caustic Soda Lime Synergic
Bactericides	Biocide Biocide Paraformaldehyde	Aldecide Surflo-B19, 33 Various
Defoamers	Aluminum stearate Salt water defoamer Salt Water defoamer Nonsurfactant defoamer	------- Defoamer 23 Imco-Defoam LD-7
Emulsifiers	Crude oil emulsifier Crude oil invert emul. Mud detergent Oil mud stabilizer Petroleum sulfonate Neutralized soap Invert oil mud conc. Salt water emulsifier	Economagic Imco Crude-X Conc. Imco-MD Invermul Magconate Mil-Olox Protecto-Mul Salinex
Filtrate Reduction	Wyoming bentonite Pregelantinized starch Oil base mud conc. Basic oil base mud Sodium carboxymethyl cellulose Lignitic material Organic polymer Oil mud filtration control Proc. lignosulfonat Causticized lignite Ferrochrome lignosulfonate Oil Base gel material Invert emulsion	Various Various Bascoil Black Magic CMC ------- Various Dextrid Duratone Imco RD-111 Imco-Thin Imco VC-10 OB Gel Stabilmul

USE OF BENTONITE IN MONITORING WELL CONSTRUCTION

A monitoring well measures the physical and chemical properties of ambient groundwater without adversely affecting its quality. The cleanliness of well construction and the collection of meaningful data are the goal of a properly installed monitoring well.

Among various available drilling methods, hollow stem augers are preferred for well installation. The advantages of hollow stem augers include drilling without fluids, installing wells within a temporary casing and obtaining accurate soil samples. The disadvantages of using hollow stem augers are that they are limited in depth capabilities and cannot be used in consolidated formations. A diagram of a typical hollow stem auger system is shown in Figure 5.

Bentonite clays are used extensively in the construction of monitoring wells. A typical well construction diagram showing the different applications of bentonite in a monitoring well is found in Figure 6.

Bentonites currently have two distinct purposes in the role of monitoring well construction: (1) to provide a low permeable seal (permeability values will range from 1×10^{-7} to 1×10^{-9} cm/sec for a bentonite grout) that will not adversely affect ambient groundwater quality and prevent the mixing and migration of interaquifer and surface fluids;[14] and (2) to create a drilling fluid that will not adversely impact ground-water quality, lubricate the bit, provide borehole stability, lift cuttings, reduce fluid loss and provide a filter cake during mud rotary drilling.[15-17]

Bentonite clays in a dry tablet form are placed on top of the filter pack to provide a seal so that water samples can be extracted from a discrete zone in the formation and to control the migration of overlying grouts into the filter pack.

Bentonite in powdered form is mixed with fresh water to form a high solids clay grout. This mixture can be used to fill boreholes for abandonment or seal the annular space overlying the filter pack between the casing and formation in a monitoring well. When augers cannot be used, monitoring wells are often drilled using the mud rotary method. Powdered bentonite (without any polymers or additives) is added to fresh water to form a natural drilling mud. Powdered bentonite can also

be added to cement to form a cement bentonite grout. This mixture is also used to fill boreholes and the annular space of wells. Although this method is widely used, it has recently been questioned because of the following disadvantages:[16,17]

- Excessive heat of hydration during curing
- High pH values and questionable levels of trace heavy metals
- Excessive loss to formation
- Permeability values greater than the formation
- Cracking and shrinking
- Incompatibility of the cement and bentonite

In the past, bentonite has been misused due to a lack of accurate terminology, education about its use, competitive pricing and product variety. Slurries of bentonite and water that resemble drilling fluids have been misused to abandon boreholes and seal casings. Due to the low solids content of these mixtures, the bentonite could separate and settle out, leaving an inadequate borehole seal.
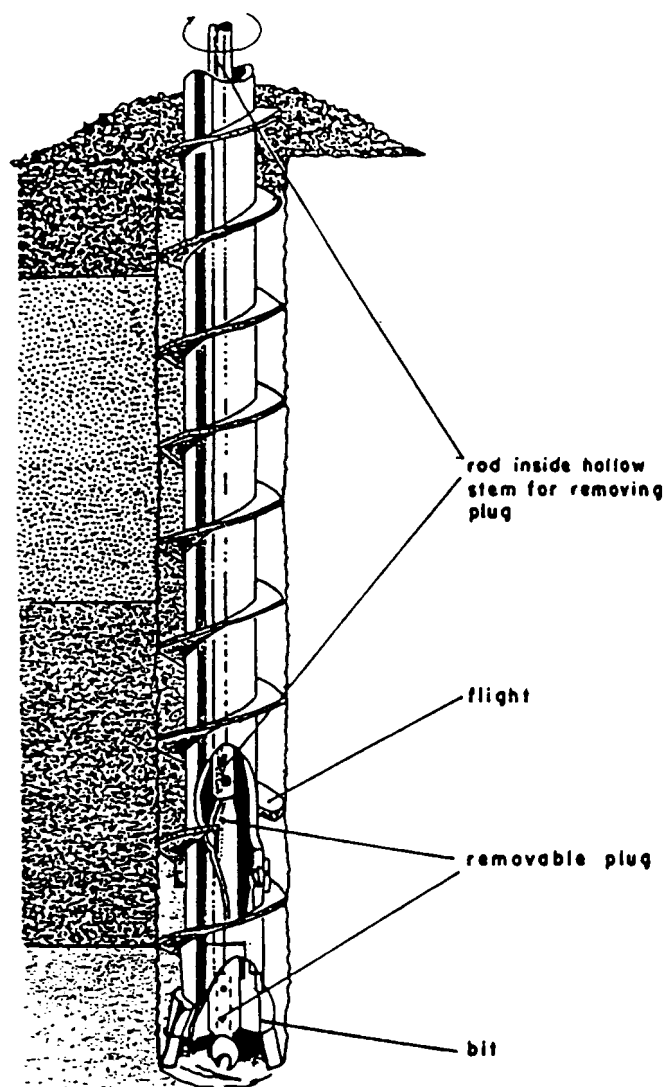
Figure 5
A hollow-stem continuous flight auger bores into soft soils carrying the cuttings upward along the flights. When the desired depth is reached, the plug is removed from the bit and withdrawn from inside the hollow stem. A well point (1/4 inch or 2 inches) can then be inserted to the bottom of the hollow stem and the auger pulled out leaving the small diameter monitoring well in place

- **Mud Weight** - Refers to the density of the slurry. This measurement is normally expressed in either lb/gal or lb/ft^3.

Mud weight of a slurry can be calculated using the following formula:

$$\frac{\text{Weight of Bentonite (lb)} + \text{Weight of Water (lb)}}{\text{yield (gal)}} = \text{mud weight lb/gal} \qquad (2)$$

- **Viscosity** - The internal resistance offered by a fluid to flow. This phenomenon is attributable to the attractions between molecules of a liquid and is a measure of the combined effects of adhesion and cohesion to the effects of suspended particles and the liquid environment. The greater this resistance, the greater the viscosity. Viscosity can be reported in centipoise when measured on a viscometer or in seconds when measured on a marsh funnel.

High Solids Clay Grouts

High solids clay grouts were first used in the mid-1980s as a substitute for cement in the annular space of monitoring wells. The ease of mixing the clay grouts, pumpability, low permeability values, no heat of hydration during curing, neutral pH and plasticity make them highly desirable. Properties that are important for distinguishing a grout from a drilling fluid are:

- **Permeability** — Values should range between 1×10^{-7} to 1×10^{-9} cm/sec and should be lower than those of the surrounding formation.
- **Solids Content** — Values should range between 20 to 30% solids by weight of water.
- **Mud Weight** — Values should range between 9.5 to 10.0 lb/gal and are directly proportional to the solids content. As solids increase, so does the mud weight.
- **Chemical Purity** — The mix should be free of polymers or additives that will adversely affect groundwater quality.

CONCLUSIONS

Bentonite occurs on all continents in the deposits of Cretaceous to Recent age. It is made up chiefly of the clay mineral montmorillonite, which gives it many useful physico-chemical properties. The chemical purity of this naturally occurring mineral with high swell capacity and plasticity, adsorptive and absorption properties and low permeability, allows for many uses in the environmental industry. This paper explored the use of bentonite as a drilling fluid, a high solids grout and as a sealant.

Sodium bentonite also can be used as an admixture with native soils to construct low-permeability liners, cutoff walls and caps for waste impoundments, landfills and contaminated sites. The latest development in containment is the thin geotextile-bentonite mat, which has seepage control characteristics equivalent to several feet of low-permeability soils.

To differentiate the application and type of bentonite needed, one must be familiar with its properties, relevant terminologies and product use. We hope the supplied definitions will help minimize the misuse of bentonite and allow the installation of monitoring wells that yield meaningful data.

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Identification of Previously Unrecognized Waste Pits Using Ground Penetrating Radar and Historical Aerial Photography

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ABSTRACT

To investigate whether wastes were buried in a portion of the property of a manufacturing facility located in the Mid-Continent, an investigation was conducted using ground penetrating radar (GPR) and historical aerial photographs. Analysis of historical aerial photographs provided information on previous patterns of land use and on changes in topography over time. Acquisition and analysis of GPR data confirmed the presence of subsurface disturbances and thus permitted identification of no longer existing or only partially existing topographic depressions, indicative of pits that are believed to have been used for waste disposal.

Four anomalous topographic depressions, clearly visible on aerial photographs acquired in 1966, 1967 and 1972, are only partly apparent on 1980 and 1985 aerial photographs. This finding indicates that these depressions were partially or completely filled and wastes may have been buried on the property. The aerial photographs do not have sufficient resolution to reveal whether debris was contained within the topographical depressions. However, the photographs did reveal that the depressions were devoid of vegetation and had irregular topography that varied for each photo acquisition date, typical of waste pits being filled over time.

Because some of the historical depressions are not apparent now on the land surface, GPR data were obtained along traverses crossing the entire project area. Zones of subsurface disturbance or signal loss, typical of buried waste, were apparent in GPR data obtained at the same locations as those where depressions were apparent on the historical aerial photographs. Thus GPR data provided information, prior to drilling, which confirmed the existence of zones of subsurface disturbance that are believed to mark buried waste. These data delineate partially buried waste pits and also provide a method to identify the optimum drilling locations for investigating potential impacts of buried waste on groundwater.

INTRODUCTION

The purpose of this investigation was to discover whether waste was buried in trenches or pits in a portion of the property of a manufacturing facility. The portion of the property investigated is approximately 62,500 square feet in area and is bounded by a chain link fence delineating the southern and eastern property boundaries (Fig. 1). The investigation consisted of four elements: (1) analysis of historical aerial photographs, (2) acquisition and analysis of ground penetrating radar data; (3) field observations; and (4) installation of monitoring wells and collection and analysis of samples of soil and groundwater. Only the first three elements of the investigation are discussed in this paper.
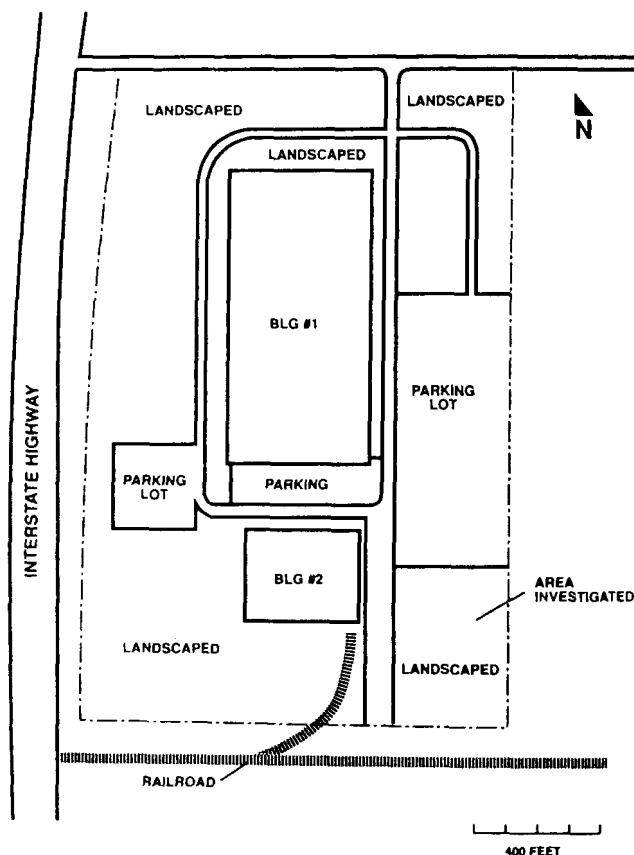
Figure 1
General Layout of Facility Property Showing
the Specific Area Investigated

ANALYSIS OF AERIAL PHOTOGRAPHS

Stereoscopic pairs of black and white aerial photographs obtained from the State Department of Transportation were analyzed to identify previous patterns of land use and to characterize changes in topography over time. The dates of the aerial photographs used are April 1950, November 1955, May 1961, March 1966, April 1967, April 1972, May 1981 and September 1985. The scales of the photographs range from 1 inch equals 2,000 feet to 1 inch equals 400 feet. Photographs from different dates were compared to establish a chronology of land use

and topographic patterns in the area investigated. This chronology is summarized below.

The portion of the property investigated is clearly visible in the aerial photographs as relatively flat, largely grass-covered undeveloped land. The 1966, 1967 and 1972 photographs reveal several small topographic depressions that are slightly different in appearance, shape and size on each of these photographs, indicating that the morphology of these features changed between 1966 and 1972 (Figs. 2c and 2d). These depressions are light-colored, irregularly shaped with sharply defined edges and devoid of vegetation. Some depressions have angular boundaries and appear similar to excavated pits that are dry. Others have slightly rounded boundaries, similar in appearance to partially liquid-filled pits. The topographic depressions range in size from approximately 20 by 30 feet to 30 by 100+ feet. These depressions appear in the 1981 photographs (Fig. 2b) as water-filled ponds and in the 1985 photographs (Fig. 2a) as a flat-lying, partially grass covered area, with a few large deciduous trees.

Dirt roads are visible on the 1966, 1967 and 1972 photographs (Figs. 2c and 2d). One road passes to the south from the parking lot and splits into two roads, with each road terminating at a specific depression. Another dirt road circles the entire area. The presence of these roads indicates that vehicular access to these depressions was maintained.

Although the aerial photographs were not of sufficient resolution to reveal whether debris was within the depressions, the photos did reveal that the depressions had features typical of waste pits. The areas identified in earlier photographs as depressions are clearly visible in earlier photographs as flat lying land, indicating that the former depressions were subsequently filled in. Additionally, the depressions were devoid of vegetation, their internal topography and shape were different in each the aerial photograph and they were connected by dirt roads to each other and to the main facility.

FIELD OBSERVATIONS

Field reconnaissance was performed to help characterize nature of
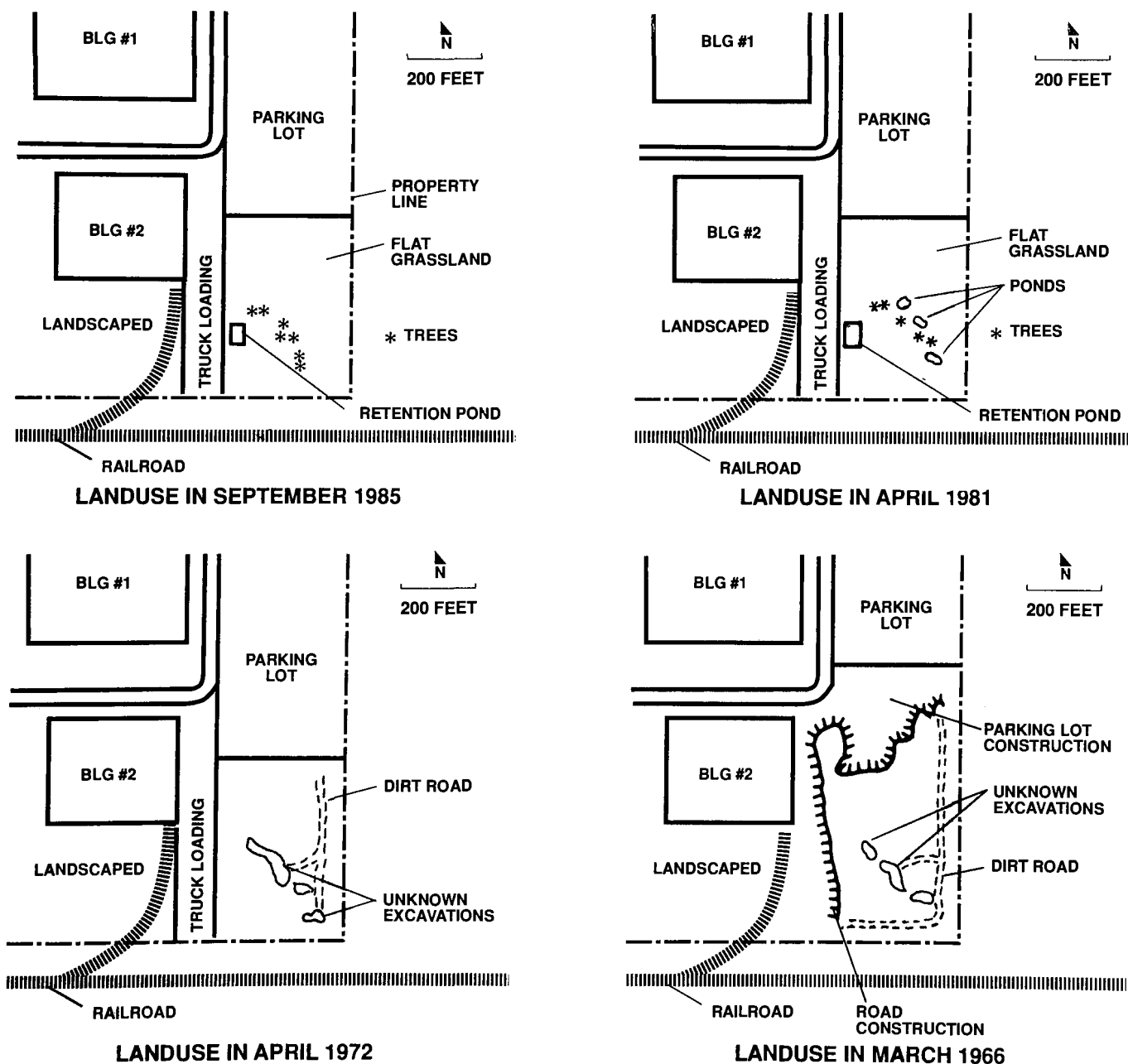
Figure 2
Land Use Patterns Interpreted from
Historical Aerial Photographs

the features observed on the aerial photographs. Portions of three of the topographic depressions identified on the 1966, 1967 and 1972 aerial photographs were located by field observations. These features are labeled "1, 2 and 3" on Figure 3. Portions of one feature identified on the 1972 aerial photographs also were located by field observations and are labeled "4" on Figure 3.
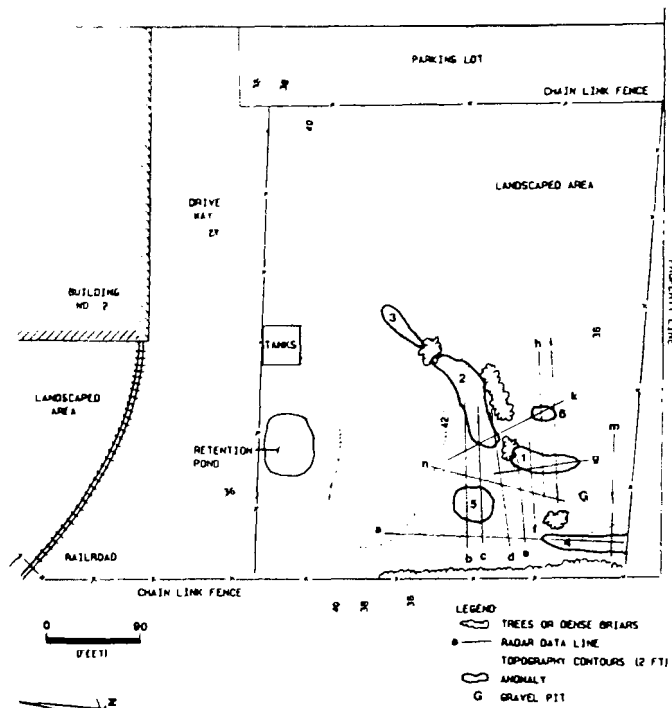
Figure 3
Area Investigated Showing Topography,
Radar Data Lines, and Anomalies

Features 1, 2 and 3 are curvi-linear topographic depressions with less than 2 feet of relief. These depressions range between 0.5 and 2 feet deep, have relatively flat bottoms covered with mud and leaves and act to collect surface water run-off. Feature 1 and the southeastern portion of Feature 2 are devoid of the grass that grows in the adjacent flat terrain. Most of the large deciduous trees in the portion of the property investigated are located along the edges of these depressions. A gravel pile covers the southeastern portion of Feature 1. The northern portion of Feature 2 and most of Feature 3 are covered by debris consisting of broken blocks of concrete, pieces of metal pipes and bricks.

Feature 4 is located in the southeast corner of the area investigated. This feature is as flat as the surrounding terrain; however, it has only sparse grass cover and is partially marked by a rust colored, hard, cinder-like, gravel-size material covering the ground surface. A dense growth of briars covers the northern and southern portions of Feature 4 and a gravel pile covers part of the northern portion, obscuring the locations of the northern and southern edges.

GROUND PENETRATING RADAR

Background

Ground penetrating radar (GPR) is a geophysical investigation technique that provides data which are used to characterize the subsurface without disturbing the ground. This GPR investigation was performed to help assess the nature of the depressions observed on the historical aerial photographs. Because some of the depressions observed on these photographs were partially apparent or not apparent at present-day land surface, the GPR data was obtained in a grid pattern that traversed the entire project area.

GPR is a device that transmits a pulse of radio frequency electromagnetic energy into the ground, records the radio frequency

response of the subsurface and displays this response on paper as a graphic record. The propagation of radio wave energy into the subsurface is governed by the electrical properties of the subsurface. When the radio frequency energy encounters a variation in the electrical properties of the subsurface, a portion of the energy is reflected back up toward the ground surface while the remaining energy continues to propagate downward. The radar response printed on the graphic record is a function of the amount of time required for the radio energy to propagate from the radar antenna into the ground, to reflect off of an interface between two subsurface layers of different electrical properties and to propagate back up toward the radar antenna.[1]

The pulse of radar energy transmitted by the radar antenna interacts with subsurface interfaces and is recorded several nanoseconds (ns: 10^{-9} seconds) later by either the same antenna (in a monostatic radar system) or by a different antenna (in a bistatic system). The intensity of the radar signal recorded by the antenna and displayed on the graphic record increases as the difference in electrical conductivity between adjacent layers increases. Any pulse of energy detected by the antenna in excess of a threshold value is displayed by the graphic recorder as a shaded spot on the graphic record. Interfaces between subsurface layers detected by the radar signal are represented on the radar graphic record by two to four black lines (Fig. 4).[1] Therefore, GPR can be used to produce an approximation of a subsurface cross-section showing layers that have different electrical conductivity.
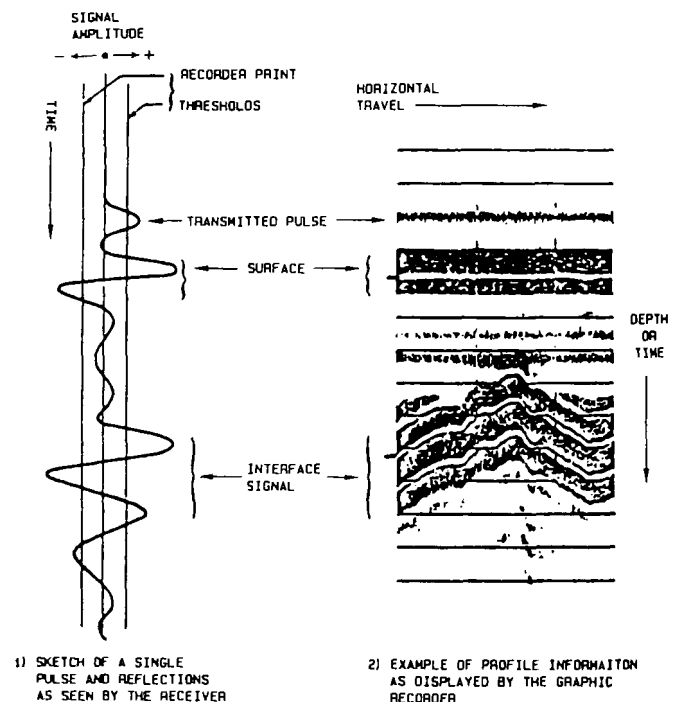
Figure 4
Example of a Single Radar Waveform 'and
Resulting Graphic Record
(from Geophysical Survey System, Inc.)

The horizontal scale of the radar graphic record is governed by the rate the antenna moves across the ground surface and by the rate at which paper feeds through the graphic recorder. Typical rates for moving the antenna across the ground surface range between 1/2 and 2 miles per hour.[2] Vertical lines (markers) placed on the graphic record that correspond to survey flags located at regular intervals along the line of traverse can be used to indicate the distance traversed.

The vertical scale of the graphic record is a function of the amount of time required for the radar signal to propagate from the antenna through the subsurface and then back to the antenna. This is known as "two-way travel time" and is a function of the velocity that radar

energy propagates through a medium; the travel time is governed by the electrical conductivity of that medium.[1] The velocity (V) of radar energy through a medium is related to the velocity of light (C) by a constant termed the dielectric permittivity (Er) through the following:

$$Er = \frac{C^2}{V^2} \qquad (1)$$

because C = 1 ft/ns

$$Er = \frac{1}{V^2} \qquad (2)$$

where V is ft/ns

Radar energy velocity (V) is related to two-way travel time (t) and the distance (D) traveled by:

$$V = \frac{2D}{t} \qquad (3)$$

Therefore, when the dielectric permittivity is known, the effective propagation velocity is:

$$V = \frac{C}{(Er)^{-2}} \qquad (4)$$

where C = 1 ft/ns

and the depth (in feet) to any radar interface is:

$$D = \frac{Vt}{2} \qquad (5)$$

The radar data are displayed on the graphic record in nanoseconds (ns) of two-way travel time. The maximum two-way travel time recorded is established manually on the radar unit by setting the range dial to a specific range. Ten equally spaced horizontal lines are printed on the graphic record and can be used as a vertical scale in nanoseconds of two-way travel time. Thus, the depth to any radar interface displayed on the graphic record can be calculated by picking the travel time where the radar event occurs and substituting this value for t in the above equation.

The value for radar velocity (V) used will depend on the dielectric permittivity (Er) of the material that the radar propagated through. Values of dielectric permittivity (dielectric constant) tabulated from Morey[1] and radar velocity calculated using the above formula are shown in Table 1.

Table 1
Approximate Conductivities, Dielectric Constants and Radar Velocities for Various Earth Materials

Material	Approximate Conductivity (mho/m)	Approximate Dielectric Constant	Two-Way Interval Time (ns/ft)	Velocity (ft/ns)
Air	0	1	2	1
Fresh Water	10^{-4} to 3×10^{-2}	81	18	0.11
Fresh Water Ice	10^{-4} to 10^{-2}	4	4	0.50
Permafrost	10^{-5} to 10^{-2}	4 to 11	4-5	0.50-0.45
Granite	10^{-6} to 10^{-3}	5.6 to 8	5-6	0.42-0.35
Dry Sand	10^{-7} to 10^{-3}	4 to 6	4-5	0.50-0.41
Sand, Saturated (Fresh Water)	10^{-4} to 10^{-2}	30	11	0.18
Silt, Saturated (Fresh Water)	10^{-3} to 10^{-2}	10	6	0.32
Clay, Saturated (Fresh Water)	10^{-1} to 1	8 to 25	6-10	0.35-0.20
Average "Dirt"	10^{-4} to 10^{-2}	16	8-10	0.25-0.20

Approximate values for conductivity and dielectric constant are tabulated from Morey (1974) and two way interval time from Benson et al (1982). The values for velocity are calculated from the formula V = 1/(Er)$^{-2}$ as discussed in the text. Two way interval time is defined in ns/ft as twice the reciprocal of radar velocity. It is used for convenient calculations of depth to a radar interface: divide the travel time of a radar interface picked from the graphic recorder by the medium's two-way interval time.

For convenience of field calculations, some workers[2] use a parameter called two-way interval time (Table 1), which is defined in ns/ft as two times the reciprocal of velocity. Hence the depth (in feet) of a radar interface is calculated by dividing the two-way travel time picked from the graphic record by the two-way interval time of a given material. However, if the mineral composition or the moisture content of the subsurface changes with depth, then the velocity is not constant with depth and the vertical depth scale is not uniform.

The depth of penetration of the radar signal is inversely related to the radar frequency and to the conductivity of the ground surface. Conductivity is directly related to groundwater salinity and to the amount of clay minerals present in the subsurface. Penetration depths typically range between a few feet and tens of feet, unless the subsurface is nearly devoid of clay minerals. However, examples of penetration depths of more than 75 feet have been reported in areas where the subsurface consists exclusively of sand and gravel.[3,4]

Methods

A Geophysical Survey Systems, Inc. SIR System 3 Ground Penetrating Radar (GPR) unit was used with a single 80 megahertz antenna. The antenna was connected to the radar unit by 100 feet of electric cable and the unit was powered by a standard car battery. The radar unit was operated with print polarity set to +/−; paper take-up set to off; paper speed set to 200 lines per inch; radar antenna scans set to 16 scans per second; surface gain set to 3.3; mid-depth gain set to 2.2; deep gain set to 3.5; and range set to either 100 or 50 ns

Before obtaining radar data, the position of each line along which data were to be obtained was accurately identified in the field and its position placed on the field map. Additionally, survey flags were placed every ten feet along each line. Figure 3 shows the locations of the data lines. Because of the rough terrain and the debris in Feature 3 and in the northern end of Feature 2, radar data could not be obtained in these areas.

Radar data were acquired by rolling the radar antenna at a constant rate along the ground following the predetermined lines. Registration marks were placed on the graphic record (vertical dashed lines on Figures 5 and 6) to denote the location of the antenna as it was rolled past each of the flags along the data lines. These registration marks provide a horizontal scale on the graphic record of the radar data.

Based on examination of the published geological map[5] of the area and on observations made in the field, we concluded that the subsurface is predominately composed of clay with minor amounts of silt and sand. Such material typically has a radar velocity of approximately 0.20 ft/ns[1] or a two-way interval time of approximately 10 ns/ft.[2] If we assume that the subsurface has relatively uniform electrical properties to the depth of radar penetration for the radar range used, then the vertical scale for the radar graphic records obtained for data acquired with range set to 100 ns is approximately 1 foot per each horizontal calibration line and the vertical scale for the data acquired with the range set to 50 ns is approximately 0.5 feet per each calibration line. Thus, the radar data acquired when the range was set to 100 ns were from a maximum depth of approximately 10 feet, and data for the 50 ns range was from a maximum depth of approximately five feet.

A preliminary interpretation of the radar graphic record was made in the field immediately after acquisition of radar data from each line. Annotations were made directly on the graphic record. This preliminary interpretation permitted making initial judgments on data quality and on where additional data might be needed to better define features detected by the radar.

Interpretation

The radar data were interpreted for the presence of zones of subsurface disturbance and zones of signal loss (Figs. 5 and 6). Zones of subsurface disturbance are recognized by the sudden irregular disruption of the uniformly horizontal bedding pattern present in undisturbed layers. These zones may mark areas that have been disrupted by man-induced processes such as digging. Zones of signal loss are recognized by large white areas on the graphic record. Signal loss can appear in a radar

graphic record if two laterally adjacent subsurface areas have very different electrical conductivities, which causes the radar velocity to be very different in each of the adjacent areas of the subsurface. Man-induced processes (e.g., digging followed by filling) that result in placing materials of substantially different conductivities adjacent to one another in the subsurface may result in signal loss.
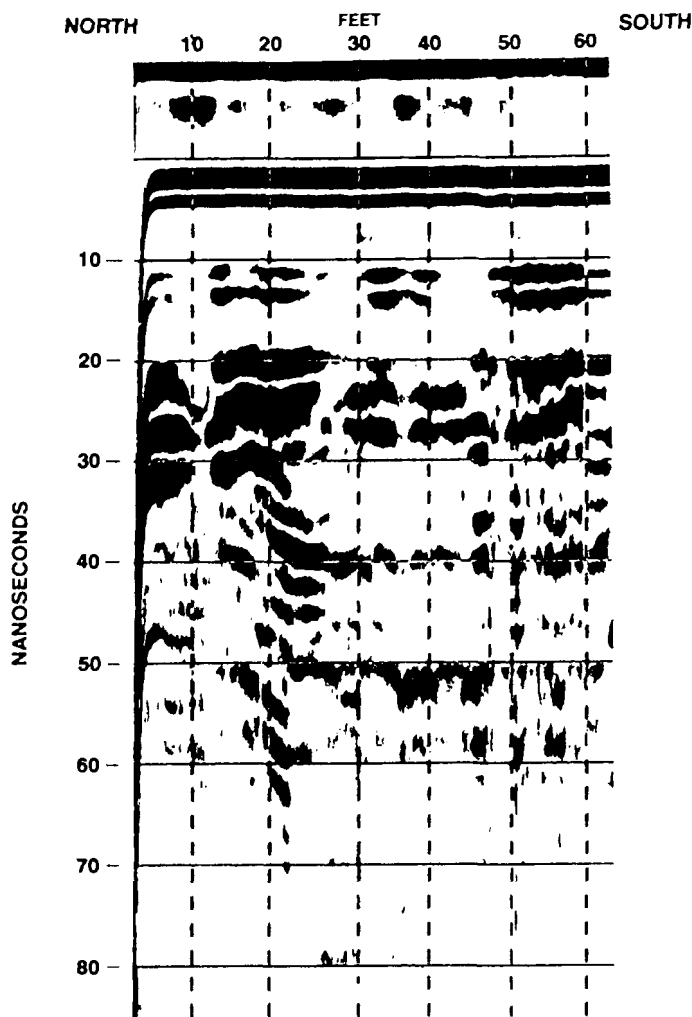
Figure 5
Radar Graphic Record Crossing Feature #1. The Distance Traveled Along the Traverse is Posted in Intervals of 10 Feet. Data was Collected Using an 80 Megahertz Antenna with the Range Set at 100 ns. Note the Loss of the Signal Between Approximately 26 and 50 Feet Along the Traverse.

Three Features (Features 1, 2 and 4 in Figure 3) identified on the 1966, 1967 and 1972 aerial photographs and during the field reconnaissance as areas of concern each show evidence of subsurface disturbance and signal loss on the radar graphic records. Two additional areas (Features 5 and 6 in Figure 3) show evidence of subsurface disturbance on the radar graphic records. Features 5 and 6 lack any obvious surface indications.

Features 1 and 2 are visible on the 1966, 1967 and 1972 aerial photographs as depressions and are partially marked on current ground surface by a lack of grass. Feature 1 appears in radar data lines E, F, G, H and I as a zone of signal loss occurring at the same location where the ground surface is devoid of grass cover. Figure 5 is a portion of radar data line F showing such a signal loss. Assuming a radar velocity of 0.20 ft/ns for the subsurface material at this location, the zone of

signal loss extends to approximately between 3 and 5 feet below the ground surface.
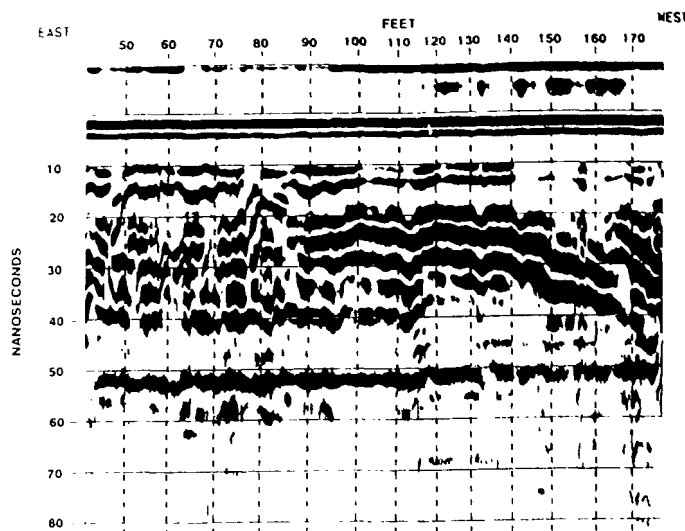
Figure 6
Radar Graphic Record Crossing Feature #4. The Distance Traveled Along the Traverse is Posted in Intervals of 10 Feet. Data was Collected Using an 80 Megahertz Antenna with the Range Set at 100 ns. A Subsurface Disturbance Occurs Between Approximately 40 and 85 Feet Along the Data Line. The Subsurface is Apparently Evenly Bedded Between Approximately 85 and 180 Feet. The Gentle Upward Slope of the Ground Surface Toward the West Creates a Dip in the Radar Data from Approximately 130 Feet West Continuing Toward 180 Feet Along the Traverse.

Feature 4 is visible in the 1972 aerial photographs as a depression and is partially marked at the present-day ground surface by the presence of a rust-colored material. This feature appears clearly in radar data line A (Fig. 6) as a subsurface disturbed zone extending approximately 85 feet west from the chain link fence near the eastern property boundary. The rust-colored material at the land surface extends approximately 70 feet west of the chain link fence. Thus, based on the radar data, Feature 4 extends approximately 15 feet further to the west in the subsurface than is apparent by surficial observations. Assuming a radar velocity of 0.20 ft/ns for the subsurface material at this location, the zone of subsurface disturbance extends to at least 4 feet in depth.

Features 5 and 6 are marked by a slight subsurface disturbance on data lines B and C, and K and H. These features are not visible on the historical aerial photographs and they have no distinguishing surface characteristics. This slight subsurface disturbance is of concern because it has the same character as the subsurface disturbance apparent on the radar data lines that cross historical topographic depressions (e.g., Features 1 and 4).

CONCLUSIONS

Six features were identified on historical aerial photographs as topographic depressions, similar in character to dug pits. Four of these historical depressions are partially marked on the current surface by slight topographic depressions and/or a partial lack of grass cover. The remaining two features lack any evidence on the current land surface that historical depressions may have been existed. Five of the six historical depressions were located within the area investigated using ground penetrating radar. All of those five features show evidence of subsurface disturbance or signal loss visible on the radar graphic records. Furthermore, the only locations with the area investigated using GPR that show subsurface disturbances or signal loss are the areas where these five historical depressions were located.

Thus, using both historical aerial photographs and ground penetrating radar provided complementary information that permitted identifying pits that may have been used to bury wastes in a portion of this property. The historical aerial photography permitted initial identification of areas of concern as possible waste pits. Acquisition and analysis of GPR data provided confirmation of the presence of subsurface disturbances and thus permitted identification of no longer existing or partially existing topographic depressions that are believed to have been used for waste disposal. These data provided information, prior to drilling, to allow us to delineate (partially) buried pits and provided us a method to identify the optimum (and safe) drilling locations for investigating potential impacts the waste may have on groundwater.

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RD/RA Sampling Strategies for the Field Verification of Waste Disposal Areas

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ABSTRACT

The strategy for developing and obtaining U.S. EPA acceptance of a verification sampling program for the identification of the lateral extent of a source area is discussed, along with the problems encountered with the execution of the program at the project site. The sampling program features the use of discrete and composite sampling of excavation faces, along with the development of a grid system for tracking and registering of sample collection grids.

The project site is an active aluminum reduction facility in the western United States. Historical waste management and handling practices resulted in the contamination of surficial sediments and the shallow groundwater horizon. U.S. EPA requirements for the remediation of the site identified soil cleanup criteria and required a sampling and analytical program be established to verify that the remediation criteria were attained. The boundaries of the waste management and handling areas were defined by the location of existing plant structures, surface drainage features and plant boundaries (the historic limits of waste placement). Other factors interacting in the verification sampling program were the rocky fill materials encountered within the sampling areas and the impact of the active plant structures.

The verification sampling program was implemented successfully and identified the need for additional soil removal in selected areas. The verification sampling program successfully identified the horizontal and vertical distribution of contaminants in the shallow soil horizon and provided assurance to the U.S. EPA that the soil remediation activities addressed the lateral extent of waste placement at the site.

INTRODUCTION

A strategy for verification of the historic limits of waste management and handling areas was required such that impacted areas at the site would be isolated and removed for long-term management, in accordance with the recommended alternative presented in the Record of Decision (ROD). In response to the need for verifying the removal of surficial soils impacted by previous waste management and handling practices, a verification sampling program (VSP) was developed, accepted by the U.S. EPA and implemented as an element of the CERCLA Remedial Actions.

The selection and application of verification sampling techniques at the site was facilitated by the identification of several sampling constraints. The location of active plant operating units (structures or capital facilities), the historic location of plant structures defining the limits of waste management and handling, and the confines of the actual plant area were all used to define the scope of the overall approach to implementing the verification sampling program.

BACKGROUND

Geologic Setting

The project site is located adjacent to the Columbia River in northern Oregon and was constructed in the river floodplain. Due to the impoundment of the Columbia in this reach, flooding is no longer a concern in the area. The surface stratigraphy of the site is dominated by deposits of volcanic basalt described as the Columbia River Basalt Group (CRBG). The CRBG, formed from approximately 300 basalt flows that erupted from linear fissures in the Columbia Plateau, and was deposited between approximately 6 and 17 million years ago. The surficial basalt formations in the area of the project site are characterized by undulating and often jagged and angular surface profiles created by environmental conditions during the spreading and cooling of the lava flows and by the process of weathering of the exposed materials. Portions of the basalt rock are present at elevations above the general ground-surface elevation, which is established by the wind-blown sands and sediments which occupy the pockets and crevices of the basalt surface. Based on the results of regional geologic investigations and site-specific hydrogeologic assessments, the upper basalt formations serve as a confining unit, separating surface and subsurface waters from deeper and more transmissive units below. The surficial basalt tended to dip in the direction of the river, and some generalized surface drainage features are present in the area.

Plant Activities

The project site is the location of an operating aluminum reduction facility. The waste byproducts of the aluminum reduction process include spent potlining materials (also referred to as cathode waste), which are the protective lining materials placed between the reduction vessels and molten aluminum. The management of these materials was accomplished by commercial recycling from 1961 to 1971. Potlining waste materials were managed on-site within designated areas between 1971 and 1984.

The aluminum reduction facility uses the Herroult process for the reduction of aluminum oxide to elemental aluminum, which utilizes an anodic/cathodic cell to separate the elemental aluminum and oxygen ions. The magnetic field is established and maintained in the reduction cells with the use of electrical current. The elemental aluminum in the reduction vessels exists in a molten state and is separated from the vessel by lining materials consisting of carbon blocks, refractive bricks and carbon paste, collectively referred to as the potlining. At the end of the useful life of a reduction vessel (when skin temperatures on the vessel indicate that the breakdown of the protective lining is imminent), the vessel is removed from service and dismantled once the spent lining materials have cooled.

Spent potlining materials were managed at the site and contained within designated waste handling and storage areas. The characteristics of the spent potlining materials made them useful as a general fill material. Therefore, as the need for additional work area increased, work areas occasionally were expanded using spent potlining materials.

In 1983, the State of Oregon Department of Environmental Quality listed spent potlining material as a hazardous substance. A waste storage facility was constructed in 1984, and the spent potlining materials previously stockpiled at the site were relocated to this interim status storage facility.

RI/FS Summary

In 1983, the U.S. EPA performed a hazardous ranking of the site after cyanide concentrations above detection limits were detected in one of the plant production wells located adjacent to the spent potlining storage area. In 1985, the principal responsible party entered into a consent order to conduct an Remedial Investigation and Feasibility Study (RI/FS).

A total of 23 individual study areas of the site were included in the scope of the Remedial Investigation (RI) which included the sampling of soil, groundwater, stream sediments and surface waters. In addition, perched water (water trapped on the surface of the basalt rock) was identified beneath four potlining handling and management areas. The perched water was an accumulation of leachate that had been generated from the open storage of spent potlining materials in direct contact with the ground and/or general fill. An electromagnetic survey of the spent potlining handling and storage areas was performed to estimate the volume of perched water estimated that between 0.5 and 2.0 million gallons of perched water were present.

The primary constituents associated with spent potlining materials were polynuclear aromatic hydrocarbons (PAHs), cyanide and fluoride. The sources of the PAHs are the raw carbon materials in the carbon block and pastes used to assemble the cell and reaction of the materials in the reduction environment, while cyanide is created as an undesired product of the reduction of atmospheric nitrogen with carbon dioxide and the carbon blocks. Fluoride is a residual waste from the catalytic agents used in the reduction process.

Applicable or Relevant and Appropriate Requirements (ARARs) were identified during the RI/FS process for fluoride, cyanide and PAHs to determine which study areas were impacted by spent potlining materials handling and management and to provide cleanup criteria. The Risk Assessment (RA) evaluated the three constituents of concern. Cyanide concentrations present within the soil matrix were below the risk threshold value and were not applied as a soil ARAR. There were no discernible risks associated with fluoride in the soil matrix. However, the ARAR for fluoride in the soil matrix was derived utilizing a conservative approach for the protection of groundwater. Urban background concentrations for PAHs were determined to be acceptable soil ARARs. ARARs for cyanide concentrations in surface water were statutory and, based on an EPA health advisory for adults for groundwater, the ARARs for fluoride were statutory for both surface and groundwaters. PAHs were not detected in the surface or groundwaters.

Soil samples taken from the former spent potlining handling and management areas revealed only one study area which exceeded ARARs
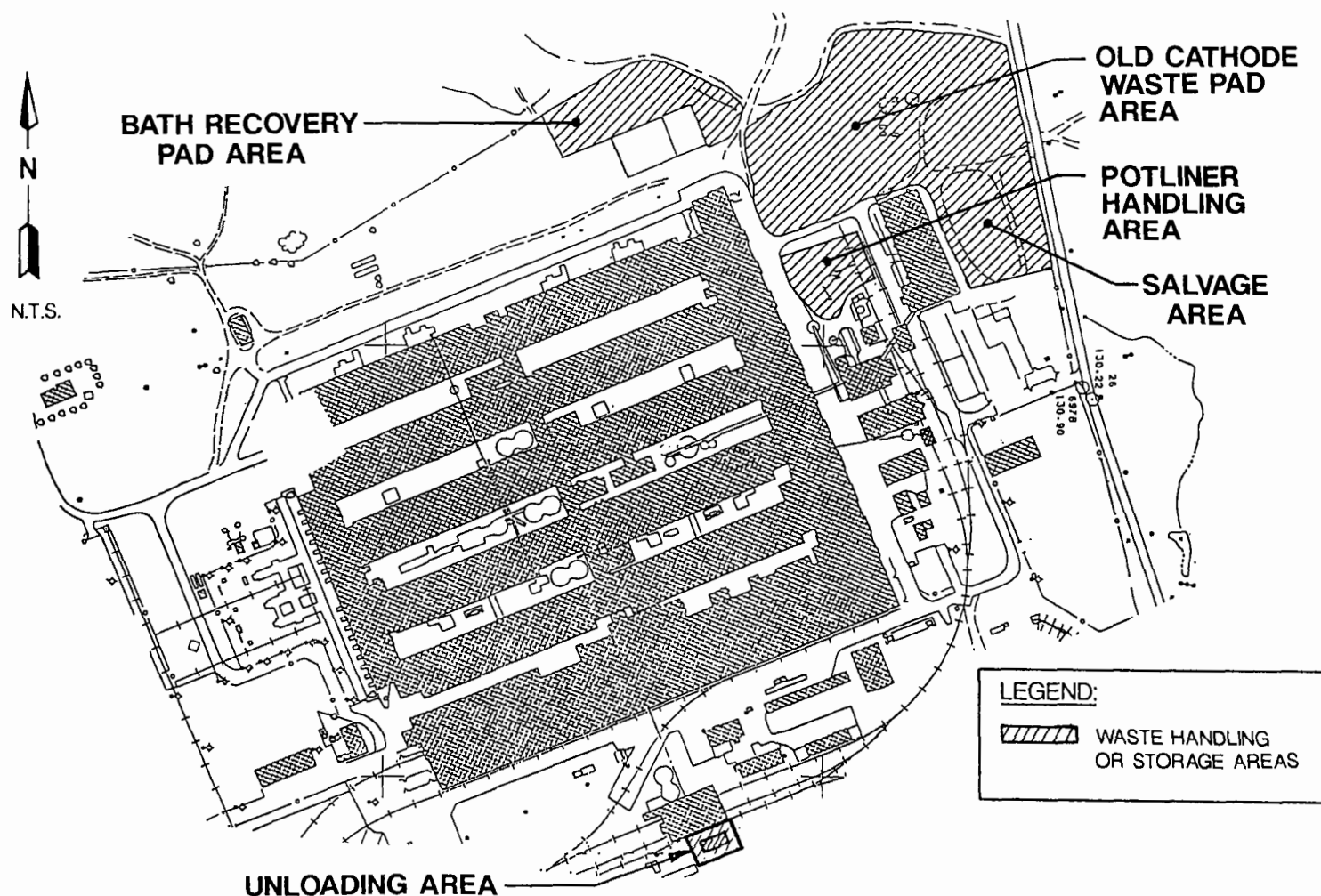
Figure 1
Location of Waste Handling and Storage Areas

based on known waste characteristics of spent potlining materials. The perched water exceeded ARARs for cyanide and fluoride when compared to surface and groundwater standards. Since spent potlining materials had been used as general fill in areas where perched water was present, an important strategy was developed to treat the perched water as a source, rather than as a shallow groundwater system. This strategy required the removal of the fill materials and a one time collection and treatment of the perched water. The strategy involved the collection and treatment of a concentrated and potentially mobile source and was determined to be the preferred alternative when compared to other options requiring containment (capping and other source controls) with long-term groundwater management.

DEVELOPMENT OF THE VERIFICATION SAMPLING PROGRAM

The verification sampling program (VSP) was developed based on the analysis of site-specific conditions and the previously-established needs for assurance that the limits of waste placement were determined. The purpose for the VSP was to: (1) establish and document the physical extent of soil and perched water contamination at the site; (2) establish an appropriate methodology for detecting the presence of contaminated materials; and (3) implement the plan, including the contingent measures to be taken in the event that an exceedance of the sampling criteria occurred. The process utilized in the development of the VSP required that the following site data be collected and interpreted in the approximate order as presented in the following items:

- Definition of the historic areas of spent potlining materials placement at the site
- Establishment of verification sampling constituents and the respective concentration limits
- Identification of the vertical and lateral constraints to verification sampling
- Selection of areas for verification sampling
- Detailed analysis of the verification sampling areas
- Selection of an sampling strategy, based on implementability and effectiveness
- Development of sampling procedures and establishment of field procedures
- Establishment of quality assurance protocol

Definition of Historic Areas of Spent Potlining Materials Placement

The areas of the project site in which spent potlining materials handling and storage activities occurred are presented in Figure 1. The principal waste handling and storage area is bounded by plant buildings and access roads, a surface drainage ditch and a county road. The identified Salvage and Bath Recovery Pad Areas both possessed a boundary which could not be accurately defined based on historic data. The Unloading Area is a site area in which waste materials were used as general backfill during the development of a parking and storage area. The intent of the VSP was to provide assurance that these boundaries represented the lateral limits of contamination.

Definition of Sampling Constituents and Sampling Criteria

Two spent potlining material constituents were identified as a primary concern in the verification of soil remediation at the site: fluoride and PAHs. Research into the types of PAHs which were present in the spent potlining materials identified seven individual PAH compounds which were known or believed to exhibit the characteristics of carcinogens in the human body at reference doses and identified periods of exposure. These individual PAH compounds were referred to as carcinogenic PAHs (cPAHs). The verification sampling concentration criteria for these two classes of constituents were developed as Applicable or Relevant and Appropriate Requirements (ARARs) for the site remediation. The verification sampling criteria were:

Fluoride ≤ 2200 mg/kg

cPAHs ≤ 175 mg/kg (cumulative)

Identification of Sampling Constraints

The identification of constraints used to guide the development of

the VSP occurred as a result of the determination of active, operating units of the facility and the evaluation of historic and institutional land uses on the site. Historic waste placement at the project site was defined by the limits of the areas used for spent potliner materials storage. As presented previously in Figure 1, the spent potlining placement areas were bounded substantially by the locations of plant buildings and facilities. The delineation of areas in which perched water contamination was expected (due to perched water travel in the general direction of the Columbia River) identified that the active plant structures were located in areas hydraulically upgradient of the expected direction of travel. The active plant structures and facilities represent significant capital assets of the reduction facility and were a consideration in the definition of excavation and verification sampling limits. Based on these data, the active operating structures were not considered for demolition or for verification sampling.

Figure 1 shows that an eastern boundary of the facility is a county roadway. The historic alignment of the roadway was useful in defining the limits of waste placement at the site. As areas east of the county road were not used for spent potliner materials handling or storage, samples collected and analyzed during the RI verified these areas were not impacted by spent potlining materials or residuals. Selected areas east of the roadway were excavated to determine what, if any, perched water transport may have occurred. The roadway alignment was considered a limit of waste placement for the purposes of waste excavation and verification sampling.

Physical constraints encountered during VSP development included compliance with OSHA excavation requirements and the presence of site utilities in the verification sampling areas. OSHA requirements were observed during the establishment of stable trench-face configurations for the areas. Railroad, electric and potable water utilities were accommodated or relocated during design and implementation of the VSP.

Verification Sampling Areas

In consideration of the identified boundaries established by data generated during the RI and the historic land uses at the site, three verification sampling areas were established. Figure 2 presents the locations of the verification sampling areas proposed to the U.S. EPA for inclusion in the program.

Two separate areal configurations were required to address the needs for verification sampling. The verification sampling areas identified in Figure 2 as the Salvage and Bath Recovery Pad Areas represent a lateral boundary defined by the historic limits of spent potlining materials handling and management. The third verification sampling area, referred to as the Unloading Area, received spent potlining material as general site backfill during expansion of the plant. In order to fully verify the limits of the spent potlining materials placed as general backfill, a boundary completely surrounding the Unloading Area was required.

Sampling Strategy and Quality Control

In developing a program which would achieve the goals of the verification sampling at the site (to provide assurance that any spent potlining materials or residuals would be excavated), be implementable at the site and be practical from a standpoint of providing useful and determinative data, a system of discrete sampling units with supporting quality assurance protocol was established. The process of proposal to and acceptance by the U.S. EPA of strategies for the sampling evaluation involved the combination of several sampling objectives into one cohesive and rational approach. The considerations included in the development of the strategy are identified as follows:

- Definition of sampling cells or units (intended to detect "hot spots" or spikes along the sampling line)
- Selection of sample cell size
- Development of the methodology for collecting and combining samples, based on the results of literature evaluation on the sampling of soil matrices
- Provisions established for the further remedial actions required in response to an identified exceedance

The strategy proposed to the U.S. EPA for the sampling of the soil
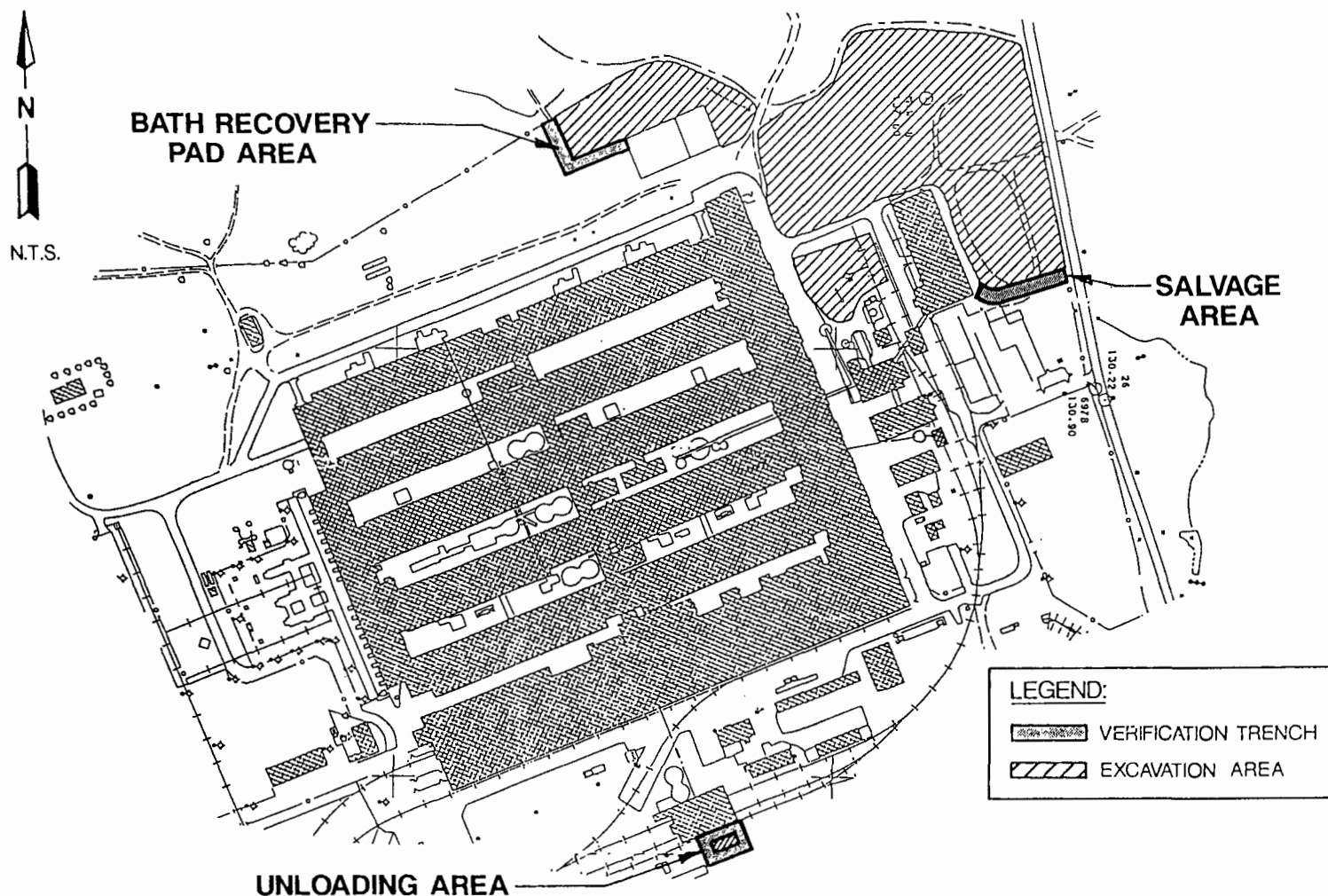
Figure 2
Location of Verification Trenches

column left by the removal of material within the excavation areas involved the division of the exposed face into 500-square foot areas. The individual sampling cells were constructed by measuring the distance along the excavation slope from the ground surface to the competent basalt rock and the calculation of the length of the cell by dividing this length by the 500-square foot area.

One of the primary difficulties encountered in the application of basic sampling principles to the soil matrix (consisting of basalt rock, wind-blown sediment and general backfill components such as spent potlining materials and residuals) was understanding the behavior of the contaminants in the soil matrix. Unlike a liquid matrix in which contaminants are customarily diluted by osmosis into an approximately homogenous mixture, contaminants in a soil matrix are customarily bound or associated with discrete soil particles. The importance of this characteristic to the development of the sampling program is that a soil sample may be composited without a substantial dilution effect—a contaminated soil grain selected for analysis in the laboratory will display a high level of contamination regardless of the effects of compositing. Therefore, the use of limited compositing of the collected samples prior to laboratory analysis was accepted by the U.S. EPA.

The identification of an objective and acceptable method for sample collection from an individual cell resulted in a methodology which utilized the discrete sampling of an arbitrary grid system with the use of a random number table. The sampling cell would be divided into 10 equal-sized areas, and four of these areas would be selected with the use of a random number table for sample collection. Once the four samples were obtained, the samples would be mixed completely and quartered in a sampling bowl, with the sample bottle filled from equal

and sequential aliquots from the four quarters.

The acceptance of the sampling strategy was obtained from the U.S. EPA after several modifications were made to the plan. The U.S. EPA required that the sample cell size be reduced from the original 500-square foot to the 200-square foot size, which resulted in a doubling of the number of samples collected. The strategy for sample collection was modified to reflect the U.S. EPA's concern that all four random samples could be located in one area or quadrant of the sampling cell. This concern was resolved by establishing four rectangular sub-cells within each sampling cell and then sampling each sub-cell, with the sub-samples composited to form the sample. This quartering of the sample cell assured that at least one sample would be collected from each quadrant of the cell. The U.S. EPA requested that an individual exceedance of the sampling criteria in any sampling cell would require that the cell be excavated further and resampled. These requests were incorporated into the sampling program.

Selection of Sampling Grids

The sampling grids were completed in accordance with the previously discussed procedures. Each 200-square-foot area was marked by stringing colored tape from the top of the trench to the toe of the slope. The four 50-square-foot areas were then marked using a different color of tape. The locations of each grid were presented previously in the profile figures. The individual sampling locations were selected with the use of a random number table, and each 50-square-foot area was divided vertically in half and subdivided into the 10 equal-sized grids. The length of the trench face at the sampling location was divided into five segments which determined the height of each grid. The individual

grid locations were not physically marked and a tape measure was employed to accurately identify the sampling locations.

VERIFICATION SAMPLING PROGRAM IMPLEMENTATION

The VSP was implemented at the project site over a 6-day period in 1989. Consistent with the health and safety requirements established for the remedial activities at the site, the verification samplers donned Level D protection garments, which provided a fugitive dust mask, exterior coveralls and gloves, in addition to the standard work ensemble of hardhat, steel-toed boots and safety glasses.

Certain constraints were introduced into the sampling program by the operation of the reduction facility and the ongoing remedial activities. The need for minimizing the open-trench time between excavation and sampling was anticipated; the ambient emissions from the reduction facility and the potential for fugitive dust generation from adjacent excavation activities were identified as concerns which could possibly bias sampling results. Modifications made to the program due to site conditions included scraping material from the sampling face prior to collecting the sample and covering sampling equipment until use.

Table 1
Sampling Procedures and Equipment Checklist
Verification Sampling Program

Procedures

1. Excavate verification sampling trenches at a 3:1 side slope unless otherwise directed by Corps of Engineers Construction Representative.

2. Measure depth from top of ground to basalt surface every 10 linear feet along trench length.

3. Starting at one end of the trench and using the data identified in item No. 2, determine the trench length required to obtain 200 square foot areas along the entire trench.

4. Drive stakes (tied with orange tape) at limits of the 200 square foot areas.

5. Divide each 200 square foot area into four 50 square foot areas. Mark these limits with a stake tied with blue tape.

6. Use a tape measure to locate the previously identified, randomly selected, 5 square foot sampling locations within each 50 square foot area.

7. Collect samples from each 50 square foot area.

8. Mix, quarter, and composite sample. Provide label with all pertinent information.

9. Prepare all samples for shipment to pre-selected analytical laboratory.

Equipment

1. Cargo type mini-van for transportation of supplies

2. 400' of plastic sheet (5' wide) in a roll or individual sheets

3. 5 stainless steel (S.S.) spoons
   5 small (1L) S.S. bowls
   5 large (5L) S.S. mixing bowls or pans

4. 100 glass bottles (1L) wide-mouth, with lids as contained in sample packs or coolers provided by the analytical laboratory.

5. Extension ladder (rented)

6. Wooden stakes (600)

7. Flagging tape (orange and blue), or spray paint

8. 100 bottle labels

9. Coolers for shipment

10. Sample boxes (25 minimum)

11. Detergent (Alquinox, Liquinox, or equivalent)

12. Isopropanol (2 gallons)

13. Fed-Ex labels (pre-typed)

Field observations recorded during the excavation and sampling process consist of: (1) field conditions at the time and date of sampling; (2) the status of work activities and other external factors which could affect the sampling results; and (3) the general depth and composition of earth materials encountered in the sampling areas which are described in this section. A sampling equipment and procedures checklist is presented in Table 1.

Salvage Area

Figure 3 presents the location and alignment of the verification sampling trench excavated in the Salvage Area. Figure 4 presents the verification sampling profile view for the Salvage Area. The outside face was excavated to an approximate 1:1 (H:V) side slope, and the interior face was excavated to an approximate 2:1 side slope. Both faces were stable for sampling operations. The average trench depth was 15 feet resulting in an average trench face length of 13 feet. The greatest depth was at Station 1+10 with a trench face length exceeding 18 feet. The excavated material consisted of silt mixed with rock (up to 0.5 cubic yard in size). Excavation of the Salvage Area continued during sampling activities because dust generation was minimal.

Unloading Area

The limits of excavation at the Unloading Area were visually determined due to the lack of precise historical data on the limits of waste placement. The general location is shown on Figure 5, while Figure 6 is the corresponding profile view of the Unloading Area. The presence of spent potlining materials was identified by its grey-black color and the presence of refractory bricks and other potlining debris. Excavation continued until the excavation faces displayed none of these characteristics. The depth to the basalt surface varied from 5.5 to 8 feet and was excavated at an approximate 1:1 slope adjacent to the railroad tracks. An active power pole present in the northwest area of the excavation prevented the complete removal of waste materials in the Unloading Area until it could be relocated.

Bath Recovery Pad Area

The alignment of the trench excavated in the Bath Recovery Pad (BRP) Area is presented in Figure 7 and the profile is presented in Figure 8. The BRP Area trench was shallow, with trench depths ranging from 1 to 6 feet. The material excavated consisted of large rock (over 1 cubic yard in size) mixed with silt and small rock fragments. No remedial activities were occurring in the vicinity of the BRP Area; however, other construction activities conducted by the plant were ongoing approximately 200 feet west of the BRP Area.

RESULTS OF THE VERIFICATION SAMPLING PROGRAM

Table 2 summarizes the analytical results from the verification sampling program. The results listed for the cPAHs are total combined concentrations of the seven identified constituents.

Evaluation of the data reported in Table 2 identified that three of the sample cells in the program had analytical results which exceeded the concentration limits for cPAHs established in the ROD. The exceedance areas include: (1) the western face of the Bath Recovery Pad Area, sample locations BRP-4 and BRP-5; and (2) the western end of the Salvage Area, sample location SA-12. Appropriate actions were taken, as approved by the U.S. EPA, in further material removal and resampling of the exceedance areas.

The results obtained from the implementation of the program indicate that the objectives of the program were met. Through implementation of the VSP, lateral limits of soil contamination were defined and the effectiveness of the CERCLA Remedial Actions at identifying and removing spent potlining materials and residuals was verified.

The application of verification sampling at hazardous waste sites for the purpose of defining the lateral and/or vertical extent of contamination is a determinative demonstration of the effects of site cleanup. The conduct and results of a verification sampling program are also useful as a public relations tool, demonstrating to the public that the site cleanup has been effective and that verification has been obtained.

Figure 3 (Salvage Area map)

N

0 - FEET - 40
SCALE

HARDPITCH BUILDING

SALVAGE AREA

STA. 1+80
STA. 1+60
STA. 1+40
STA. 1+20
STA. 1+00
STA. 0+80
STA. 0+60
STA. 0+40
STA. 0+20
STA. 0+00

CONTRACTORS STAGING AREA

Water
132.20

MW-27

C.R. 514 (RIVER ROAD)

LEGEND:

VERIFICATION SAMPLING FACE

BUILDING

FENCE

□ □ □
MW-27   MONITOR WELL CLUSTER

CONCRETE RETAINING WALL

Figure 3
Salvage Area

Figure 4 (Salvage Area Trench Profile)

	SA-1	SA-2	SA-3	SA-4	SA-5	SA-6	SA-7	SA-8	SA-9	SA-10	SA-11	SA-12	SA-13	SA-14
FI-	168	143	99.6	252	357	69.3	260	233	170	242	291	350	277	635
cPAH-	35.6	137.1	12.0	72.4	35.1	12.0	60.6	12.0	96.5	96.2	49.8	183.6	84.6	137.6

GROUND SURFACE

LENGTH OF TRENCH FACE (FEET)

BASALT SURFACE AND TOE OF SLOPE

STA. 0+00   STA. 0+50   STA. 1+00   STA. 1+50   STA. 1+85

LEGEND: x   LOCATION OF SUB-SAMPLE   FI-921   FLUORIDE CONCENTRATION (mg/kg)   cPAH-000   CUMULATIVE cPAH CONCENTRATION (mg/kg)

Figure 4
Salvage Area
Trench Profile

LEGEND:
▨ VERIFICATION SAMPLING FACE   ┼ RAILROAD TRACK
▧ BUILDING   ⊕ POWER POLE
–·–×–·– FENCE

Figure 5
Unloading Area

LEGEND: x LOCATION OF SUB-SAMPLE   FI-921 FLUORIDE CONCENTRATION (mg/kg)
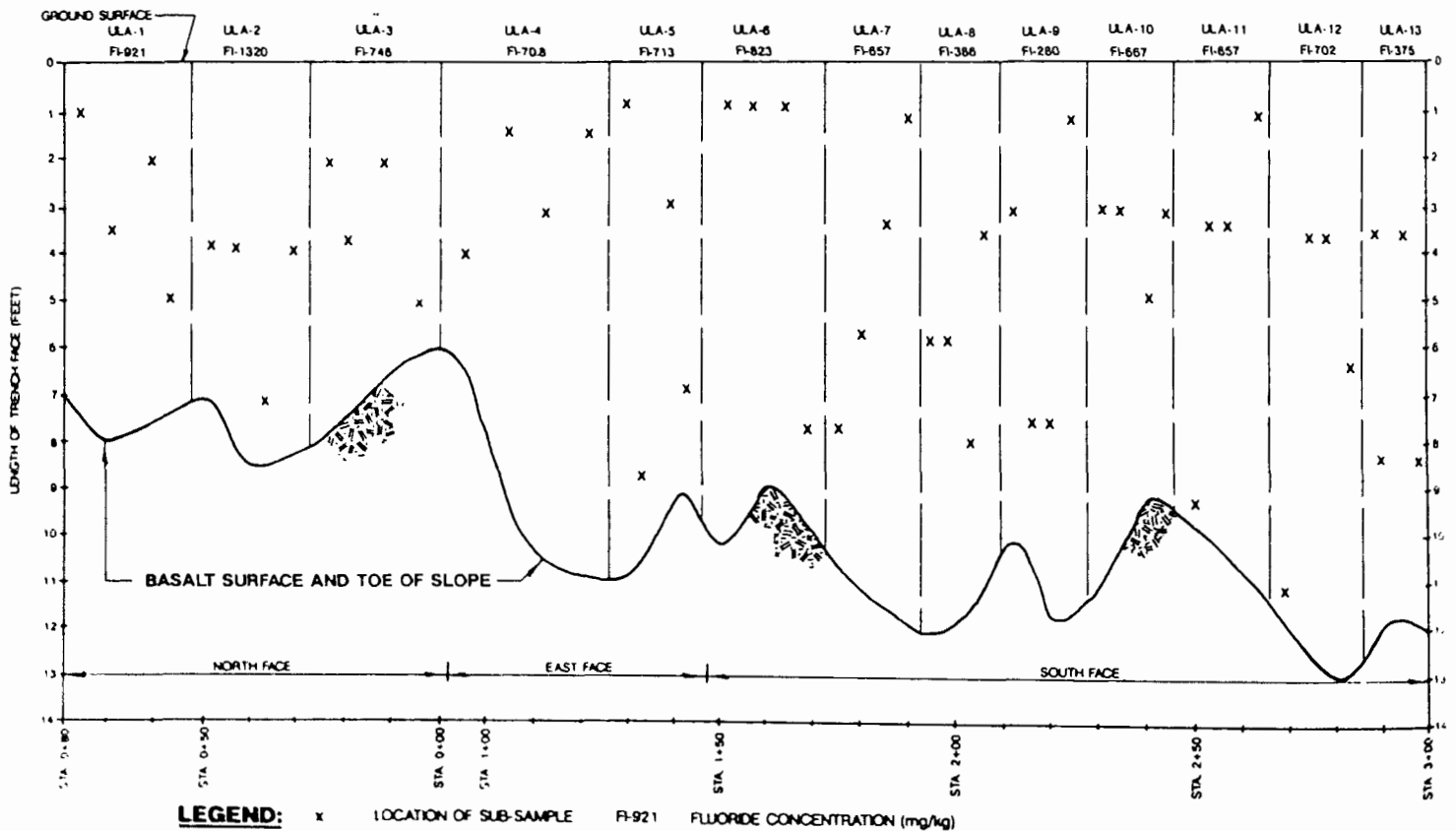
Figure 6
Unloading Area
Trench Profile

LEGEND: [VERIFICATION SAMPLING FACE]   ------- OPEN CHANNEL DITCH
         —x—x— FENCE   vvvvv CONCRETE RETAINING WALL
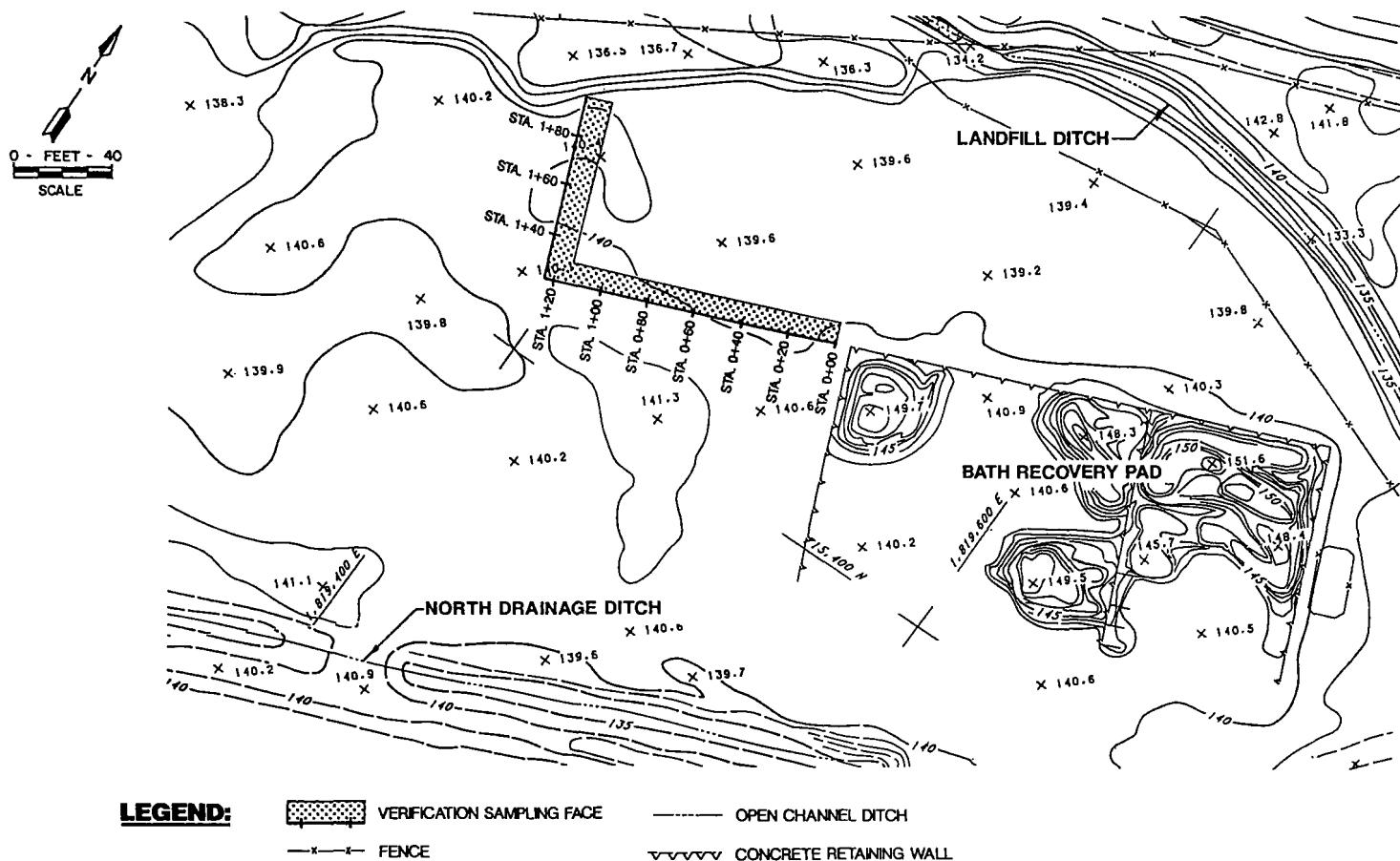
Figure 7
Bath Recovery Pad Area

LEGEND: x LOCATION OF SUB-SAMPLE   FI-921 FLUORIDE CONCENTRATION (mg/kg)   cPAH-000 CUMULATIVE cPAH CONCENTRATION (mg/kg)
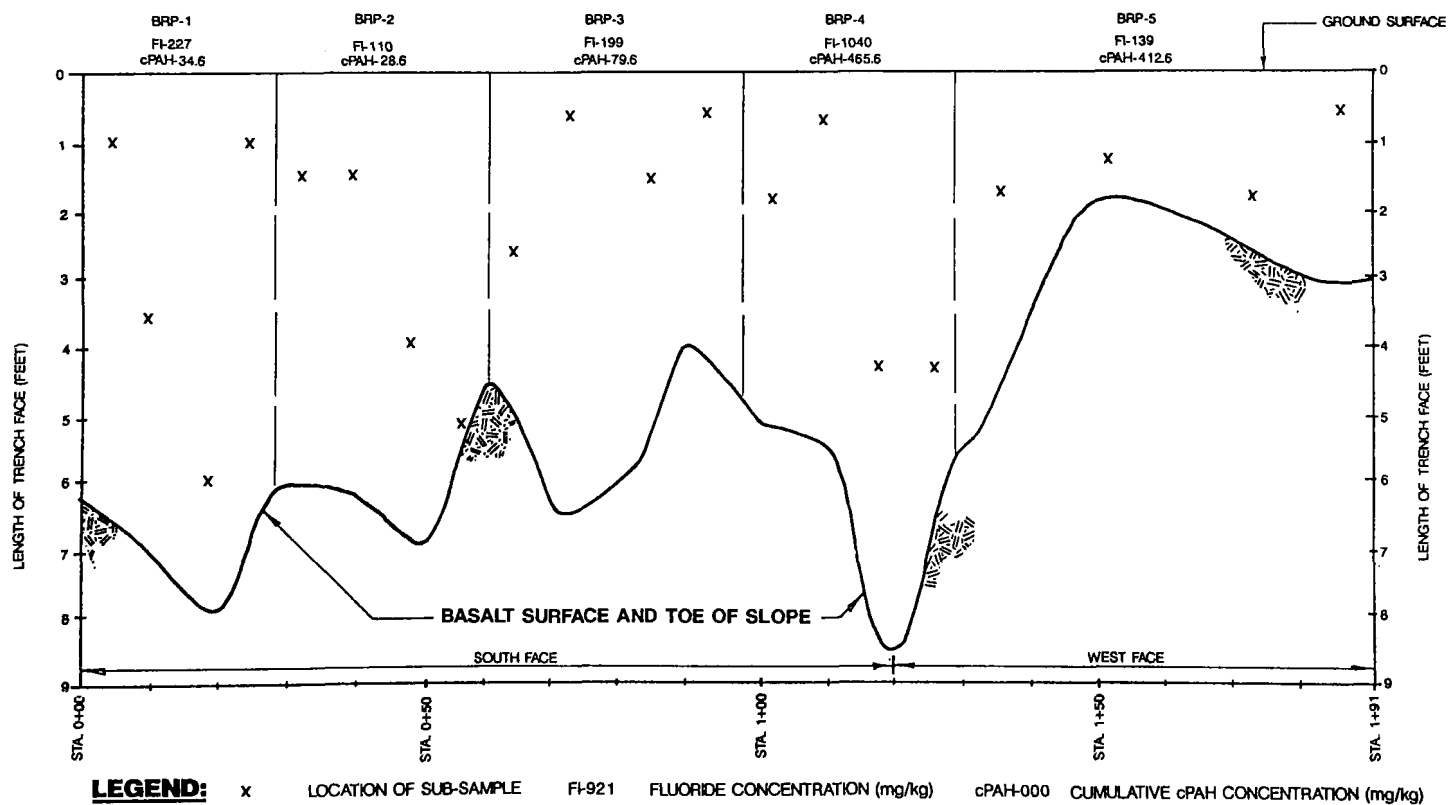
Figure 8
Bath Recovery Pad Trench Profile

Table 2
Summary of Analytical Results
Verification Sampling Program

Sample	Total cPAH Concentration[1] (mg/kg)	Fluoride Concentration (mg/kg)
SA-1	35.6	168
SA-2	137.1	143
SA-3	12.0	99.6
SA-4	72.4	252
SA-5	35.1	357
SA-6	12.0	69.3
SA-7	60.6	260
SA-8	12.0	233
SA-9	96.5	170
SA-10	96.2	242
SA-11	49.8	291
SA-12	183.6	350
SA-13	84.6	277
SA-14	137.6	635
ULA-1	NA	921
ULA-2	NA	1,320
ULA-3	NA	746
ULA-4	NA	70.8
ULA-5	NA	713
ULA-6	NA	823
ULA-7	NA	657
ULA-8	NA	386
ULA-9	NA	280
ULA-10	NA	667
ULA-11	NA	657
ULA-12	NA	702
ULA-13	NA	375
BRP-1	34.6	227
BRP-2	28.6	110
BRP-3	79.6	199
BRP-4	465.6	1,040
BRP-5	412.6	139

[1]   Total cPAHs are the sum of all reported cPAH compounds.

Field Test Kit for Quantifying Organic Halogens In Water and Soil

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ABSTRACT

In a continuing data-gathering program, the U.S. EPA monitors organic chemicals in the waters of the United States. The list of monitored chemicals includes aliphatic and aromatic hydrocarbons, pesticides, industrial chemicals, plasticizers and solvents. Many of these materials are halogenated, produced by chlorination of water during purification processes, through industrial and municipal run-off, natural sources and sewage purification practices.

Chlorine is a contaminant often found in oils, soils, sludges and organic liquids found at hazardous waste sites. Controlling wastewater discharges and landfilling of chlorinated compounds have become priority issues for the U.S. EPA since the passage of the Hazardous and Solid Waste Amendments in 1984.

In response to toxicological and environmental concerns of trihalomethanes and other halogenated compounds present in water and soil, a quick, accurate, easy to use, portable field test kit has been developed for quantifying organic halogens. The analytical procedure requires an extraction with a suitable solvent, followed by colorimetric chemistry to quantify the organic halogens present.

This paper discusses detail field and laboratory results, limits of detection, matrix effect and cost analysis.

INTRODUCTION

U.S. EPA regulation 40 CFR 261 establishes that any used or waste oil containing greater than 1000 ppm organic chloride may have to be classified as a hazardous waste. Chlorinated solvents are the primary contaminants found in waste oils and oily wastes.

Currently available instrumental methods of chlorine analysis (microcoulometric titration, X-ray fluorescence spectometry, oxygen bomb combustion and gas chromatography) are time-consuming and must be performed in a laboratory by trained technicians. Foreseeing the additional testing that would be required under the new regulations, the U.S. EPA Region II contracted Dexsil Corporation to develop a field-portable test kit that could be used by untrained personnel. The result was two small, disposable test kits that require less than five minutes to determine chloride contamination in waste oil. The first method is a go/no-go test, indicating over or under 1000 ppm chloride. The second method is a quantitative analysis giving an amount of contamination between 200 and 4000 ppm.

These test kits were evaluated by Research Triangle Institute in Raleigh, North Carolina) for U.S. EPA and were found to be acceptable methodology for chlorine detection. As a result, the kits were assigned U.S. EPA method 9077, to be published in the forthcoming SW-846 manual.

Interest has since increased in a test kit that would work on oil containing large quantities of water (oily waste) and, in light of the current regulations pertaining to leaking underground storage tanks, it would be useful to have a kit that would detect total organic halogens in soil. Two field-portable test procedures have been developed which address these issues of halogens in wastewater, oily waste and soils. The different methodology and apparatus will be described, the accuracy and precision of each method discussed and the costs of each method reported.

USED OIL CONTAMINATION

How do chlorinated solvents contaminate used oil? Chlorinated solvents are not ingredients of crankcase oil, but are indirectly introduced through careless management practices, such as pouring used degreasing and cleaning solvents into used oil storage drums. The most common solvents found in waste oils are dichlorodifluoromethane, trichlorotrifluoroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene.[1] Levels of contamination range from 100 ppm to thousands of ppm. The presence of chlorinated solvents can be determined by checking total chlorine, an indicator of the potentially hazardous chlorinated substances present.

The U.S. EPA estimates that more than 350 million gallons (approximately 30% of all used oil) are landfilled or dumped annually. Approximately 160 million gallons come from "do-it-yourself" oil changers, who typically dispose of their oil by dumping it on the ground, into sewers, or into waterways, or by placing it with the household trash destined for a landfill that has not been lined to protect against soil and groundwater contamination. The remaining 190 million gallons are dumped or landfilled by automotive shops and industrial facilities.[2]

OILY WASTE SOURCES

Sources of oily waste include bilge and ballast, rain run-off, washings from cleaning vehicles and tanks and cutting oils. All of these materials are predominantly water, containing from 0.1 to 10% oil.

Bilge oil is a mixture of fuel oil, lubricating oil and hydraulic oil dispersed in sea water along with dirt, rust and bacterial sludge. Ballast oil composition depends on what is carried in the ballast tanks when the ship is not in ballast, usually fuel oil, crude oil, or petroleum products. The oil usually will exist as free oil droplets in the seawater, or as a sheen on the water surface.

Rain run-off that carries oil from contaminated areas often cannot be legally discharged to storm sewers. Trucks and fuel storage tanks are cleaned with water containing detergents. This process produces oily water containing solids, emulsions, free oil, dissolved oil and detergents. Metalworking fluids are used for both lubrication and cooling in various machinery processes such as cutting and grinding.

Oily waste resulting from used oil mismanagement causes damage to streams, groundwater, lakes and oceans. For instance, the U.S. Coast Guard estimates that sewage treatment plants discharge twice as much

oil into coastal waters as do tanker accidents - 15 million gallons per year versus 7.5 million gallons from accidents. A major source of this pollution is dumping of oil by do-it-yourselfers into storm drains and sewers. A startling example of this dumping has occurred in the Seattle area, where more than 40% of the water quality trouble calls received are related to used oil and other wastes dumped down storm drains, thus contaminating water bodies.[3]

ENVIRONMENTAL IMPACT

Many contaminated sites containing oily wastes and oily waste sludges are now being cleaned up under authority of Superfund. The Superfund regulations govern the handling of oil wastes in the areas of spills and accidental releases, leaky storage tanks and abandoned storage facilities. Oils from abandoned storage facilities fall into one of three categories: (1) abandoned tank pumpings, (2) abandoned drummed oils or (3) sludge pit residues.[4]

The composition of the oils in each of these categories can vary significantly from site to site. Over time, the oils in tanks and drums absorb material from the walls of the container. This process is exacerbated by corrosion due to seasonal temperature variations, rain, mechanical abrasion. The oils are usually significantly diluted by water infiltration. In order to fall under Superfund jurisdiction, must present a danger to the public or the environment. Thus the emphasis is on quick and inexpensive analysis and disposal of the materials, rather than on recycling and reuse.[5] Ideally, hazardous waste determinations, whenever possible, should be carried out in the field to quickly identify the extent and magnitude of the contamination. The advantages of alternative simple chemical tests have been foreseen by the U.S. EPA and some procedures have, in the face of alternative instrumental methods, been examined and subsequently have been approved by the U.S. EPA.

METHOD FOR THE DETERMINATION OF ORGANIC HALOGENS IN WASTEWATER, OILY WASTES AND SOILS

This procedure requires an extraction with a suitable hydrocarbon solvent. Covalently bonded halogens present in the hydrocarbon solvent are then stripped from their solvent backbones by sodium metal according to the Wurtz reaction:

$$2Na + 2R\text{-}X \rightarrow 2NaX + R\text{-}RD \qquad (1)$$

Any halogens that are present (now in ionic form) are extracted into

Table 1
Comparison of Laboratory Prepared Sample Analyses:
Microcoulometric Titration vs Hydroclor™

Sample	Hydroclor™	Microcoulometric Titration
2000 ppm Cl⁻ as Cl₂C₂Cl₂ in 1% oil in pond H₂O	2000 ppm 2500 ppm	1980 ppm 2460 ppm
2000 ppm Cl⁻ in previous matrix + dirt	2250 ppm 2275 ppm	2250 ppm 2210 ppm
1000 ppm Cl⁻ as C₆H₃Cl₃ in 1% oil in pond H₂O	900 ppm 1050 ppm	760 ppm 980 ppm
1000 ppm Cl⁻ in previous matrix + dirt	850 ppm 900 ppm	849 ppm 897 ppm
1000 ppm Cl⁻ as CHCl₃ in 1% oil in pond H₂O + 4000 ppm Cl⁻ as NaCl	900 ppm 975 ppm	996 ppm 959 ppm
1000 ppm Cl⁻ in previous matrix + dirt	1000 ppm 900 ppm	936 ppm 871 ppm

Table 2
Comparison of Laboratory Prepared Antifreeze Sample Analyses:
Microcoulometric Titration vs Hydroclor™

Matrix	Microcoulometric Sample	Titration	HydroClor™
Tetrachloro-ethylene in antifreeze/H₂O	2740 ppm 2670 ppm	2690 ppm 2760 ppm	2900 ppm 2850 ppm
Same	1230 ppm 1140 ppm	1280 ppm 1280 ppm	1200 ppm 1350 ppm
Same	481 ppm 444 ppm	535 ppm 548 ppm	500 ppm 500 ppm
Trichloro-ethylene in antifreeze/H₂O	3000 ppm 3000 ppm	2810 ppm 2800 ppm	3000 ppm 3100 ppm
Same	1200 ppm 1200 ppm	1120 ppm 1160 ppm	1200 ppm 1250 ppm
Same	451 ppm 462 ppm	509 ppm 521 ppm	600 ppm 600 ppm
1,2-Dichloro-ethane in antifreeze/H₂O	2950 ppm 2800 ppm	2820 ppm 2800 ppm	3300 ppm 3300 ppm
Same	1400 ppm 1490 ppm	1370 ppm 1410 ppm	1550 ppm 1600 ppm
Same	697 ppm 711 ppm	693 ppm 671 ppm	800 ppm 800 ppm
1,2,4-Trichloro-benzene in antifreeze/H₂O	3260 ppm	2880 ppm 2940 ppm	2800 ppm 2800 ppm
Same	1400 ppm 1640 ppm	1510 ppm 1620 ppm	1500 ppm 1500 ppm
Same	812 ppm 791 ppm	857 ppm 856 ppm	800 ppm 825 ppm
Chloroform in antifreeze/H₂O	3090 ppm 2930 ppm	2930 ppm 2930 ppm	2900 ppm 2800 ppm
Same	1300 ppm 1310 ppm	1410 ppm 1440 ppm	1400 ppm 1350 ppm
Same	728 ppm 718 ppm	732 ppm 730 ppm	800 ppm 725 ppm

an aqueous buffer, to which is added a color reagent to measure the concentration of the resulting chloride. A solution of mercuric nitrate is added dropwise until a color change from yellow to purple is realized and the concentration (in ppm) is read directly off the dropper.

ANALYTICAL METHOD

Method for Samples Containing Water

Ten mL of the liquid sample are extracted by shaking for one minute with 10 g of an immiscible hydrocarbon and 0.5 g of a (granular) emulsion breaking material. The sample is allowed to settle until it has separated into distinct phases (approximately three minutes).

Approximately one-third of the top layer is dispensed into a vial containing a drying agent which will remove any moisture and inorganic chloride. The vial is shaken and the drying agent is allowed to settle. A 0.34-g aliquot of the dried solvent is then treated with 1.5 mL of a solution of naphthalene in ethyl diglyme followed by 0.4 mL of organic dispersion and metallic sodium and shaken for 1 minute. Buffer solution (7 mL) is then added and the aqueous layer is separated and combined with 0.5 mL of a solution of s-diphenyl carbazone in alcohol.

A solution of mercuric nitrate is added dropwise from a 1-mL microburette. When a true purple color is realized, the test is stopped and the chloride concentration of the original oil/water or wastewater sample is read directly off the microburette.

Method for Soil Samples

Ten grams of the soil sample are extracted by shaking for one minute

Table 3
Comparison of Liquid Superfund Sample Analyses:
Microcoulometric Titration vs Hydroclor™

Sample	Microcoulometric Titration	HydroClor™
TX - 563 ppm	230 ppm	200 ppm
TOX - 242 ppm	242 ppm	200 ppm
TX - 604 ppm	417 ppm	300 ppm
TOX - 315 ppm	396 ppm	350 ppm
TX - 2260 ppm	1187 ppm	1350 ppm
TOX - 1400 ppm	1425 ppm	1400 ppm
TX - 1910 ppm	1539 ppm	1600 ppm
TOX - 1690 ppm	1518 ppm	1700 ppm
TX - 6420 ppm	5750 ppm	5800 ppm
TOX - 5690 ppm	5900 ppm	5600 ppm
TX - 4940 ppm	3270 ppm	3600 ppm
TOX - 3980 ppm	3870 ppm	3400 ppm
TX - 1560 ppm	774 ppm	900 ppm
TOX - 712 ppm	748 ppm	800 ppm

Table 4
Comparison of Laboratory Prepared Sample Analyses:
Microcoulometric Titration vs TerraClor™

Sample	TerraClor™	Microcoulometric Titration
500 ppm Cl⁻ in dry soil	600 ppm / 500 ppm	515 ppm / 509 ppm
600 ppm Cl⁻ in dry soil	650 ppm / 650 ppm	635 ppm / 624 ppm
700 ppm Cl⁻ in dry soil	850 ppm / 650 ppm	700 ppm / 727 ppm
800 ppm Cl⁻ in dry soil	800 ppm / 800 ppm	784 ppm / 790 ppm
900 ppm Cl⁻ in dry soil	950 ppm / 900 ppm	931 ppm / 948 ppm
1000 ppm Cl⁻ in dry soil	1000 ppm / 950 ppm	960 ppm / 979 ppm
1500 ppm Cl⁻ in dry soil	1500 ppm / 1450 ppm	1450 ppm / 1490 ppm
500 ppm Cl⁻ in wet soil	500 ppm / 450 ppm	558 ppm / 595 ppm
600 ppm Cl⁻ in wet soil	700 ppm / 650 ppm	689 ppm / 719 ppm
700 ppm Cl⁻ in wet soil	750 ppm / 800 ppm	654 ppm / 677 ppm
800 ppm Cl⁻ in wet soil	800 ppm / 800 ppm	861 ppm / 883 ppm
900 ppm Cl⁻ in wet soil	900 ppm / 950 ppm	960 ppm / 946 ppm
1000 ppm Cl⁻ in wet soil	1100 ppm / 1000 ppm	1070 ppm / 1080 ppm
1500 ppm Cl⁻ in wet soil	1600 ppm / 1600 ppm	1520 ppm / 1520 ppm
2000 ppm Cl⁻ in wet soil	2050 ppm / 2000 ppm	1860 ppm / 1910 ppm

Table 5
Comparison of Laboratory Prepared Sand Sample Analyses:
Microcoulometric Titration vs TerraClor™

Sample	TerraClor™	Microcoulometric Titration
300 ppm Cl⁻ in wet sand	350 ppm / 300 ppm	312 ppm / 315 ppm
400 ppm Cl⁻ in wet sand	400 ppm / 450 ppm	421 ppm / 429 ppm
500 ppm Cl⁻ in wet sand	500 ppm / 550 ppm	452 ppm / 457 ppm
500 ppm Cl⁻ in dry sand	400 ppm	533 ppm / 528 ppm
600 ppm Cl⁻ in wet sand	575 ppm / 650 ppm	633 ppm / 632 ppm
700 ppm Cl⁻ in wet sand	775 ppm	823 ppm / 812 ppm
1000 ppm Cl⁻ in dry sand	1050 ppm / 1050 ppm	1110 ppm
1186 ppm Cl⁻ in dry sand	1200 ppm / 1250 ppm	1220 ppm
1200 ppm Cl⁻ in dry sand	1200 ppm	1200 ppm / 1200 ppm
1500 ppm Cl⁻ in dry sand	1500 ppm / 1550 ppm	1570 ppm / 1510 ppm
2000 ppm Cl⁻ in dry sand	1800 ppm	1880 ppm

with 12 mL of a mixture that contains 2 mL of distilled water and 10 mL of an immiscible hydrocarbon. The soil is then allowed to settle and the supernatant liquid is filtered through a column containing florisil to remove any moisture and inorganic chloride. A 0.34-g aliquot of the dry filtrate is then treated with 1.5 mL of a solution of naphthalene in ethyl diglyme followed by 0.4 mL of organic dispersion and metallic sodium and shaken for 1 minute. Buffer solution (7 mL) is then added and the aqueous layer is separated and combined with 0.5 mL of a solution of s-diphenyl carbazone in alcohol.

A solution of mercuric nitrate is added dropwise from a 1-mL microburette. When a true purple color is realized, the test is stopped and the chloride concentration of the original soil sample is read directly off the microburette.

ANALYTICAL TESTS, RESULTS AND DISCUSSION

The samples chosen were both laboratory mixtures and Superfund samples containing a range of 125 ppm to 6500 ppm chloride. The procedures employed were the same as those described above, except a packed kit was used (HydroClor™, Dexsil, Hamden, Connecticut). All reactions with this kit are carried out in sealed plastic tubes and all reagents are contained in crushable glass tubes to obviate any need to handle the reagents. This procedure is advisable, as some of the reagents are hazardous to handle in the normal manner. The results obtained from the laboratory samples are shown in Table 1 and Table 2 and the results from the Superfund samples are shown in Table 3. All three tables include results from the microcoulometric titration (U.S. EPA method 9076) of the same samples. The results from both the test kit and the microcoulometric titration of the samples agree very well. It is also clearly demonstrated that no interference occurs in the presence of inorganic chloride.

Laboratory soil samples were also tested in the same manner using an analytical kit (TerraClor™, Dexsil, Hamden Connecticut). This kit is a similar to the one used for liquids, but also provides a simple balance

for weighing out the soil. The procedures previously described were used. The results obtained for wet and dry soils are shown in Table 4 and the results for wet and dry sands are shown in Table 5. Microcoulometric titration results of the same samples are shown in each table, agreement is good between the two methods.

The cost of each kit is $10-15 and no capital investment in instruments is needed. The kits can easily be used in the field and little skill is needed. The test takes approximately ten minutes. With increasing testing requirements, laboratory fees and laboratory turn-around times, the field-portable chemical test with colorimetric end-point would be the first choice for a suspect site or container, prior to laboratory analysis.

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Analytical Field Screening of Soil and Water
By Thin Layer Chromatography

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INTRODUCTION

Thin Layer Chromatography (TLC) has been in use for decades in the chemical industry where it has been used to identify many compounds. Law Environmental, Inc., has employed TLC as a screening tool for on-site environmental analyses. The technique is both qualitative and quantitative for a variety of semivolatile organic compounds, including petroleum distillates, polynuclear aromatic hydrocarbons (PNA), chlorinated pesticides, PCBs, phenols and explosives in soil and water. Low parts per million detection limits can be achieved for most of these compounds through the use of concentration techniques and compound-specific development sprays. TLC is fast, inexpensive, simple to implement and versatile when used as a screening tool.

Currently most screening analyses are accomplished through Gas Chromatography (GC) or colormetric tests. TLC cannot match the detection limits of the more expensive GC for many compounds; however, the sensitivity of a GC may not be required by all projects. TLC is comparable in cost, speed and simplicity to colormetric tests, but is not as susceptible to false positives that often plague the colormetric tests. This paper provides a discussion of the TLC methodology we have employed, a presentation of results and a summary discussion of the advantages and disadvantages of TLC as a field screening tool.

METHODS

This section contains a brief description of sample preparation, procedures and analyses. The methods are mainly based on a modification of the method described by Friedman and Bruya.[1]

Groundwater Sample Preparation—Petroleum Hydrocarbons

Groundwater samples suspected of containing JP-4 and No.2 fuel oil were prepared for analysis by using a modified California Department of Health Services preparation for the semivolatile compound portion of the Total Petroleum Hydrocarbons.[2] A 250 mL sample of groundwater was extracted with two 20 mL aliquots of pesticide-grade methylene chloride. The two extracts were combined and concentrated to 5 mL with a Kuderna-Danish apparatus to yield a 50 to 1 concentration factor.

Soil Sample Preparation

Soils suspected of being contaminated with petroleum products were prepared using the following procedures. A 10 gram soil sample was mixed with 1 to 2 grams of silica gel and then mixed with a 10 mL portion of methylene chloride in a 40 mL vial. The mixture was agitated for 90 seconds. Polynuclear aromatic and pesticide compounds also were extracted by this method.

Soils suspected of containing PCBs were extracted with a mixture of deionized water, methanol and hexane (1:4:5) according to the method

of Spittler.[3] This mixture and soil were shaken for 90 seconds and the solids were allowed to settle out. The hexane layer was then collected.

The concentration method involved decanting the hexane or methylene chloride extract and evaporating the solvent with a hot air blow dryer. Concentration factors were 5:1 or 10:1 depending on the analyte. This concentrate was applied to the silica gel TLC plate. The TLC plate was then eluted in a glass developing chamber containing hexane as the eluting solvent. Methylene chloride was used as the eluting solvent for more polar compounds, such as phthalate, cresol and nitroaromatic compounds.

Analysis

Once the TLC plate was eluted, it was air-dried and developed for compound-specific analysis. The development consisted of exposing the plate to iodine vapor and ultraviolet light. The dried plate was placed in a second glass iodine-charged development chamber. This iodine-charged chamber contained a purplish-red iodine vapor. After 5 minutes, the plate was observed using a 254 nm UV light source, which was placed directly above the glass development chamber. Dark spots appeared against a fluorescent green background if detectable contamination was present.

The detection of all categories of tested compounds was enhanced by using a 7,8-benzoflavone based development spray. Approximately 30 seconds after the removal from the iodine chamber, a mixture containing 1.5 grams of 7,8-benzoflavone in 95 mL of ethanol and 5 mL of 30% sulfuric acid was lightly sprayed onto the TLC plate. This quantity of spray was adequate for observation of several plates and lasted at least eight hours.[4]

Contamination was evaluated by measuring standards (Rfs) and comparing the intensity of the spots to multiple known concentrations of standards. Rfs were measured according to the classical methods.[6,7,8] The origin of the material was assigned a value of 0.0 and the solvent front was assigned a value of 1.0. The center of a developed spot was measured with a ruler for its distance from the origin. This value was divided by the distance of the solvent front from the origin to produce an Rf value for that compound. Intensities of ovals were judged against those produced by standards that were analyzed on the same plate. For example, a sample spot might have appeared to be more intense than the 200 mg/L standard, but less than the 300 mg/L standard oval. This sample was assigned a concentration value of 250 mg/L. Figure 1 depicts the eluted compounds of interest with associated Rf values. An example of the calculation for the Rf of Aroclor 1242 is also included on the figure.

RESULTS

This section briefly describes the results of the TLC experiments

which stem from a groundwater contaminant survey a soil contaminant survey and laboratory investigations.
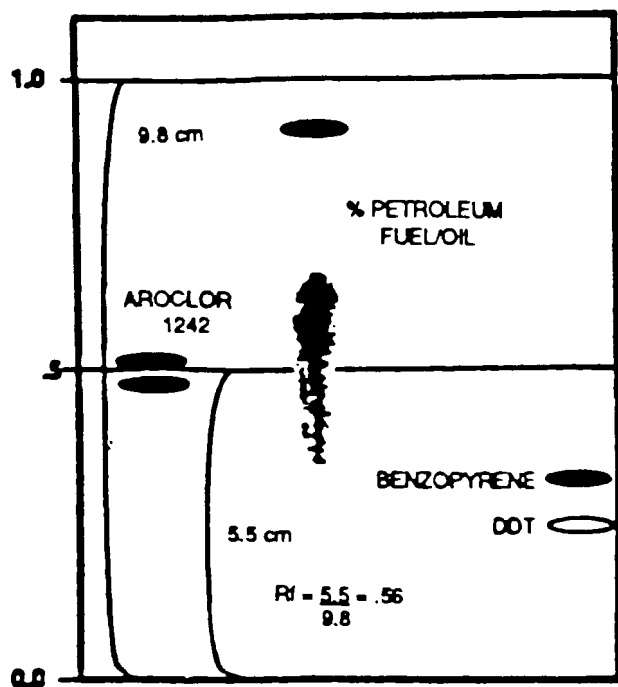
Figure 1
TLC Representation Showing Aroclor and
Petroleum Products Patterns. A Rf Calculation
is Made for Aroclor

Groundwater Samples

The results of the analysis of groundwater samples for fuels were compared to GC-FID results for samples from the same locations. High concentration (percent level) standards of diesel, JP-4 and No.2 fuel oil yielded identical TLC Rf values; however, the appearance of the developed TLC chromatogram pattern was dissimilar. The heavier the fuel, the more intense and streaked the chromatogram appeared at the Rf 0.5 value. The lighter the fuel, the more intense the spot appeared at the Rf 0.9 value. As the concentration of the standards approached environmental concentrations (e.g., 1,000 mg/L), only the 0.9 Rf spot was visible.

Contamination by JP-4 and No.2 fuel oil was not detected at the test site by GC. In order to test the effectiveness of TLC vs. GC on the these fuels, 100 mg/L spiked samples of No.2 fuel oil and JP-4 were prepared and analyzed by TLC and GC-FID. The TLC analysis yielded spiked sample results of 40 mg/L and 60 mg/L on two samples for No.2 fuel oil and 20 mg/L and 40 mg/L for JP-4. These values were confirmed by the GC-FID.

Soil Samples

A screening program was undertaken where 100 soil samples from a second site were screened by TLC for petroleum lubricants and heavy fuels. The objective of this screening program was to aid in the selection of soil boring placement. The soil boring samples were later sent to the laboratory for analysis. Field samples, quality control samples and samples known to be contaminated with petroleum products were analyzed.

A positive result was defined as any sample that exhibited an oval-shaped iodine-stainable material in the 0.8 to 0.9 Rf value region. Standards analyzed for the petroleum products suspected of being present showed chromatographic patterns indistinguishable from each other at detection limits of 100 mg/L. Positive results were obtained for 19 field samples; 7 samples were judged to be in the 100 mg/L range, 10 samples in the 200 mg/L to 400 mg/L range and 2 samples were greater than 1,000 mg/L. Soil samples known to contain used motor oil were com-

parable to high concentration standards of motor oil, except that the 0.5 Rf constituents were clearly more elongated or "stretched."

Quality control samples were analyzed in addition to the standards. These samples included matrix spikes, duplicates and soil blanks. Duplicate samples were analyzed for 10 of the positive samples, with all 10 reconfirmed as positive. Blank samples, consisting of commercial grade sand, were negative for all fuel analyses. Four soil matrix spiked samples were tested for motor oil. All four TLC analyses indicated an approximate recovery of 70% of the motor oil.

A comparison of TLC results for PCBs to a commercially available colormetric test was completed with soil samples from the two sites. The colormetric test yielded a purple color if a sample contained PCBs at concentrations less than 50 mg/L. A pale yellow color was observed if the soil contained PCBs at levels greater than 50 mg/L. One drawback to the colormetric test is that it is subject to interferences from chlorinated compounds found in fuels.[5]

The TLC standards were analyzed with Aroclor 1242, which yielded a detection limit in soil of approximately 35 mg/L. The TLC chromatogram for Aroclor 1242 produces a purplish "dual oval" at an Rf of 0.5. Samples were spiked with a 50 mg/L mixture of Aroclor 1242 and 1,000 mg/L motor oil. The PCB were recovered well and were clearly distinguishable from the motor oil. Analysis times using the PCB test kit and TLC were similar. Thus, simultaneous analysis of fuel and PCB was achieved using the TLC within the same time frame as the PCB test kit. A lower detection limit was also achieved using the TLC method versus the PCB colormetric test.

Soil samples from a site that previously had been characterized by contract laboratory analysis for semivolatiles were tested by TLC. Soils from this site were heavily contaminated with a wide range of polynuclear aromatic compounds. Soils for the TLC analysis were selected from the "hot spots" identified by the contract laboratory analysis results. Benzopyrene was common to many of the analysis results and for this reason this compound was chosen as the primary standard. Standard analysis of benzopyrene established a 1.0 mg/L detection limit with an Rf value of 0.15. Benzopyrene produces dark blue spots when treated with 7,8-benzoflavone spray. Standard mixtures of polynuclear aromatic compounds varied considerably in Rf values due to the differing polarities of each compound.

Two samples were selected for TLC analysis. One laboratory-analyzed sample contained fourteen different PNAs with a total concentration of 0.4%. The other laboratory-analyzed sample contained eight PNAs for a total concentration of 30 mg/L. The 0.4 PNA concentrated level soil sample saturated the TLC plate. That is, the sample chromatogram appeared as a large "slurr" that extended from the 0.0 Rf point to the 1.0 Rf or solvent front end point. The 30-ppm sample showed a column of five oval spots, one of which had an Rf value identical to that of benzopyrene. Benzopyrene was indicated in the results from the laboratory analysis of soil from this area. The TLC chromatogram was judged to be between 30 mg/L and 50 mg/L total PNA content. A sample that was free of PNA compounds was spiked with 200 mg/L of benzopyrene and indicated no detectable loss of this compound when chromatographed.

The pesticide 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT) was analyzed from soil samples obtained from two different sites. A 100-ppm sample was easily detected. DDT appears as a purple oval with an Rf value of 0.25. The detection limit for DDT was determined from the lowest visible standard as 3 mg/L. DDT produces white spots on a light blue background when treated with the 7,8-benzoflavone spray.

The spiked samples included a laboratory-analyzed sample (SS-1) and a previously TLC screened sample (I2) that had not been tested for pesticides. Each sample was analyzed with its corresponding spike sample. Both the SS-1 sample and the spike saturated the plate such that a determination of DDT for each was not possible. The I2 sample did not show DDT; however, the I2 spiked sample showed complete recovery of DDT for the 100-ppm spike.

DISCUSSION

Our study of TLC shows that this method is superior to a soil colormetric test for PCBs, is effective in the analysis of other semivolatile

compounds in soil and is comparable to gas chromatographic analysis of petroleum products in soil. TLC's clearest advantage over GC is cost. Table 1 compares the cost of a typical on-site analysis of 100 soil samples using GC and TLC. GC is approximately twice as expensive as TLC. In addition, much of the TLC's cost are one time purchases (i.e., development chambers, UV lamps, etc.). TLC becomes more cost effective the more it is used. Other factors directly affecting cost are speed and reliability. Since TLC is faster, support personnel should have less time in the field, therefore, reducing the cost associated with personnel time. TLC does not require field maintenance and does not suffer the down time that can be associated with field instrumentation. A timely and inexpensive analysis is very important for site remediation activities.

Table 1
Comparison of GC vs. TLC:
Field Summary of One Hundred Soil Samples

	GC	TLC
Labor*	4,800	2,160

Other Direct Cost** (ODC)

	GC	TLC
GC Rental	2,000	0
Shipping	1,350	625
Columns	300	0
Autosampler	1,200	0
Gases	200	0
Regulators	400	0
Hood	450	450
Syringes	250	250
Glassware	400	400
Chemicals	700	750
Heating mantle	150	0
Heat Gun/Blow Dryer	0	20
Phone	90	90
Refrigerator	75	75
Trailer	500	500
Tubing	50	0
Sample bottles	500	500
Safety Equipment	100	100
Development chambers	0	450
TLC Plates	0	100
UV Lamp	0	150
Total ODC	8,715	4,460
Overall Total	13,515	6,620

* Labor cost are based on $60 per hour billing rate for one person; 80 hours GC (12 samples per day), 36 hours TLC (40 samples per day).

** Rental cost are based on one month rental.

TLC can, in the analysis of some semivolatile compounds, compare favorably with laboratory analysis. The method is very practical for PNA compounds, as indicated by our results from TLC vs. soil samples analyzed by a contract laboratory. Again, cost is a consideration. TLC analysis for semivolatile organic compounds in the soil was accomplished at approximately 1/30 the cost of a laboratory analysis. This is based on $50 per sample analyzed on-site (including labor) vs. $1500 for an average 24 hour turnaround time from laboratory analysis for semivolatile compounds.

TLC was shown to be superior as a screening tool when compared with the soil colormetric test. The cost is similar, but, TLC has the advantages of yielding qualitative and quantitative information. TLC offers simultaneous analysis of multiple components and, most importantly, is not as susceptible to interferences from nonspecific compounds. The colormetric test does offer convenience and ease of use.

In summary, the TLC method is a cost-effective tool for the field screening of samples. It should be considered for use, especially for soils, when low detection limits are not required. The TLC method will have its greatest utility if low cost, fast screening techniques are of premium importance and slightly higher detection limits will meet the need of the data quality objectives of a particular project.

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Monitoring Mercury-Contaminated Soils For Monomethylmercury

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ABSTRACT

Hazardous waste sites that are found to be contaminated with mercury should be further characterized by determining the presence or absence of monomethylmercury. The health risks are greater for the methylmercury than inorganic mercury, and it has been shown that inorganic mercury can be converted to monomethyl and dimethylmercury under anaerobic conditions. A procedure was developed in our laboratory using Gas Chromatography with an electron capture detector to determine monomethylmercury in soils. Hydrochloric acid is used to hydrolyze dimethyl and monomethylmercury to the monomethylmercury chloride. The acidic solution is extracted with benzene and concentrated prior to analysis. The gas chromatography requires conditioning of the GC column with mercury chloride to ensure reliable peak resolution. A method detection limit of 14 ppb (14 ug/kg) was determined. The accuracy ranges from 82 to 117%. The procedure is described.

Using this analytical procedure, nine hazardous waste samples known to be contaminated with mercury were evaluated to determine the presence of organic mercury contamination. Total mercury versus methylmercury concentrations for these samples was nine randomly selected samples, a probability of finding methylmercury appears to be greater than 75%. Risk assessments should include mercury speciation.

INTRODUCTION

The purpose of this paper is to describe a procedure to test for dimethyl and monomethylmercury in soil/solid matrices and the application of this test procedure on six randomly selected mercury-contaminated soil/solid matrices. The Superfund Program, RCRA and NPDES require testing for mercury. A site investigation will usually include the determination of mercury as part of the assessment. Rarely is speciation of mercury into its various organic compounds required. However, determining the mercury species present can help evaluate the potential means of transport from the site via air or water, further delineate the toxicology and/or provide evidence of the source of contamination. Dimethyl and monomethylmercury have been analyzed for frequently in biological species, particularly fish.

Mercury and its compounds are frequently occurring contaminants in the enviroment whose toxicity is well known and characterized. Since 1900, it has been estimated that more than 170,000,000 pounds of mercury have been used in the United States. Major uses of mercury and its compounds include the electrical industry (switches, lamps and rectifiers), producers of chlorine and caustic soda, paint manufacturers (fungal retardants), agriculture (fungicides), paper and pulp (slimicides), catalytic uses pharmaceutical and cosmetic industries.

A U.S. EPA validated procedure does not exist for determining methylmercury in soils. The Food and Drug Administration has been testing for methylmercury for a number of years in fish with a method described in *Official Methods of Analysis of the Association of Offical Analytical Chemists.*[1] The method described is a modification of the AOAC procedure.

ANALYTICAL METHODOLOGY

Solid samples are extracted with benzene and the extract containing any dimethyl and monomethylmercury is transferred to a second test tube and mixed with a warm solution of 70:30 hydrochloric acid: ASTM Type II water. The acid/benzene mixture is heated at 60°C for 2 hours. During the 2 hour span, the mixture should be shaken vigorously. The dimethyl and monomethylmercury chloride in the presence of hydrochloric acid.

The benzene layer containing the methylmercury chloride derivative is concentrated to 10 mL or less by Kuderna Danish or nitrogen evaporation. From 3 to 5 μL of the concentrated extract are analyzed on a gas chromatograph equipped with an electron capture detector. The gas chromatographic column must be conditioned and equilibrated prior to analysis with multiple injections of mercury chloride. The extraction procedure is outlined in Figure 1. A cleanup procedure using an LC-18 solid phase extraction was developed to cleanup sample extracts which may contain interfering compounds.

Solvents/Reagents

Pesticide grade benzene is used for extraction. Toluene probably is an acceptable solvent, but the lower boiling benzene results in faster concentrations. Hydrochloric acid should be ultrapure reagent grade. Ultrex grade from J.T. Baker has a trace amount of mercury that will result in an artifact at the retention time of methylmercury chloride. This trace amount of mercury must be removed prior to use of the acid as a derivatization reagent.

Prepare a 70:30 mixture of hydrochloric acid and distilled deionized water. Extract this mixture five times with a 25% volume of benzene. The acid should always be extracted immediately prior to use. The final volume of benzene wash is concentrated to 10 mL and analyzed by GC-EC to determine the presence of artifacts in the area that methylmercury chloride elutes. A noncontaminated hydrochloric acid mix will result in a nondetectable GC response. Any acid left over from a series of extractions can be stored for later use. However, the acid should be extracted again prior to use because, on standing, an artifact is generated in a lesser yet still detectable amount.

Calibration

For best performance of this procedure, calibration is performed by derivatization of dimethylmercury to the methylmercury instead of the use of purchased methylmercury chloride. Dimethylmercury for for-

tification and calibration may be purchased from Aldrich. A calibration mix from 0.05 mg/L to 1 mg/L of dimethylmercury is prepared in benzene. Each calibration standard is derivatized in the same manner and at the same time as the samples. Experiments were performed which indicate that a derivatization efficiency of approximately 50% to 60% results after acidification at 60 °C for 2 hours. Experiments to improve the efficiency of approximately 100% were not performed. It is assumed more rigorous conditions of temperature, pressure and greater mixing would increase the derivatization efficiency.

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┌─────────────────────────────────────┐
│  PREPARE 70:30 HCL WATER AND         │
│  EXTRACT 5 TIMES WITH BENZENE        │
│  AT A 1:4 BENZENE :ACID RATIO        │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  SAVE FINAL BENZENE WASH AND CHECK   │
│  FOR PURITY BY GC\EC                 │
│  REPEAT CLEANUP IF NECESSARY         │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  WEIGH 10 GR. OF SAMPLE INTO A SCREW │
│  CAP TEST TUBE                       │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  HEAT 10ml OF ACID TO 60C            │
│  IN A SCREW CAP TEST TUBE            │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  EXTRACT SAMPLE 3 TIMES WITH         │
│  10ml OF BENZENE                     │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  TRANSFER EACH BENZENE EXTRACT       │
│  IMMEDIATELY TO THE WARM ACID AND    │
│  SHAKE WELL                          │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  HEAT BENZENE:ACID FOR 2 HOURS.      │
│  SHAKE SAMPLE FREQUENTLY             │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  TRANSFER HEATED BENZENE EXTRACTS    │
│  TO A KUDERNA DANISH AND CONCENTRATE │
│  TO 10ml                             │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  CLEAN UP SAMPLE IF NECESSARY        │
│  BY LC-18 SOLID PHASE EXTRACTION     │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  CONDITION GC\EC WITH 20ul           │
│  INJECTIONS OF MERCURY CHLORIDE      │
└─────────────────────────────────────┘
                 │
┌─────────────────────────────────────┐
│  CALIBRATE INSTRUMENT AND            │
│  ANALYZE SAMPLES                     │
└─────────────────────────────────────┘
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Figure 1
Soil Extraction and Analysis for Methylmercury

Extraction/Derivatization/Concentration

Ten gram soil/solid samples are weighed into a Teflon-lined screw cap test tube. Ten milliliters of the hydrochloric acid derivatization reagent are trasferred to another screw cap test tube, and the acid solution is placed in a 60 °C water bath. The test tubes used should be large enough to hold sample and extracts. When the acid reaches 60 °C, begin extraction of the sample using three 10 mL aliquots of benzene. Shake or vortex the sample vigorously for 3 to 5 minutes. Extraction with benzene may produce emulsions. Centrifugation for 2 minutes at 2000 rpm will reduce the emulsion. Transfer each aliquot of benzene directly to the acid and begin shaking vigorously. Continue to shake the benzene/acid mixture every 10 to 15 minutes for at least 2 hours. Transfer the benzene layer to Kuderna Danish concentrator or another test tube for nitrogen evaporation. The results reported here are based upon a 10-mL final volume. A final volume of 1 mL is easily attained and can result in a 10-fold reduction in the detection limit. Approximately 20 samples can be extracted in eight hours.

Gas Chromatography

Analysis is performed on a gas chromatograph with an electron capture detector. The packing of the separation column should be diethyleneglycol succinate (DEGS) 5% on 100/120 Supelcoport (Supelco, Inc., Catalog Number 1-1870M). The column should be six foot glass with a 2-mm ID and 6.4-mm OD. The instrument conditions use a flowrate of 60 mL/min of argon-methane (95*5), inlet temperature of 235 °C, detector temperature of 325 °C and isothermal runs of 155 °C. By increasing the temperature to 165 °C after 5 minutes, the column can be quickly cleaned of any extraneous compounds prior to the next sample analysis. To prevent carryover, the run times were set at 20 minutes.

The conditioning of the column prior to analysis is critical. Failure to perform the conditioning steps described here will result in poor or no resolution/detection of the monomethylmercury chloride derivative. Various experiments were performed on a number of columns, and the chromatographic conditioning procedure of the AOAC produced the best results. The AOAC procedure recommends first conditioning a new column with a 0.5 hour flush of carrier gas at 30 mL/minute at room temperature, heating to 100 °C for 1 hour, then heating the column at 4 °C/minute until 200 °C and holding overnight. The column is then ready for mercuric chloride treatment.

A mercuric chloride solution (1000 mg/L) is prepared and five 20-uL injections are made onto the column at 10 minute intervals. The oven temperature should be 160 °C. Large, broad peaks will elute and approximately 1.5 to 2 hours after the last injection a large peak will elute. A methylmercury chloride standard at 0.1 mg/L should be injected until the retention time and peak height are stable. The temperature should be adjusted to 155 °C and analysis can begin.

The column should be treated periodically during use to ensure that peak resolution and retention times do not degrade. After the initial treatment, an end of work day single injection of 20 uL of mercuric chloride at a temperature of 115 °C will prepare the column for analysis the following day. A large peak will elute 11 to 15 hours after the injection.

Use of these AOAC-derived chromatographic conditioning procedures resulted in very stable retention times of 2.0 to 2.2 minutes. The peak heights for calibration standards on a day-to-day basis resulted in the variabilities recorded in Table 1. Over the 10-day span there was less than 12% variability in peak heights.

Quality Control

Analyses performed using these procedures must include a method blank that consists of hydrochloric acid extracted in the same manner as the samples. The method blank is absolutely necessary to avoid reporting false positives. Early experiments with improperly prepared hydrochloric acid resulted in an artifact at the same retention time as the methylmercury chloride.

In addition, it is recommended that the calibration standards be prepared by derivatization of dimethylmercury and not from purchased

methylmercury chloride. At least one sample matrix in 10 should be spiked in duplicate with dimethylmercury to determine the precision and accuracy of the extraction. A calibration standard should be run after every 10th sample to ensure peak height and retention time stability.

Table 1
Stability of Day-to-Day Calibration

| | Concentration | |
Day Number	mg/L	Peak Height
1	0.500	21583
2	0.500	18264
3	0.500	20170
4	0.500	18884
5	0.500	16870
6	0.500	23336
7	0.500	15834
8	0.500	21393
9	0.500	22737
10	0.500	20363
Relative Standard Deviation		**11.7%**

Health and Safety

Mercury and its compounds are toxic. Methylmercury and its various salts are especially toxic because they are completely absorbed via breathing or ingestion and not eliminated from the body. All mercury compounds have neurotoxic effects and can cause kidney and liver damage.[2,3,4]

Anyone using this procedure should use extreme care in preparation of standards and handling extracts. The chromatographic column should be vented directly into a carbon trap. A glovebox should be used whenever possible and an efficient fume hood at a minimum. Under the new OSHA requirements for laboratories, technicians should inform their colleagues that methylmercury is in use and establish an area that only authorized personnel may enter.

Extract Cleanup

Extracts of heavily contaminated environmental samples may require some type of cleanup to ensure that there are no organic interferences during analysis. The electron capture detector is prone to fouling if excessive concentrations of compounds other than the target compound are present in the extract. For a quick cleanup procedure, pass the benzene extract through a solid phase extraction column. Several sample extracts analyzed for this paper were highly colored, and passage through a Supelclean LC-18 column (Supelco, Inc., catalog number 5-8298M) resulted in a dramatic reduction in color. Recovery from the Supelclean LC-18 column was validated by quadruplicate analysis of four soils that were fortified with 1 ppm dimethylmercury, extracted and derivatized as described. Table 2 indicates a recovery average of 101% with a standard deviation of 18%.

Table 2
Recovery of Dimethylmercury After LC-18 Cleanup

Sample Designation	Spike Concentration mg/Kg	Found Concentration mg/Kg	Percent Recovery
MDL 1	1.000	0.962	96.2%
MDL 2	1.000	0.763	76.3%
MDL 3	1.000	1.270	127.0%
MDL 4	1.000	1.058	105.8%

Method Validation and Detection Limit

The method was validated by fortification of a silty/clay soil with dimethylmercury. The soil was approximately 40% silt and 60% clay. A batch of seven fortifications was prepared by weighing 10 g of sample aliquotes into test tubes and spiking each with 1 ml of 1 ppm dimethylmercury solution which results in a 0.1 ppm final concentration in the soil. The soil was shaken to mix well and the solvent was allowed to evaporate. Extraction and analysis of these samples resulted in an average recovery of 97.3% with a standard deviation of 9.9%. Table 3 lists the found versus true concentrations. Figure 2 is a representative calibration curve.

The same data were used to derive a method detection limit.[5] The method detection limit for these data is 14 ppb. Since a 10-mL final extract volume was used, it can be assumed that concentration to a final volume of 1 mL should produce a 1.4 ppb method detection limit. Because 14 ppb was an acceptable detection limit for this project, further validation and procedure development to achieve a lower limit was not done.

Table 3
Total Mercury and Methylmercury Results of Selected Environmental Samples

Sample Designation	Spike Concentration mg/Kg	Found Concentration mg/Kg	Percent Recovery
MDL 15	0.100	0.094	94.2%
MDL 16	0.100	0.094	93.5%
MDL 17	0.100	0.082	82.2%
MDL 18	0.100	0.088	88.1%
MDL 19	0.100	0.088	88.0%
MDL 20	0.100	0.092	92.4%
MDL 21	0.100	0.096	96.3%
MDL 22	0.100	0.107	106.5%
MDL 23	0.100	0.105	105.5%
MDL 24	0.100	0.106	106.1%
MDL 25	0.100	0.117	117.2%
Average Percent Recovery			**97.3%**
Standard Deviation			**9.9%**
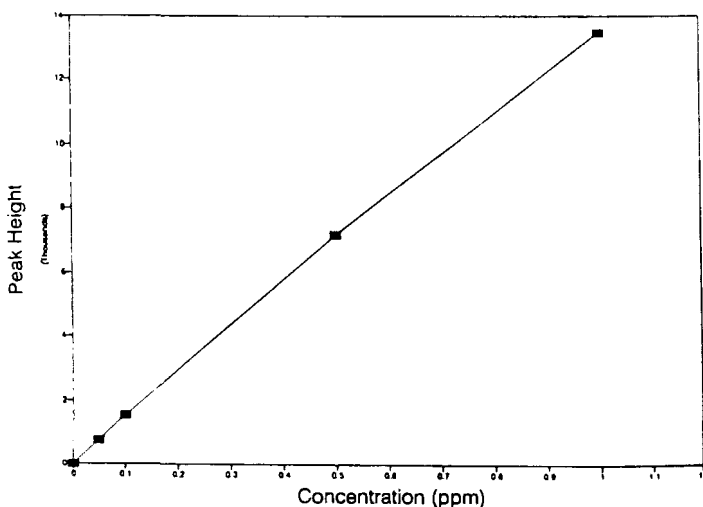
Figure 2
Example Calibration Methylmercury

DISCUSSION

Our laboratory performed 3250 total mercury analyses over an 18-month period from July 1988 to February 1990. Of these tests, 1375 were digested samples and 1080 were RCRA EP Toxicity Leachates.

Of these, 24% had mercury concentrations >0.0002 mg/L. Only one mercury leachate failed to pass the RCRA regulatory limit of 0.2 mg/L. Only 6% of the samples had mercury concentration >0.5 mg/L.

For the purposes of this paper, nine samples with positive mercury concentrations were selected for methylmercury analysis. At the time of analysis, no information about the sample or site the sample was collected from was known. The tests were performed, results were tabulated and then the clients who provided the samples were contacted to inquire about the samples' history.

The results of the methylmercury analyses are reported in Table 4 with the total mercury concentration for camparison. The sample histories are:

- Sewage Plant Debris - During an expansion of local sewage plant, soil and debris were removed from old sludge digester pits. The debris was tested for RCRA parameters for disposal.
- Utility Fly Ash - Fly ash collected during coal burning operations at a local utility was tested to meet RCRA disposal regulations.
- Cement Kiln Dust - This sample was supplied as a solidification medium for an engineering treatability study. Total mercury was tested to characterize the sample prior to solidification tests.
- Soil and Debris (Tool and Die) - The samples were part of a site investigation for a real estate transfer. The soil samples were contaminated with a heavy oil like substance. Originally the site was a tool and die manufacturing facility.
- Soil from Army Arsenal - The sample was provided for RCRA analyses. History of the sample site is unknown.
- Soil from Munition/PVC Plant - The sample was provided for RCRA analyses. The sample site was a munition plant from 1915 to 1950. From 1950 to the present, the site has been a manufacturer of polyvinyl chloride products.

Table 4
Total Mercury and Methylmercury Results of Selected Environmental Samples

Sample Type	Total Mercury (mg/Kg)	Methyl-Mercury (mg/Kg)
Sewage Plant Debris	1.8	0.899
Utility Fly Ash	0.33	<0.015
Utility Fly Ash	0.30	<0.015
Cement Kiln Dust	0.87	0.018
Soil & Debris (Tool & Die) 1	0.5	1.612
Soil & Debris (Tool & Die) 2	4.3	0.706
Soil & Debris (Tool & Die) 3	4.3	0.542
Soil from Army Arsenal	0.77	0.594
Soil from Munition/PVC Plant	1.4	1.584

The expected concentration of methylmercury should be less than equal to the total mercury concentrations. A soil and debris sample from the tool and die site and the soil from the munition/PVC plant did not meet this criterion. The soil and debris tool and die sample concentration of 1.612 mg/kg methylmercury versus 0.5 mg/lg total mercury may be the result of two factors. The first is nonhomogeneity of the sample and the second is the large difference in sample size used for the total mercury analysis (0.2 g) versus the methylmercury analysis (10 g). A 10 g sample would be much more representative than 0.2 g. On the other hand, the soil from the munition plant had a total mercury result of 1.4 mg/kg versus 1.584 mg/kg of methylmercury. This is well within the error limitations of the two analyses.

That seven of nine randomly selected samples with total mercury present also had concentrations of methylmercury was unexpected. However, each sample had a history that would indicate the potential for organomercurials. The sewage plant debris methylmercury concentration may have been the result of all the incidental uses of mercury-containing products that are disposed of by individuals and businesses. Metallic or inorganic mercury in sewage sludge can be converted to methylmercury via anaerobic methylation[6] and, therefore, could be the source of the methylmercury-contamination.

The two samples with a munition background may have mercury present as a result of the manufacture of mercury fulminate. In addition, the site where polyvinyl chloride is manufactured has a high probability of methylmercury since the source of methylmercury-contamination that resulted in Minamata disease in Japan was the catalytic use of mercury in preparing vinyl chloride and acetaldehyde.[7] The tool and die samples may have been contaminated by mercury leaking from electrical units or cleaning/fumigation which occurred at the site, as well as metabolic methylation of inorganic mercury.

As might be expected, the presence of mercury in fly ash from a coal burning utility is not surprising since trace amounts of mercury are present in coal. That these samples had no methylmercury was also reassuring because of the thermal processes involved in producing the fly ash.

The presence of methylmercury in the cement kiln dust was surprising since cement kiln dust is a byproduct of cement manufacturing where high temperatures are to be expected. A finding of 0.018 mg/kg of methylmercury is at the detection limit of the method and may in fact be a false positive. The result for the cement kiln dust is not discounted, however, because the concentration of total mercury of 0.87 mg/kg is high enough to warrant the presence of methylmercury. The process which may have produced this methylmercury is not known.

Although a sample population of nine is small, it is significant that seven of nine sample tested positive for methylmercury. The collection and handling of samples which contain mercury should be considered potentially more hazardous than expected since methylmercury is much more readily absorbed than mercury and apparently has a great potential for being present in any mercury-contaminated sample. Testing for methylmercury should be considered when mercury has been identified as a site contaminant and a risk evaluation should be made based upon the presence of both inorganic mercury and methylmercury.

CONCLUSION

The test procedure for methymercury described here can produce valid results for the detection and quantification of methylmercury in soil. Results of this test performed on randomly selected soil samples resulted in the detection of methylmercury in seven of nine samples that had total mercury concentrations. As a result of the greater biological risks associated with methylmercury, site investigations should include a test for this mercury species.

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Use of High Resolution Passive Soil Gas Analyses to Characterize Sites Contaminated with Unknowns, Complex Mixtures, and Semi-Volatile Organic Compounds

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ABSTRACT

Soil gas methods are recognized to be useful tools for reconnaissance testing of underground storage tanks and shallow groundwater contamination by volatile organics. Advanced, high resolution soil gas techniques, exhibiting multiple vapor collection and analytical methods, can dramatically expand the applicability of soil vapor surveys into more difficult chemical and lithologic environments. Where photoionization detectors and even probe/GC methods fail to yield reliable results, a combination of passive sampling with mass spectrometry and GC/MS, and multivariate statistical chemometric tools can identify and differentiate a broad range of volatile and semivolatile organic compounds, fingerprint multiple sources and assist in pinpointing industrial activities and waste disposal practices.

Applications that are of greatest importance include landfills and other waste disposal sites, property conveyance studies where detection of unknowns is vital and assessment of sites with a historical use of industrial products containing semivolatiles or characterized by non-priority organic pollutants.

An overview of different vapor collection techniques is presented along with the use of multiple analytical methods illustrating how such compounds and mixtures can be detected in a reconnaissance mode using soil gas. Two case histories are outlined illustrating the application of these principals: (1) property conveyance showing the existence of both on- and off-site sources of contamination; and (2) fingerprinting of hydrocarbon mixtures to differentiate between diesel and creosote contamination. In addition, several examples of semivolatile compounds detected in soil gas will be presented.

INTRODUCTION

Evolutionary changes in the methods of environmental site investigations have been gaining momentum nationwide over the last decade. Both the environmental manager and consultant are utilizing a variety of lower cost, reconnaissance techniques that provide upfront insight into potential problem areas that exist at a site. These methods afford the investigator a data base from which he can develop effective Phase II subsurface investigations and proceed efficiently to remediation.

One method that has gained an increasing acceptance is soil gas surveying. Soil gas sampling and analysis was first developed as a petroleum exploration tool dating back to the early 1900s.[1] A number of different sampling and analytical methods emerged during the ensuing years. These analytical techniques include free soil gas sampling, desorption of sorbed and occluded gases from soils and the use of adsorbent materials for passive collection.

Early analytical methods were based on simple combustion and manometry techniques, becoming more sophisticated with the development of the gas chromatograph in the 1950s.[1] Ultimately, the applica-

tion of two state-of-the-art, high technology analytical methods, (such as mass spectrometry and gas chromatography/mass spectrometry) were introduced as geochemical problem solving tools in the late 1970s to early 1980s.[1] Subsequently, several environmental researchers applied the basic soil gas systems to volatile organic compound (VOC) contaminant plume tracking, underground storage tank (UST) assessments and source delineation problems.[2-5]

Now the next generation of methods has emerged: rapid, high resolution soil gas techniques that are additionally capable of detecting many semivolatile organic compounds (SVOC) and utilizing a variety of sophisticated computerized data processing techniques.[6]

STANDARD SOIL GAS METHODOLOGIES

All soil gas methods involve varying sampling and analytical techniques. Two primary types of sampling methods are utilized by environmental soil gas practitioners: active and passive. Active sampling systems withdraw an aliquot of gas from a sampling location at a given instance of time, while passive systems incorporate a sample collection medium to sample the migrating gases as they propogate towards the atmosphere. Several company specific variations to each of the primary sampling method types are currently being practiced.[4,5] A summary of the different sampling types, advantages and limitations as compiled by Eklund[4] for the American Petroleum Institute is provided in Table 1.

Table 1
Comparison of Soil Gas Sampling Techniques
(Modified from Ekland[4])

Technique	Disturbance Of Soil Gas Equilibrium Small	Large	Suitable For Rocky Soil Yes	No	Sampling Time Hour(s)	Days	On-Site Analysis Pratical Yes	No
1) Grab Sampling of Soil Cores								
- Auger		X	X		*X		X	
- Driven Sleeve	X	X		X	X		X	
2) Surface Flux Chamber	X		X		X		X	
3) Subsurface Flux Chamber								
- Auger/Enclosure		X	X		X		X	
- Groundprobe type	X			X	X		X	
4) Accumulator Device								
- Curie Point Wire	X		X		X	X		X
- Absorbant/Pump		X		X	X			
5) Groundprobe								
- Passively Emplaced		X	X		X			
- Driven	X			X	X			
- Driven, small Volume	X			X	X			X

In addition to the two primary types of sampling methods that are commonly utilized, a multitude of analytical methods also is employed.[4,5] Analytical methods include total volatile screening, analysis of pathfinder analytes by using field or laboratory gas chromatographs with varying detectors, mass spectrometry and standard gas chromatography/mass spectrometry techniques. Table 2 is a compilation of the various types of analytical methods commonly employed, their uses, advantages and limitations.[4,5]

HIGH RESOLUTION SOIL GAS SURVEYING

During the last four years, Northeast Research Institute, Inc. (NERI),

has adapted a soil gas surveying system (PETREX Technique) developed at the Colorado School of Mines for application at sites with complex contamination histories.[1-3] The basic system utilizes a passive soil gas sampler that continuously collects VOCs and SVOCs over a few hours to several days. During this sampling period, VOCs and SVOCs are sorbed onto a specially treated substrate, thereby decreasing the lower limit of detection for many compounds. The integrative nature of the passive sampler tends to smooth temporal variations that can plague most "instantaneous" sampling methods.[1]

The standard analytical system uses a Curie-point desportion inlet interfaced to a quadruple mass spectrometer (CpD-MS) for fast, adequately reproducible analyses. During each analysis, all VOCs and SVOCs collected in a mass range of 30 to 240 (C2-C16) are desorbed, analyzed and stored on a computer as a composite of the VOC/SVOC compounds collected at each sampling location. These data are then downloaded onto a graphics workstation where data processing and interpretation are conducted.

Analytical flexibility is another advantage afforded by such a high resolution soil gas system. An enhanced version of the PETREX sampling system often is combined with other analytical techniques such as specific detector—gas chromatography, gas chromatography/mass spectrometry and gas chromatography/mass spectrometry/mass spectrometry for enhanced individual compound sensitivity or complex mixture resolution. This advanced sampler incorporates multiple adsorption wires in the same collection device. One adsorption wire is analyzed by Cpd-MS, while the others are available for another analytical method depending on the results of MS analysis and the objectives of the survey.

The ability to readily adjust the analytical program during the interpretative stages of a survey offers tremendous advantages over stan-

Table 2
Comparison of Analytical Techniques

Method	Uses	Advantages	Limitations
VOA/HNU	Total Volatile Screening	Minimum Operator Training; Inexpensive	Poor Sensitivity No Compound Discrimination
Gas Chromatography (GC)	Light MW Organics	Good Sensitivity Low Equipment Costs	Tentative IDs; Knowledge of Contamination Necessary to Obtain Maximum Sensitivity
Mass Spectrometry (MS)	C2 - C20 Organics & Some Inorganics (Hg,S)	Good Sensitivity; Rapid analysis Non-discriminatory; Allows ID of Discrete Chem. Composition	Complex Data Output Composited Data Interference
GC/MS	Any Collectable Organic	Adequate Sensitivity Good Compound ID	High cost; Slow Analysis

Multiple Chlorinated Compounds
- - - - - Dichlorobenzotriflouride
— — — Chlorobenzotriflouride
· · · · · · Tetrachloroethylene (PCE)
———— Trichloroethylene (TCE)
—— · —— Dichlorobenzene

Figure 1
Examples of SVOCs Detected in Soil Gas

dard sampling and analytical techniques. For example, landfills frequently exhibit a large number of unanticipated compounds whose identification can be essential in differentiating PRP responsibility. Figure 1 is an example of a PETREX MS soil gas sample from a landfill site where several unanticipated SVOCs were identified. Followup GC/MS analyses confirmed the SVOC compounds tentatively identified by straight mass spectrometry. Review of a survey where the application of combining the enhanced PETREX sampling system with gas chromatography/mass spectrometry is outlined in the second case history described later in this paper.

DATA INTERPRETATION

Two different interpretation strategies are used when evaluating high resolution soil gas data. All soil gas practitioners report the relative relationships between soil gas response or concentrations for a given compound or compound class in the form of a contoured map.[2-5] These maps usually represent the soil gas distribution of a predetermined target chemical or chemical class.[4,5] However, unlike those techniques relying on gas chromatographic analysis, composite mass spectrometry does not limit the types of compounds that are detectable to predetermined or standard compounds. When analyzing by mass spectrometry, it is not necessary to select a detector to optimize sensitivity for a specific class of chemicals as with a gas chromatograph. This advantage is very important when dealing with real estate conveyance surveys where site history is often sketchy and past chemical use uncertain. In addition, the extensive library of mass spectral signatures permits reasonable identification of many unknown or unanticipated compounds.

The second type of interpretative tool focuses on treating the composite VOC/SVOC response at each sampling location as a discrete soil gas Fingerprint. Once characteristic Fingerprints are identified (e.g., diesel or gasoline), the data set is modeled using computerized pattern recognition techniques to classify the balance of the survey set relative to the likelihood of being associated with that type of contaminant occurrence. One example demonstrating the use of Principal Component Analysis (PCA) in discrimination of different hydrocarbon soil gas Fingerprints is provided in the second case history described below.

CASE STUDIES

Two case histories illustrate the value of adding a high resolution soil gas method to site investigation. The information developed in both cases either: (1) is essential data that otherwise would be unrevealed or (2) could only have been supplied at a large multiple of the costs actually incurred.

OFFICE BUILDING PROPERTY CONVEYANCE

The first case involves a property acquisition. It is now common for buyers to carry out a Phase I investigation prior to purchasing property. Phase I surveys can include a variety of activities, but too frequently only include limited evaluation of three elements essential when the property is in urban areas; namely:

- Long-term land use history for the property under investigation
- Surrounding land use, both present and historical, and its potential impact on the site
- Non-invasive sampling, including off-site sampling

This case involves NERI's conduct of a Phase I study related to the acquisition of a 15 year old office building in Denver, Colorado. After discussion with the client, the scope of work was expanded by adding more extensive off-site and on-site land use evaluation, plus a phased approach for soil gas sampling. Soil gas surveying was to be deferred to a rapidly deployed Phase "IA" depending on the preliminary results of other researches.

The office building, with underground parking garage, was constructed in the mid 1970s and sold twice thereafter without any environmental assessments. Public record searches showed no on-site or off-site environmental problems within 1/2 mile or so of the site. Even though heavy commercial and some industrial activities (including industrial dry cleaners) had been located within that distance upgradient, there were no recorded CERCLA, UST, or RCRA actions in
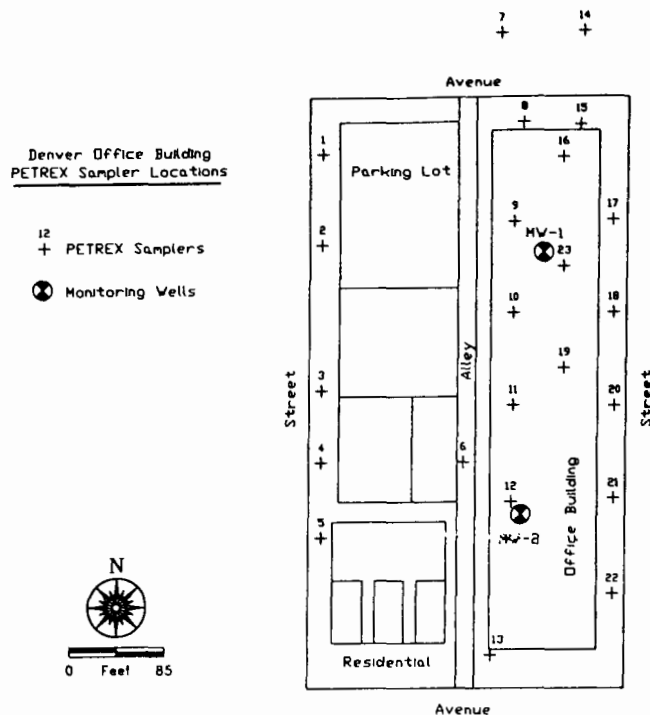
Figure 2
Denver Office Building
PETREX Sampler Locations

evidence. Neither the State of Colorado nor the U.S. EPA data bases indicated any contamination problems nearby or on the site.

Detailed historical land use research, using newspaper and other public records at the historical society and similar agencies, revealed that during the 1940s and 1950s the site had been used extensively for the manufacture of electronic and avionic components. Combined with the off-site usage history, there was sufficient circumstantial evidence to warrant the application of a rapid and broad-based soil gas survey.

Twenty-three PETREX Samplers were installed on the site and in public rights-of-way over the entire city block following acquisition of requisite permits (Fig. 2). Samplers remained in the ground for 48 hours to obtain equilibration with soil vapors. Analysis was conducted by CpD-MS.

Two principal VOCs were identified: trichloroethylene (TCE) and tetrachloroethylene (PCE). These compounds exhibited two very different distributions. Figure 3 shows that the TCE is confined to the site and does not appear to have migrated off-site. The PCE (Fig. 4) appears to be in a broad unconfined plume extending from upgradient off-site northeasterly to downgradient off-site areas.

The soil gas results confirmed some of the suspicions raised by the historical land use search within 72 hours of learning of the potential problem.

Two monitoring wells were installed to establish whether the TCE contamination had reached groundwater and to confirm that the PCE had an off-site source. MW 1 and MW 2 soils (silts and silty sands) were sampled at 5 ft intervals from the surface to the water table (20 ft BGS). Subsequently, monitoring wells were completed and developed in each of the borings and the groundwater sampled and analyzed in NERI's laboratory.

The results are shown in Figure 5, which combines the soil gas data with the soil and groundwater results. The data indicate that the site was the source of the TCS, which apparently resulted in trace amounts of TCE reaching groundwater. The PCE however, was determined to be present only in groundwater, not in near surface soils. PCE was thus confirmed to come from an off-site source only.

This study indicates the dangers of limiting Phase I property conveyance studies, particularly in urban areas. Routine record searches failed to show actual contaminant conditions. Most environmental

regulatory agency records are useful only for the past 10-20 years, depending on the location. Both older conditions and undiscovered problems hide in extensive gaps in the records.

Only direct measurements can give reliable indicators of contamination. A high resolution soil gas method effectively fulfills this need
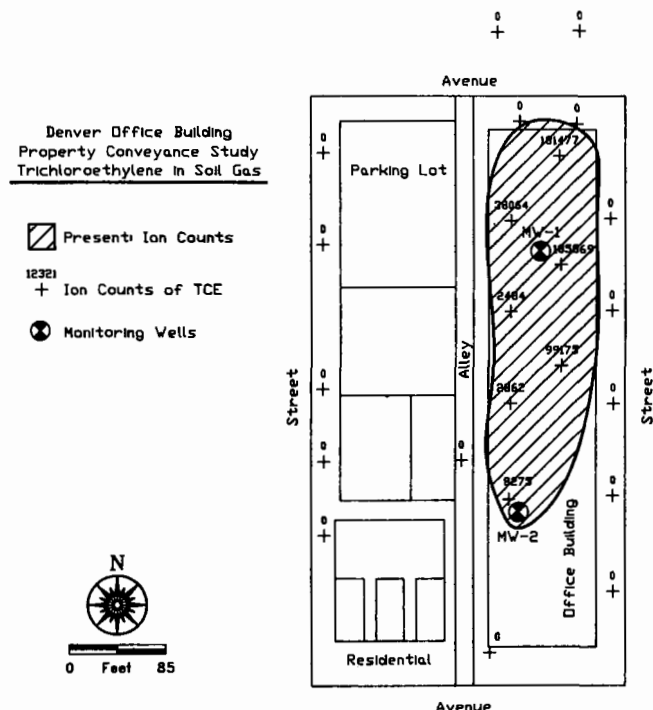
Figure 3
Denver Office Building Property Conveyance Study
Trichloroethylene in Soil Gas
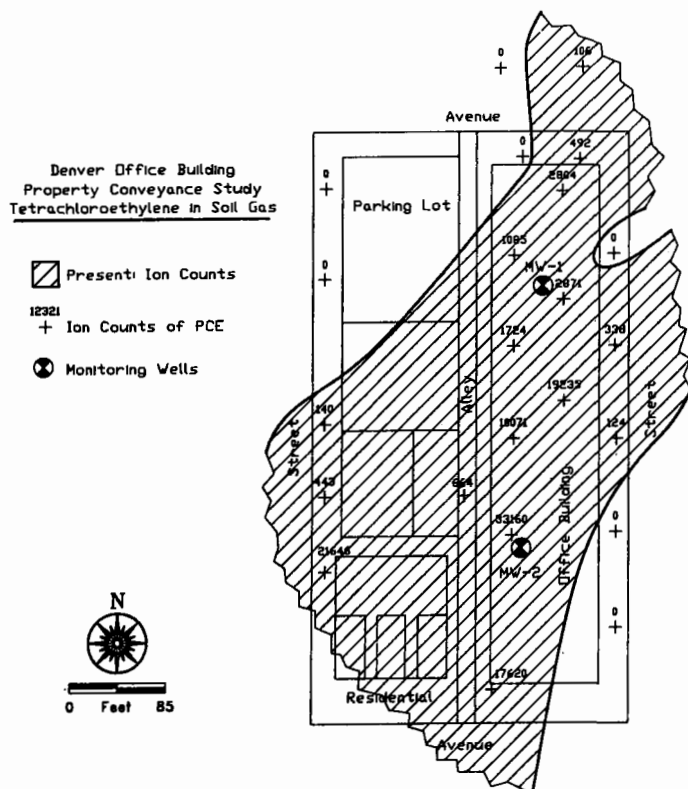
Figure 4
Denver Office Building Property Conveyance Study
Tetrachloroethylene in Soil Gas
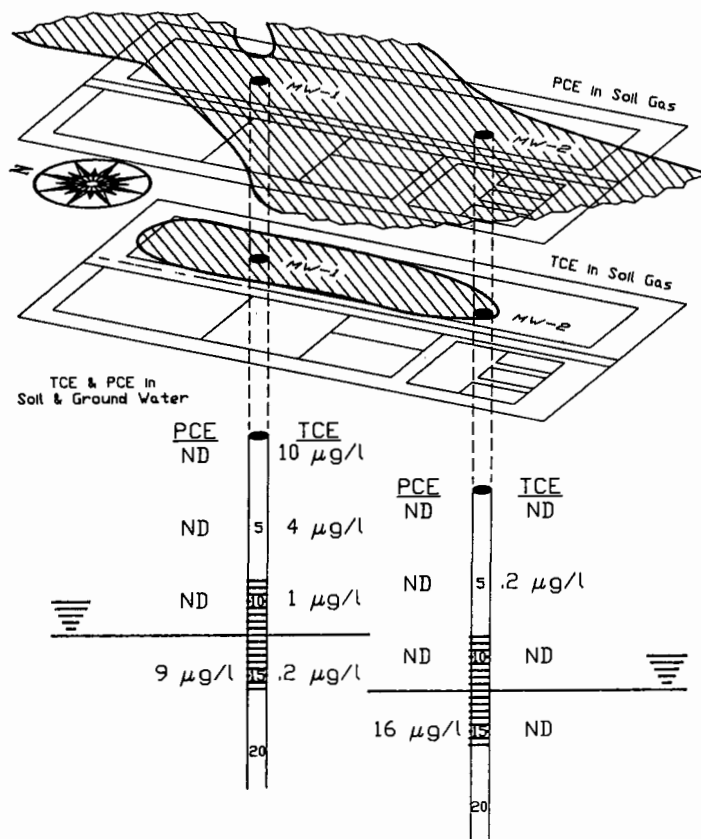
Figure 5
Composite 3-D Representation of PETREX Soil Gas
with Soil and Groundwater Analysis

for sites involving a wide range of organic contaminants. Use of VOA analyzers or an HNU would not have differentiated between on-site and off-site sourced contamination.

RAILROAD YARD ASSESSMENT

The second case involved the assessment of a former railroad yard. the assessment was difficult because of the size of the property and the nature of the potential contamination. Encompassing nearly 100 acres, the site was reportedly used in the early part of the century for railroad tie treatment, storage and disposal. In addition, engine fueling and maintenance apparently were conducted on the site. The exact locations of these activities and their areal extent were less than certain.

Assessment by traditional drilling and sampling, without advance screening, were expected to be extremely expensive. However, most soil gas practitioners report difficulty in detecting such semivolatiles as creosotes and heavy fuels.[7] Following a review of reconnaissance methods, the client selected the PETREX 2-wire sampler to screen the site prior to drilling.

Seventy PETREX samplers were placed in a two-tiered reconnaissance grid across the site (Fig. 6). Spacing was approximately 100 feet in the areas suspected to be near historical sources; it expanded to approximately 200 feet in outlying areas of the site. Samplers were allowed to equilibrate with the air in the ground for approximately one week.

A review of the MS data showed two primary hydrocarbon mixtures. Each mixture exhibited a relatively consistent composition derived from upwards of 40 different hydrocarbon constituents in the range of C_5 to C_{15}. Representative mass spectra are shown in Figure 7. Figure 7A is typical of the mixtures that generally correspond to cresote. Creosote is a generic term which includes a range of hydrocarbon coal tar compounds, but in general, the more volatile of the components are aromatic hydrocarbons, naphthalene and biphenyl and the alkyl substituted derivations of both.

Figure 6
Railroad Yard
PETREX Sampler Locations

Figure 7
Representative Spectra
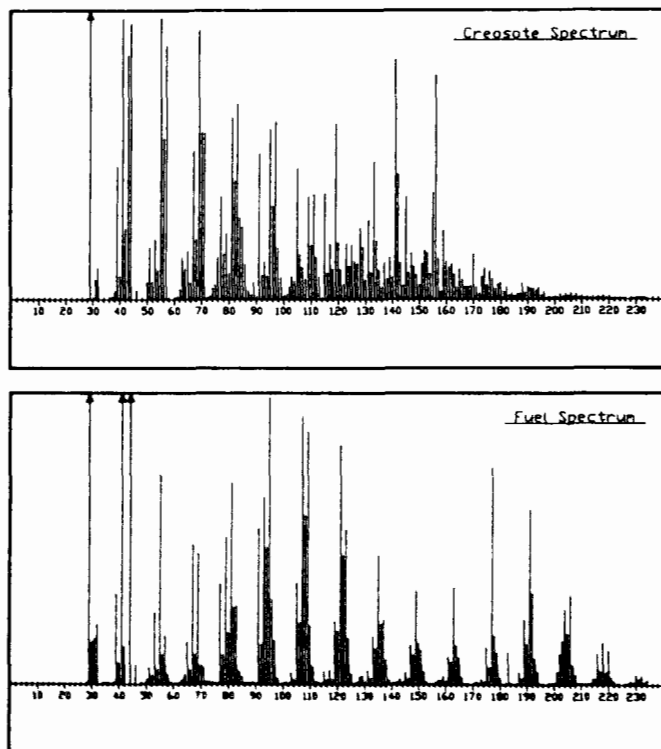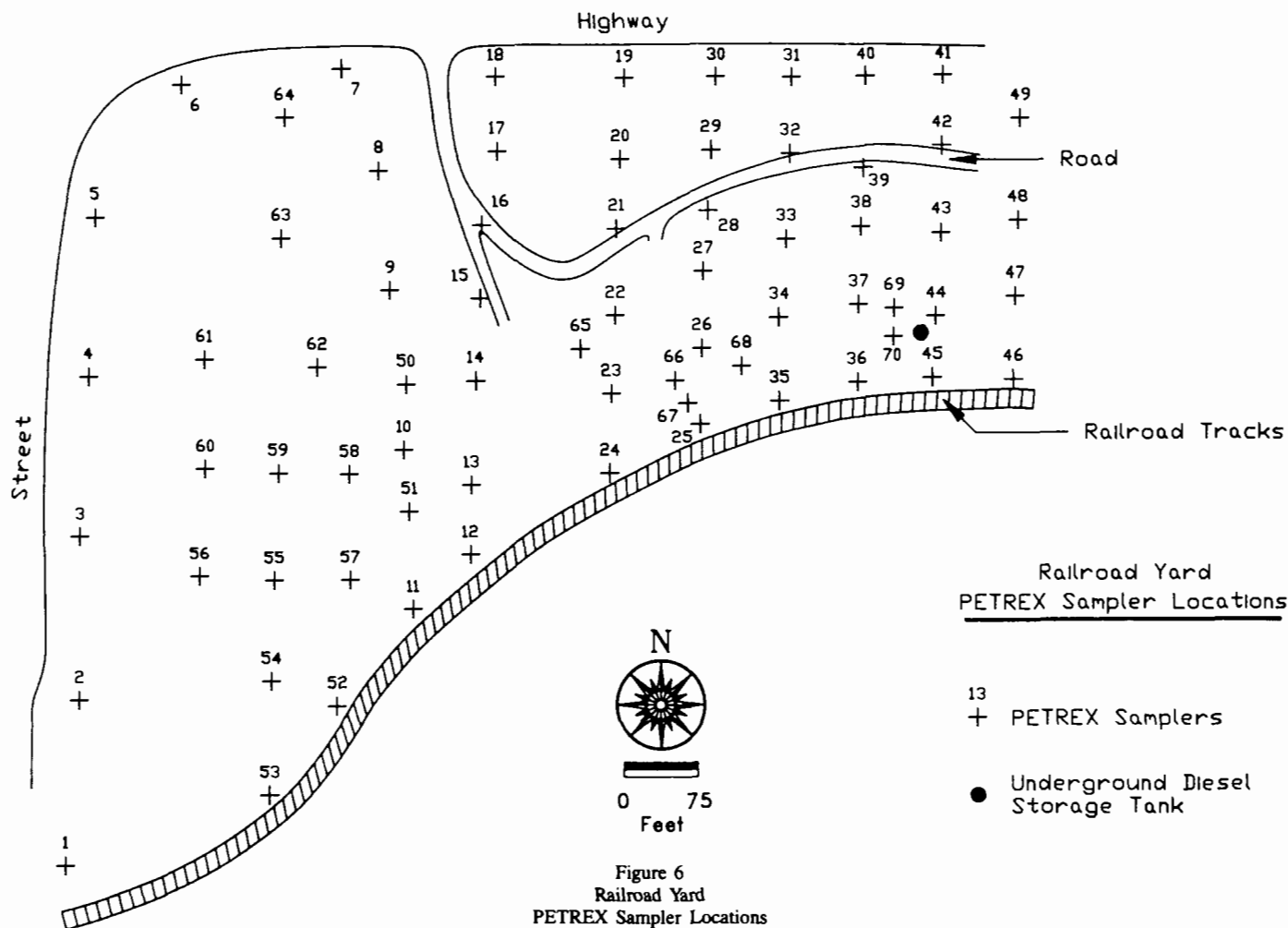
Methyl nonane
Methyl undecane
Dimethyl undecane
Dimethyl dodecane
Tetramethyl pentadecane
Methyl cyclohexane
Dimethyl cyclohexane
Ethyl cyclohexane
Trimethyl cyclohexane
Ethyl methyl cyclohexane
Propyl cyclohexane
Pentyl propyl cyclopentane
Dimethyl benzene
Xylene
Ethyl toluene
Trimethyl toluene
Tetramethyl benzene
Diethyl toluene
Ethyl dimethyl benzene
Isopentyl trimethyl benzene
Undecane
Decahydromethyl naphthalene
Naphthalene
Methyl naphthalene
Dimethyl naphthanlene
Trimethyl naphthalene
Methyl biphenyl
Diethyl naphthalene

Figure 8
Principal Compounds—Creosote Sample
Derived from GC/MS Analysis of PETREX Sampler

Pentane
Hexane
Cyclohexyl decane
Trimethyl dodecane
Hexadecane
Methyl hexadecane
Trimethyl hexadecane
Tetramethyl hexadecane
Cyclohexane
DiMethyl cyclohexane
Trimethyl cyclohexane
Tetramethyl cyclohexane
Diethyl methyl cyclohexane
Ethyl dimethyl cyclohexane
Dimethyl cyclooctane
Hexyl trimethyl cyclobutane
Dimethyl cyclopentane
Dibutyl cyclopentane
Butyl propyl cyclopentane
Pentyl propyl cyclopentane
Diethyl dimethyl cyclohexane
Butyl trimethyl cyclohexane
Dimethyl cyclopentyl cyclohexane
Tetraethyl cyclohexane
Benzene
Toluene
Xylene
Dimethyl propyl benzene
Ethyl trimethyl benzene
Triethyl toluene
Isopentyl trimethyl benzene
Phenyl methyl diemthyl benzene
Dimethyl propyl trimethyl benzene
Hexadiene
Methyl pentadiene
Dimethyl pentadiene
Heptamethyl heptene
Octadecene
Decahydro diemthyl naphthalene
Tetrahydrodimethyl naphthalene
Tetrahyro trimethy naphtalene
Naphthalene
Trimethyl naphthalene
Methyl bihenyl
Dimethyl biphenyl

Figure 9
Principal Compounds—Diesel/fuel Sample
Derived from GC/MS Analysis of PETREX Sampler

Figure 10
Factor Spectrum Creosote vs. Diesel

Figure 7B reflects a fuel type mixture, in this case dominated by diesel fuel, but including fuel oil components as well. The mixture is largely aliphatic and alicyclic, although there are quantities of alkyl aromatic hydrocarbons. The naphthalenes and biphenyls that were found in the creosote mixture are present only at trace levels.

These general chemical characterizations were made on examination of the CpD-MS results. A number of duplicate wires were selected for CpD-GC/MS analysis to confirm these identifications. The results of each analysis were given in Figures 8 and 9, listing the primary compounds identified by GC/MS.

The Analytical results were used in conjunction with Principal Component Analysis to develop a geochemical model of each mixture. The chemistry of each "model" is illustrated in Figure 10. Mass peaks extending upwards are characteristic of the creosote. Those peaks reaching down reflect the principal discriminating components of the fuel (diesel). These correspond closely to the compounds identified in the GC/MS analysis.

It should be recognized that both mixtures contain some common compounds. This is to be expected with numerous hydrocarbon mixtures. However, PCA permits identification of those compounds which either by presence or relative abundance discriminate between mixtures.

Each individual grid sample in the data set was then compared with the model using discriminant analysis and a Similarity Value (Discriminate Function) was calculated and mapped. Geostatistics were used to determine the cutoff point. The mapped results are given in Figures 11 and 12.

Figure 11 shows an E-W zone of intense fuel (diesel) contamination lying between the two primary trackages known to have entered the site. Investigation revealed a former underground diesel storage tank at the center of the zone. Drilling and sampling near PETREX sample 69 showed 1.5 feet of free product fuel on groundwater some 8 feet below surface.

Creosote contamination is found scattered across the site, reflecting the more diffuse nature of treatment, storage and disposal of RR ties. Two areas are indicative. The first contaminated area is along both sides of the fueling area where trackage was known to run prior to site clearing. The second area was near sample 54, where soil analyses revealed low ppm levels of creosote components.

CONCLUSIONS

Rapid, high resolution soil gas surveys can effectively yield reconnaissance data regarding the presence of VOCs and many SVOCs and can then direct subsequent investigations at a fraction of the cost of traditional drilling and sampling. Soil gas surveys are extremely sensitive to low levels of such volatiles as TCE, PCE and light petroleum hydrocarbons (BTEX). The sensitivity is not projected to be as good for semivolatile compounds. Depth to sources, lithology and contaminant concentration are all limiting factors to consider.

Insufficient research data makes it impossible to firmly define the

Figure 11
Samples Similar to Creosote Soil Gas Model

Railroad Tracks

Railroad Yard

Samples Similar to
Creosote Soil Gas Model

N

0   75
Feet

▨ Similar to Creosote Model

13 Similarity Values
+   Based on Model

▲ 'Creosote Like'
    Soil Contamination

●   Underground Diesel
    Storage Tank

Figure 12
Samples Similar to Diesel Soil Gas Model

Highway

Road

Railroad Tracks

Railroad Yard

Samples Similar to
Diesel Soil Gas Model

Street

N

0   75
Feet

▨ Similar to Diesel Model

13 Similarity Values
+   Based on Model

■ 'Oil Like' Soil Contamination

●   Underground Diesel
    Storage Tank

lower limits of SVOC detection at this time. As a result, more experimentation and trial studies are required before we can confidently delineate the limits of such applications. Despite these limitations, investigators should be encouraged to carefully apply high resolution soil gas methods to such problems, being cautious to integrate sampling, analytical and statistical methods into the overall investigative programs for optimum interpretation reliability.

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Geochemical Techniques for Site Characterization and Monitoring

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ABSTRACT

Groundwater geochemistry data (major anions and cations) are widely used as an interpretive tool for groundwater quality and water resources studies on the regional scale. Applications in the field of contaminant hydrogeology, however, have been largely overlooked even though the analyses are inexpensive and do not require extensive validation. Ionic data were collected during hydrogeologic characterization and contaminant assessments at two hazardous waste sites (including one on the NPL) to determine the feasibility of applying these techniques on a smaller scale. The data provided useful information at each site, including delineation of variation in groundwater quality related to the introduction and migration of contaminants that were undetected through "full scale" analyses and better definition of circulation patterns in fractured rock. Hydrochemical facies were used to correlate monitored intervals in on-site wells and nearby residential wells and document variations in background groundwater quality controlled by off-site sources of contamination. The results of this study indicate that geochemical techniques should be given full consideration for the majority of site characterization/monitoring studies.

INTRODUCTION

The use of groundwater geochemistry data as an interpretive tool for characterization of groundwater quality and circulation patterns is a widely accepted practice for water resources evaluation and regional aquifer studies.[8] These techniques are not often used for contaminant-related studies that typically involve relatively small study areas, in most cases because the sampling and analysis that occurs is heavily biased toward constituents recognized by the U.S. EPA as priority pollutants or listed on its target compound list; the emphasis is nearly always on contamination rather than natural groundwater quality. This natural water quality is broadly defined on the basis of the ionic composition of the water, typically expressed as the distribution of the major anions and cations. Although standard metals analyses quantify the major cations, anionic analyses are rarely employed even though the analyses themselves are relatively inexpensive and do not require extensive validation procedures.

Interpretations of groundwater quality on the basis of ionic concentrations are usually accomplished using graphical methods. These methods require that the concentrations of the ions be converted from mg/L to milliequivalents per liter (meq/L), based on the gram formula weight of the compound and its valence. The meq/L data can be graphically plotted in several ways, following the methods of Piper,[7] Stiff,[8] or Collins.[3] The graphical representations can then be compared and used to detect and identify mixing of waters of different chemical composition and to identify some of the chemical processes that occur as natural waters circulate.[4,6] The concept of hydrochemical facies as

developed by Back[1] is a means of grouping water compositions into identifiable groups or categories. The hydrochemical facies are distinct zones that are characterized by particular compositions of anions and cations. The facies are commonly based on subdivisions of the trilinear diagram.[2] Evaluation of the different types of facies and their areal and vertical distribution in the vicinity of the sites support interpretations regarding the mixing of groundwaters.

The objective of this study was to determine the feasibility of applying these techniques on a smaller (i.e., site-level) scale. To this end, samples were collected from monitoring and/or residential wells at two sites and analyzed for major anions and cations. The resulting data were plotted graphically on trilinear diagrams and used to construct Stiff diagrams.

Monitoring well samples were collected with stainless steel bailers following purging of 3-5 well volumes and stabilization of temperature, pH and specific conductance parameters measured in the purge waters. Residential well samples were collected from taps closest to the well, in most cases at the base of the pressure tank. The residential wells were purged 10-15 minutes to remove stagnant water from the plumbing and well.

Monitoring well samples were filtered in the field with 0.45 μm filters and placed into polyethylene sample bottles. Residential well samples were not filtered. The filtered and nonfiltered samples selected for cation analyses were acidified with concentrated HNO_3 at the rate of 0.5 mL/100 mL of sample. All samples were stored in sealed ice chests and shipped to the laboratory for ion analyses. At four of the five sites, bicarbonate analyses were performed in the field using standard alkalinity titration methods.

Samples were analyzed in the laboratory for major cations and anions (except bicarbonate) in accordance with standard procedures. For the cations, atomic absorption methods were used; for the anions, ion chromatography was used. Major cations quantified included calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+) and potassium (K^+); major anions included chloride (Cl^-), bicarbonate (HCO_3^-) and sulfate (SO_4^{-2}). Nitrate (NO_3^-) was also measured at both sites and phosphate (as PO_4^-) was identified at the two Hohenfels landfills.

SITE BACKGROUND

The two sites utilized in this study are the Greenwood Chemical Company site in Virginia and the Hohenfels Training Area in the Bavarian State of West Germany.

Greenwood Chemical Company

The Greenwood Chemical site is an abandoned chemical manufacturing facility located in Albemarle County, Virginia, between the cities of Waynesboro and Charlottesville, approximately four miles east of

Rockfish Gap at the foot of Bear Den Mountain and the Blue Ridge Mountain Range (Fig. 1). The site is located on the southeastern edge of the Blue Ridge physiographic province and just west of the Piedmont province.
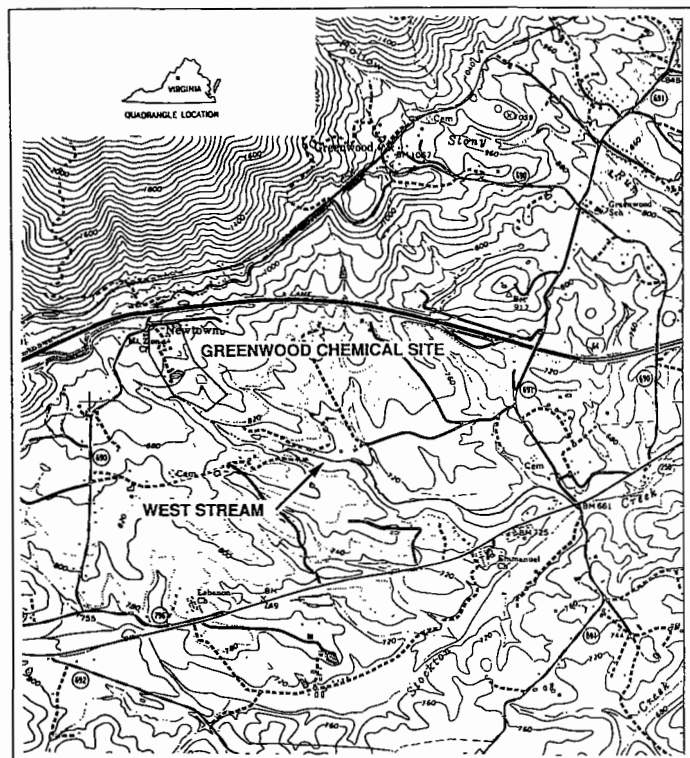
Figure 1
Site Location
Greenwood Chemical Company

Site History

The Greenwood Chemical Company site was investigated as part of the U.S. EPA's Superfund Program. The work discussed herein was part of the Remedial Investigation conducted at the site from 1988-1990.

The Greenwood site has extensive soil, groundwater, surface water and sediment contamination. The source of this contamination has been attributed to improper waste handling and disposal activities during the operational life of the facility, which extended from approximately 1947 until 1985. Waste handling and disposal activities centered around the five shallow lagoons (Fig. 2) used for wastewater disposal and various areas around the site used for burial of containerized waste.

Releases of hazardous chemicals to the environment have been documented over a period of at least 15 years. A direct consequence of these releases has been extensive soil and groundwater contamination over an area of approximately 7 acres. Continued release of this contamination to groundwater is occurring in response to downward percolation of precipitation waters through these contaminated soils.

Geohydrology

The bedrock at the Greenwood site consists of coarse-grain granodiorite with gneissic texture.[5] The bedrock is moderately to highly fractured at shallow depths, with decreasing fracture intensity with increasing depth. Overlying the bedrock is an unconsolidated overburden horizon comprised of colluvial soils and saprolite; its thickness ranges from zero (at an outcrop on the southern portion of the site) to nearly 100 feet in the central portion of the site.

Groundwater at the Greenwood site is present in both the bedrock and overburden horizons, with the water table occurring in the overburden at depths between 5 and 35 feet below ground surface. Aquifer
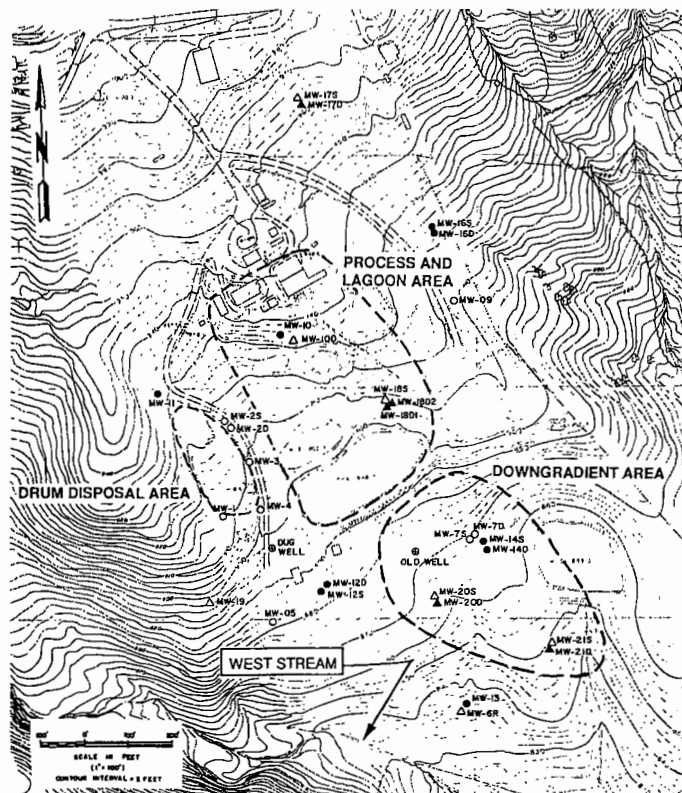
Figure 2
Site Layout
Greenwood Chemical Company

test results from monitoring wells on the site indicate that these two units exhibit a high degree of hydraulic connection; however, potentiometric data indicate that the overburden is acting as a confining layer over much of the site. Groundwater flow directions in the overburden and bedrock are to the southeast, reflecting the topographic slope of the site. The vertical direction of flow is downward in the central part of the site but upward elsewhere. Discharge of groundwater from the bedrock into the overburden is followed by surface discharge of overburden groundwater near a small stream along the southern border of the Greenwood property. Flow velocities in the overburden and bedrock are estimated to average 0.04 and 0.21 feet per day, respectively.

Hohenfels

The Hohenfels Training Area is a U.S. Army installation located in central Bavaria, approximately 60 kilometers southeast of Nurnberg and 115 kilometers north of Munich (Fig. 3). The 17,800 hectare Training Area is located in the Franconian Alps geographic region, which is characterized by high limestone plains, deeply incised valleys and relatively few perennial streams or rivers.

Site History

The Training Area contains two solid waste landfills; one is active (the Operating Landfill), and the other was closed in 1965 (the Old Landfill). Both landfills are located near the main field camp, which contains the administrative, residential, logistical and maintenance facilities for the installation. Investigation of groundwater quality at the Operating and Old Landfills was undertaken in response to a request from the Bavarian State Water Authorities after volatile organic contamination was detected in a water supply well for a nearby village.

The Operating Landfill consists of approximately 4.8 hectares. The landfill has no liner, leachate collection system, or other engineered structures for the containment or diversion of leachate or run-off. There is some evidence that waste may have been placed directly on the exposed bedrock at the site. Landfilling operations at the Operating

Figure 3
Site Location
Hohenfels Landfill

Landfill began in 1965. Wastes reportedly included municipal solid waste generated by the Hohenfels military community (approximately 4,500 soldiers and their families), construction/demolition debris and wastes from vehicle maintenance activities.

The Old Landfill is approximately 1.5 kilometers north of the Operating Landfill. The landfill area comprises approximately 0.7 hectares and, similar to the operating landfill, does not have a liner, leachate collection system or other diversion systems for leachate or run-off. Landfilling operations at the Old Landfill began in the early 1940s and continued until 1965. The majority of the wastes placed in the unit were domestic refuse and construction debris. Given the period of operation for the Old Landfill, other waste types, including explosives, petroleum products and chemical wastes such as solvents also may have been placed in the landfill.

Geohydrology

The Malm Formation is the uppermost bedrock unit and principal aquifer in the Hohenfels area. It consists of thinly bedded to massive limestone which has been dolomitized to varying degrees and karstified. The Malm aquifer is confined, with groundwater occurring generally in the fractures, joints and solution cavities associated with the karst. The top of the aquifer beneath the Operating and Old Landfill occurs at a depth between 40 and 60 meters below ground surface. Groundwater flow is to the northeast with an average gradient of 0.021 (2.1%). Transmissivity values for the Malm range from 0.44 to 380 m^3/m/day. Seepage velocities ranged from 0.001 to 6.3 m/day. Groundwater geochemistry was found to be largely controlled by the limestone and dolomite of the aquifer.

DISCUSSION OF RESULTS

Results from ionic analyses of samples from Greenwood and Hohenfels were reported in concentration units of mg/L and converted to meq/L for graphical plotting and analysis. Because of space limitations, the actual concentration data are not presented here.

Greenwood Chemical

A trilinear diagram presenting ionic data from the Greenwood site is shown in Figure 4; separate trilinear diagrams for overburden and bedrock were developed. The trilinear plots show that the groundwater geochemistry is quite variable at the site. The bedrock monitoring and residential wells were classified as either calcium bicarbonate type waters (i.e., calcium and bicarbonate are the dominant cations and anions, respectively) or as calcium chloride water (due to replacement of bicarbonate by chloride as the predominant anion).

All of the bedrock monitoring wells plotted in the calcium chloride field on the trilinear diagram are contaminated with a variety of organic contaminants including trichloroethene, toluene, carbon tetrachloride and chloroform. Bedrock monitoring wells in the calcium bicarbonate field are either free of contamination or contain significantly lower levels of contaminants than do those in the calcium chloride field. The bedrock monitoring wells plotted in the calcium chloride field are directly downgradient of the principal source areas of the site.

The overburden groundwater plotted across a much wider spectrum of chemical facies, with samples falling into the calcium bicarbonate, calcium chloride and sodium chloride fields on the diagram. All of the samples classified as calcium bicarbonate-type water were from wells on the western portion of the site near the drum disposal area. The majority of the remaining overburden wells had chloride as the dominant anion and either calcium or sodium as the major cation. Three monitoring wells and an old hand-dug well on-site had sulfate as the dominant anion.

The separation of hydrochemical facies between the eastern and western portion of the site is not readily explained. The boundary between these two areas is more or less defined by a major lineament identified in a fracture-trace study completed by the U.S. EPA's Environmental Photography Interpretation Center in 1987. The presence of chloride as the dominant anion in overburden groundwater to the east of the lineament probably is due to its introduction into the environment through waste disposal activities in the process area and lagoons. The absence of chloride in wells to the west of the lineament would not be expected, given the potential for groundwater flow toward the buried drum area in response to topographic variations as well as mounding of the water table beneath the lagoons.

Evidently, the feature identified as a lineament is acting as a hydraulic barrier (in this case a drain) which is preventing groundwater on either side of the fracture-trace from mixing. The contrasting hydrochemical facies caused by the absence of chloride in the groundwater to the west of the lineament is a strong argument in support of this interpretation.

Another trend obvious from the trilinear plots is the divergent nature of bedrock and overburden water chemistry, particularly with regard to anionic constituents. The majority of these differences can probably be attributed to site-related, inorganic contaminants. Given the apparent degree of hydraulic interconnection that exists between overburden and bedrock based on pump test data, the groundwaters from these units should be more homogeneous due to the mixing that should be occurring in response to this connection. The geochemical data suggest that the mixing is not as significant as the pump test alone would suggest. The differences in chemistry are further illustrated in Figure 5, which utilizes another method of graphical interpretation[8] to present the contrast between overburden and bedrock groundwater chemistry.

A final interpretation regarding groundwater geochemistry concerns on-site bedrock monitoring wells and off-site bedrock residential wells. Groundwater at the Greenwood Chemical site is contaminated with both volatile and semivolatile TICs (Tentatively Identified Compounds), including many compounds classified as unknown constituents. Residential well data collected in 1988 and 1989 included several unknown TICs. Initially thought to be evidence of site-related contamination, these results were subsequently discounted on the basis of ionic data from the same residential wells.

The conclusion that site-related contamination has not impacted nearby residential wells was supported by examining individual ionic concentrations in samples from the wells with TIC contamination. Certain anionic constituents are considered to be nonreactive and
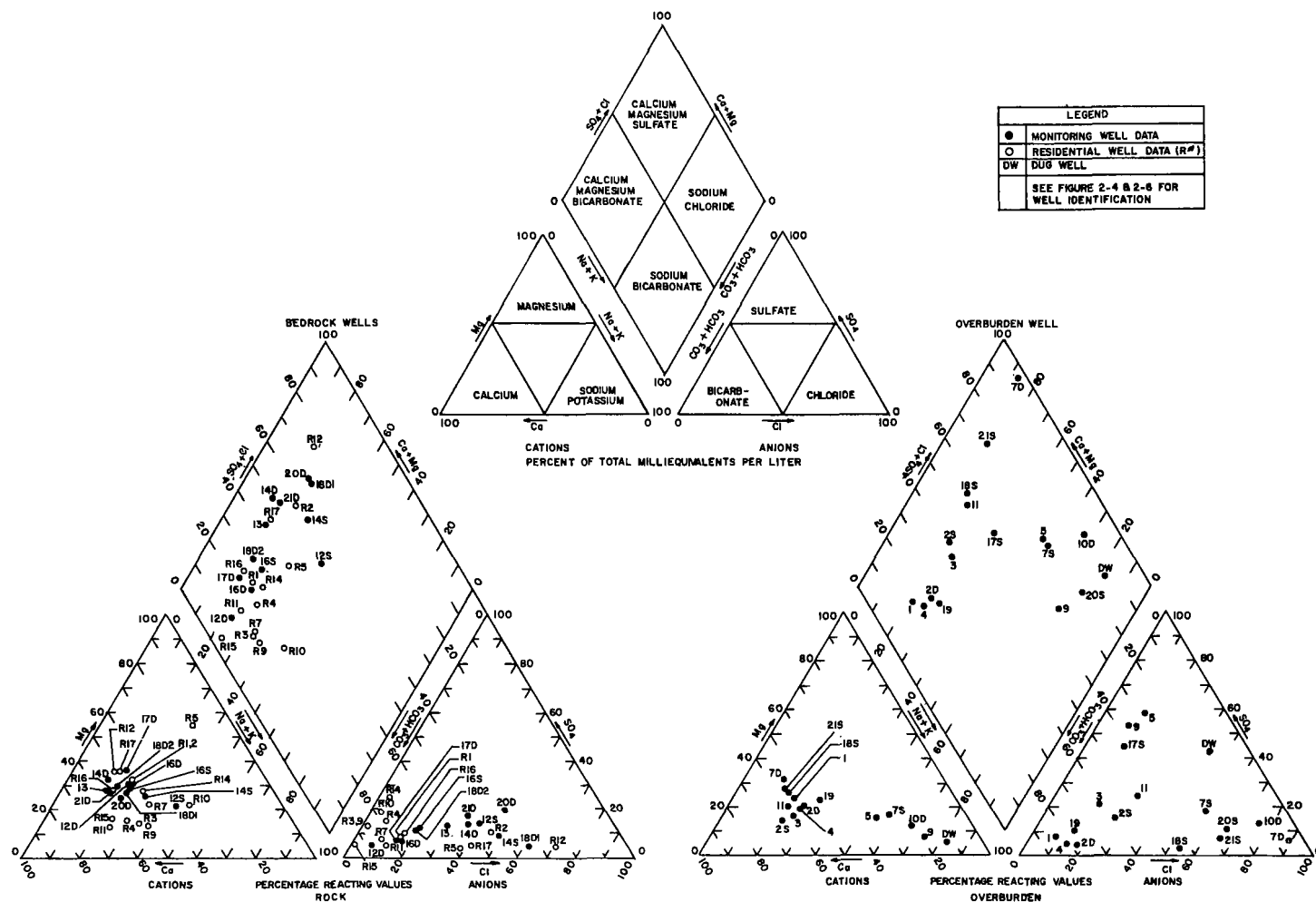
Figure 4
Hydrochemical Facies
Greenwood Chemical Site

therefore capable of rapid transport by groundwater. These nonreactive constituents, specifically chloride and sulfate, are thus able to migrate faster than the organic components of the contaminant plume at the site and would likely mark the leading edge of any such plume emanating from the Greenwood site.

Most of the residential wells containing TICs were downgradient of the primary source area at the site and also downgradient of the monitoring wells with elevated chloride concentrations. The fact that the nonreactive constituents have not been detected above background levels in any of the residential wells (Fig. 6) containing unknown TICs is evidence that these compounds are not site-related and that in general site-related contamination has not affected these wells.

Hohenfels

The investigation conducted at the Hohenfels Sanitary Landfills included the analysis of organic, inorganic and water quality parameters. Water samples were collected from the six on-site monitoring wells and from two water supply wells located off-site (5 and 8 km away). The two off-site water supply wells were considered to be representative of background groundwater quality. The interpretation of these analytical results concluded that neither the Operating Landfill nor Old Landfill were contributing contamination to the groundwater of the Malm aquifer. Water quality data were instrumental in this determination, as they strongly suggested that the contamination detected in the groundwater was not site related.

At both of the landfills, low levels of organic contamination were detected in the groundwater. However, no trends were apparent in

distribution of the organics data, i.e., upgradient and downgradient wells contained similar contaminants present at similar concentrations. The two off-site water supply wells also contained similar types and concentrations of organic contaminants. These results suggested that the source of the organic contamination was not the landfills.

In contrast to the organics data, inorganic data suggested that the landfills were contributing slight amounts of heavy metal contamination to the groundwater. Results for several metals (iron, chromium, manganese, lead and nickel at the Operating Landfill) displayed a trend of increasing concentration between upgradient (B1) and downgradient monitoring wells (B2 and B3) at the Operating Landfill, suggesting that the landfill was the source of the metals. At the Old Landfill, similar concentrations of metals (chromium, lead and nickel) were present in both the upgradient (B4) and downgradient monitoring wells (B5 and B6). In all 3 wells, the concentrations were elevated relative to the concentrations detected in the two water supply wells (i.e., background). Given the uncertainty regarding groundwater flow direction at the Old Landfill (a function of the limited number of monitoring points and complex hydrogeology), the presence of contamination in an upgradient well was not wholly unexpected.

This apparent contradiction between organic and inorganic data was resolved with the use of water quality data. Figures 7 and 8 show Piper and Stiff diagrams, respectively, for the Operating Landfill and the Old Landfill. Data from the two water supply wells, considered to represent background conditions in the area, also are presented. All of the monitoring well samples collected at the site were found to have little variation with regard to geochemical composition, as indicated by the
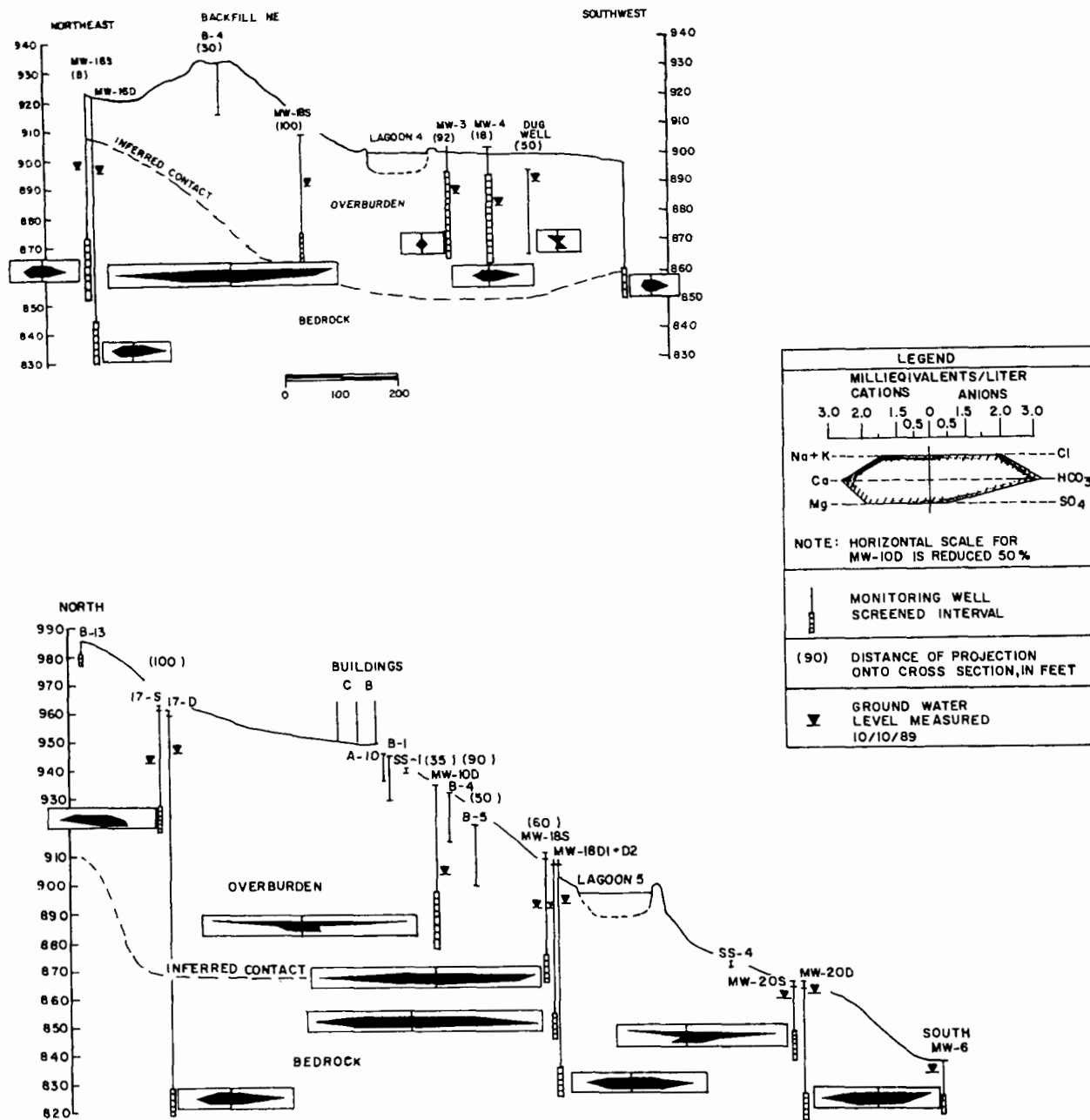
Figure 5
Vertical Profile of Groundwater Quality
Greenwood Chemical Site

tight grouping of the samples shown on Figure 7 and the similarity of Stiff polygons shown in Figure 8. Comparison of site groundwater geochemical composition with that of the two water supply wells also indicates that the waters are very similar.

Typical landfill leachate is enriched in chloride, nitrate, phosphate and ammonium. Although there are limited data available concerning the exact types of wastes buried at the two landfills, the bulk of the material is known to be ordinary domestic waste generated by the family housing and the troop billeting facilities at the Training Area. Therefore, the composition of leachate generated by the landfills should approach that described as typical. The samples collected from two landfills and the two water supply well show virtually no difference with respect to the water quality parameters of chloride and nitrate.

The source of the metals contamination was not resolved. It is unlikely that a leachate dominated by dissolved heavy metals constituents alone would be generated at either of the landfills. Equally improbable is that an ordinary leachate is being generated, but that only the heavy metals are reaching the water table. This second scenario would require significant attenuation capacity in the vadose zone. Heavy metals are much more likely to be attenuated (e.g., through ion exchange, complexation and adsorption) than are constituents such as nitrate, chloride and sulfate. If heavy metals can migrate to the water table, so should many of the other leachate constituents. The absence of these constituents suggests that neither the Operating nor the Old Landfill are the source of the heavy metal contamination.

The organic contamination, which is present in the water supply wells

OLD LANDFILL & WATER SUPPLY WELLS

OPERATING LANDFILL

NOTE: FM - Forst Meister Well
No.2 - Water Supply Well No. 2

Figure 7
Piper Diagrams for Samples from Hohenfels Landfill Study
(January 1990 Data)

and both upgradient and downgradient monitoring wells from the two landfills, suggests that there has been an area-wide degradation of groundwater quality. This conclusion is supported by the water quality data which show no effects from the two landfills.

CONCLUSIONS

The application of geochemical techniques during investigation at the sites described in this paper resulted in a more accurate characterization of the hydrogeology and a better understanding of the factors controlling contaminant transport at each site. These results support the conclusion that geochemical methods should be considered for the majority of site characterization studies and contaminant assessments. The techniques may be applied best at sites where little data are available,

where residential well data have a significant impact on the overall findings and in complex hydrogeologic settings where circulation and/or migration trends are not readily apparent. The design of monitoring programs for the evaluation of remedial actions or detection of releases from hazardous or solid waste management units are additional scenarios where geochemical data can provide highly useful (and relatively inexpensive) information concerning groundwater flow and groundwater quality on the site level.

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Figure 6
Greenwood Chemical Site

Figure 8
Stiff Diagrams from Hohenfels Landfill Study
(January 1990 Data)

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Investigations of Contract Laboratories: U.S. EPA Superfund Program Actions

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ABSTRACT

Recently, a number of laboratories under contract to the U.S. EPA's Superfund program have come under investigation for allegations of fraud. The U.S. EPA is taking action on the individual investigations, on policies and procedures related to the investigations and on further the prevention and detection of contract laboratory fraud.

INTRODUCTION

Currently, the U.S. EPA sends more than 100,000 samples a year from Superfund sites to commercial testing laboratories for analysis under Superfund's Contract Laboratory Program (CLP) contracts. The U.S. EPA's contracts with the laboratories contain extensive quality control provisions with strict limits and documentation requirements. While the CLP is not a laboratory accreditation or certification program, nor is it intended to be, other parties such as the U.S. EPA's prime contractors, states, other federal agencies and PRPs may contract independently with laboratories in the CLP for Superfund analyses they submit to the U.S. EPA. The data from these commercial laboratories are used by the U.S. EPA and these other parties in all aspects of Superfund site actions - site assessment, removal and remedial actions, enforcement and cost recovery.

Recently, some 10-17 of the approximately 100 laboratories in the CLP have become the subject of preliminary inquiries, investigations or civil or criminal actions by the U.S. EPA's Office of the Inspector General (OIG) and the Department of Justice (DOJ). These laboratories are alleged to have misrepresented the data they have submitted under their current or prior CLP contracts. Specifically, they allegedly have reported their data as having met the requirements of their contract provisions when in fact they have not. The primary examples relate to backdating and altering data to disguise time limits for analyzing the samples that were exceeded, instrument calibration requirements that were not met and results of quality control standards that were outside specification limits.

To assess the impact of this, we must first know whether or not any falsification of the testing process has in fact occurred - in most instances we only have allegations. Second we must know the nature and extent of the falsification. The falsifications may have variable or no impact on the final test result, depending on the nature and extent of the falsification in each specific instance. Finally, the impact on site decisions and actions will depend on the specific use of the data, whether results are available from other laboratories and whether independent data and information are available. The Agency is proceeding to make these determinations as the information with which to make them is made available. Only a very small percentage of the samples analyzed under the CLP is potentially affected by the allegations. Further, in the majority of cases, samples from a site were sent to a number of laboratories. The

Agency will take the actions necessary to protect public health and the environment while this matter proceeds to final resolution.

U.S. EPA SUPERFUND PROGRAM ACTIONS

The U.S. EPA's Superfund program is taking action in three major areas. It is pursuing the individual investigations of the laboratories, developing policies, procedures and guidelines related to the investigations of CLP laboratories and is implementing a data authenticity program to further prevention and detection of fraud in the CLP.

Individual Laboratory Investigations

The Superfund program has referred the allegations of fraud or laboratory self-disclosures that it has received to the Inspector General and is providing technical support to the OIG investigations and DOJ actions. We are working with other U.S. EPA offices and the OIG and DOJ to pursue criminal, civil and administrative actions. As a result, CLP samples have stopped being shipped to any laboratory that the OIG has notified us they have under investigation, five laboratories and nearly a dozen individuals have been suspended from receiving future contracts, a civil settlement with one laboratory has been reached, one individual has pleaded guilty and several indictments, pleas and settlements are pending.

Proposed Office of Solid Waste and Emergency Response (OSWER) Interim Final Policy for CLP Investigations

The proposed interim final policy outlines the actions OSWER will take to protect the integrity of data generated for OSWER's programs when a laboratory in the CLP is placed under investigation by the OIG. The provisions of the interim final policy are intended to provide the protection of OSWER's programs allowable under law and regulation, within the constraints of the criminal and civil investigative and judicial processes, while preserving the constitutional due process rights of the laboratories and the individuals. The provisions of the interim final policy, which are subject to change, are as follows:

- REPORTING
  - Report fraud allegations to the OIG
- COOPERATION
  - Cooperate with OIG investigations
- OSWER ACTION
  - Refer actions for suspension/debarment for future contracts
    Refer actions to stop CLP samples
    Refer actions to terminate CLP contracts
    Do not recommend/direct state, prime contractor,other federal agency or PRP action on their contracts
    Consider available investigation information in quality assurance project plan review/approvals

Exclude data from decisions until determine not misrepresented, unless can defend and document use
Consider referring/concurring on action to lift sample stop, suspension, etc. only when OIG/DOJ complete action

- NOTIFICATION

  Notify U.S. EPA offices of actions and information authorized by OIG/DOJ for release

  States, prime contractors, federal agencies and PRPs not notified of investigation or sample stop are notified of suspension, debarment, termination; notify states, prime contractors and other federal agencies of information authorized by OIG/DOJ for release

  Provide sample stop, suspension and other public documents upon request; will not provide Investigation Notice

  Notify states, prime contractors, federal agencies and PRPs that U.S. EPA will exclude data unless they can defend and document use

  Refer investigation inquiries from outside U.S. EPA to OIG/laboratory; give only information in public documents

  Notify all parties of completed investigation and U.S. EPA/DOJ action

The interim final policy is to be effective upon its issuance. When OSWER makes this interim final policy a final policy, it intends to issue it as a *Federal Register* Notice so that all parties involved with the CLP will be aware of the actions OSWER will take.

Other Related Policies and Guidelines

The Superfund program is also working with other Agency offices to develop guidelines that address press releases and other communications related actions. In addition, we are drafting a policy regarding the use of data from laboratories under investigation. Additional procedures and guidance will be developed as necessary.

Data Authenticity Program

To further prevent and detect fraud in the CLP, the U.S. EPA is working jointly with the Departments of Defense and Energy to identify and implement several types of measures. These measures include contract provisions related to business integrity and automated data management; oversight procedures such as tailored audits and performance indicators; and communicating the importance of data integrity, individual's responsibilities and the consequences of fraud to the laboratory community.

CONCLUSIONS

Based on the actions we have taken and the consequences to the laboratories and the individuals involved, few if any laboratories should consider misrepresenting data in the future. The Superfund program welcomes any suggestions regarding this matter.

DISCLAIMER

The proposed policies outlined in this paper are currently under Agency review and may be revised. The content of this paper is not a statement of final Agency policy and no action should be taken on the basis of it.

New Horizontal Wellbore System for Monitor and Remedial Wells

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ABSTRACT

This paper describes the development and field testing of an innovative drilling system for installing horizontal wells for groundwater monitoring and remediation. Detailed technical specifications and planning and operating considerations are presented. In addition, the paper suggests specific applications for the system.

INTRODUCTION

Over the last decade, horizontal drilling technology has been developed and applied in the petroleum industry for oil and gas production and in civil engineering projects for utility and pipeline installation. The oil industry has drilled more than 2000 horizontal wellbores since 1980. This experience has helped service companies develop new drilling technology and has helped oil companies gain a better understanding of how to use horizontal wells for petroleum production.[1]

In 1989, the authors initiated a research project to identify potential applications for horizontal drilling in the environmental industry. This study determined the industry's preferences for well construction, the geologic strata to be drilled, as well as requirements for well depth, overall length and borehole directional accuracy. Other considerations such as availability of suitable drilling rigs, site space limitations and acceptable operating schedules also were investigated. These efforts resulted in the general systems specifications listed in Table 1.

MAJOR DESIGN CONSIDERATIONS

Major considerations in designing the drilling system included:

Table 1
System Specifications

Depth of Horizontal Section: 18 ft to 300+ft below surface

Horizontal length: more than 500 ft

Screen size in the horizontal section: 6-inch nominal (6 5/8 in OD)

Casing size in the curve section: 10-inch nominal (10-3/4 inch OD)

Casing and screen material: High density polyethylene pipe

Horizontal Placement accuracy: True vertical depth +/- 5 ft

Azimuth: +/- 2 degrees

Pumping specifications: submersible pump ahead of screen

Seal specifications: sand pack or other filter

- Placement of horizontal sections at depths ranging from 20 ft to more than 300 ft.
- Installation of horizontal lengths of more than 500 ft
- Drilling in very unconsolidated formations
- Effective completions of the wells with a minimum 4-in. OD screen
- Operation with a minimum rig crew
- Use of noncontaminating drilling fluids (as close to fresh water as possible)
- The industry requirement to drill wells economically
- Personnel safety and protection of surface environment from contamination

CUSTOM DRILLING SYSTEM

After reviewing the available contract drilling service and hardware, the project team concluded that technology is not available within the water well and monitoring well industry to conduct horizontal drilling operations. In addition, mining and civil engineering technology do not meet the specific requirements of horizontal drilling in environmental applications. Because of these factors, an entirely new drilling system, including downhole technology and a custom slant drilling rig, would have to be designed and built for horizontal drilling in the environmental industry. The project team developed the concept by adapting advanced oilfield technology. The rig and downhole tools were designed to work as a system to drill to horizontal on a 100-ft radius (Figs. 1 and 2).

Important features of the drilling rig that resulted from this effort include:

- Capability to slant the rig mast from vertical to 60 degrees in 15-degree increments. Figure 3 shows how this capability enables the drilling system to place the horizontal section at any depth in this range.
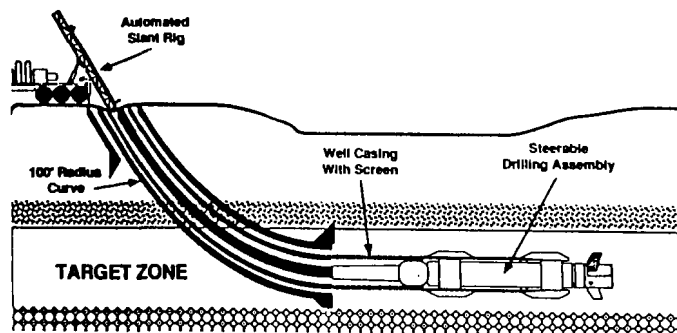
Figure 1
Horizontal Wellbore System Schematic
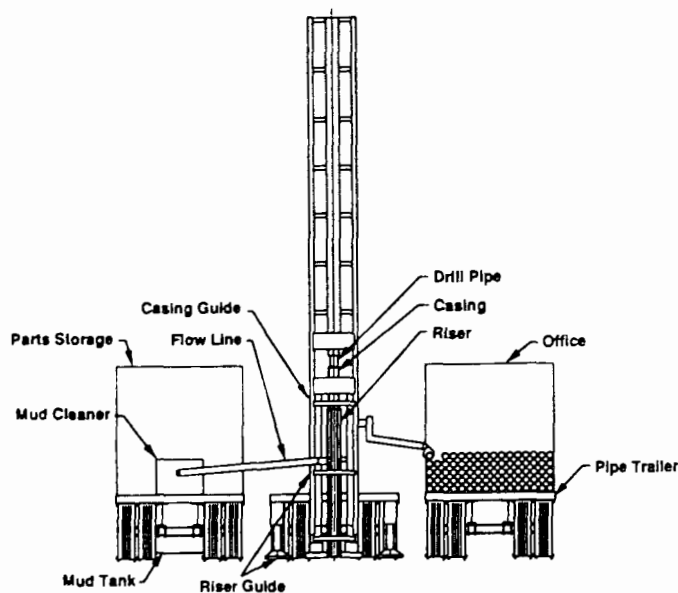
VIEW AT REAR OF TRAILERS
Figure 2
Horizontal Wellbore System Drilling Rig

- The rig is hydraulically operated for precise, automated control from a single driller's console. Rated at 2000 ft for vertical drilling, the unit has a hoisting capacity of 70,000 lb and 30,000 lb of push down capability. This gives the rig ample power for handling the system's dual drill string which may encounter significant torque and drag during horizontal drilling.
- Pipe handling is accomplished with a hydraulic pipe-handling arm and two hydraulic top drives: one for the casing and one for the drill pipe. In addition, a power tong makeup and break-out unit is incorporated for making/breaking connections. Casing tongs are provided to hold the well casing when required.
- The drilling unit's fluid system—with mud pumps, fluid tanks, solid control equipment and a grouting machine—is included in a single trailer. The circulation takes place in a closed loop and requires no earthen mud pits. At the conclusion of the job, drilling fluids and cuttings can be placed in drums for disposal.
- Rig operation requires only a three-man crew per shift, with a project engineer supervising the job.
- Pipe storage, rig-site office and electrical generator are housed in a third trailer. The site office has a computer; the office area can also be used as a laboratory as needed. The generator provides power for lights used for nighttime drilling. A small crane, mounted on the trailer, is used to move drill pipe and casing.
- All three trailers that comprise the drilling unit can be transported without special permits on highways in the contiguous 48 states.

DOWNHOLE DRILLING EQUIPMENT

Like the drilling rig, the downhole system also had to be specifically engineered to solve the unique problems associated with horizontal drilling in shallow, unconsolidated formations. The downhole drilling assembly is comprised of a dual drill string; a hydraulic downhole motor; an expanding drill bit; and a toolface indicator/inclination measurement device. (Fig. 4).

The unique drilling assembly was designed to address the problems of drilling horizontally through unconsolidated and heterogeneous formations found near the surface. Such strata make it difficult to maintain hole integrity, even in vertical drilling. In horizontal drilling, there is an even greater risk of hole collapse. This is especially true in environmental drilling applications where most drilling fluid additives are avoided. In such conditions, the horizontal hole could be lost when the drilling assembly is changed or during installation of completion hardware
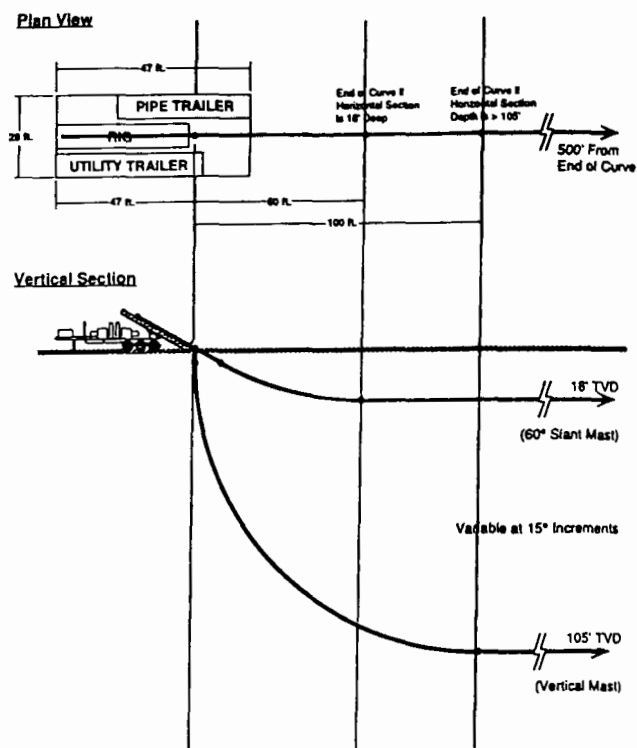
Figure 3
Layout and Depth Capability
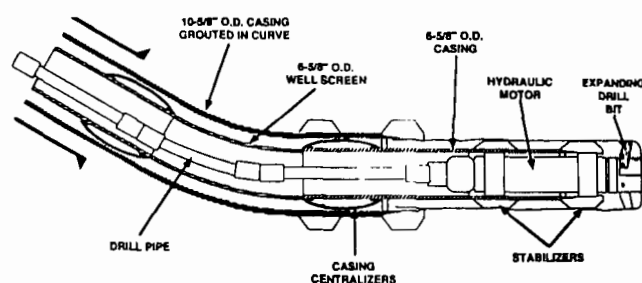
Figure 4
Horizontal Drilling Downhole Equipment

A new casing/drilling method was developed to solve this problem. An inner string of 2.875-in. drill pipe pushes the high density polyethylene (HDPE) casing/well screen into place. This casing protects the hole from cave-in during drilling and installs the well casing at the same time. (HDPE was chosen because of its unique physical properties including strength, flexibility and resistance to damage from a broad range of chemical contaminants.) The casing is centralized in the hole to permit cementing and effective well completion. Once the well is drilled to total depth, the inner drilling assembly is withdrawn from the hole and the casing is left in place.

Downhole power and the ability to guide the hole are provided by a steerable downhole hydraulic motor. The motor is based on the oilfield positive displacement moineau motor concept which converts the hydraulic energy of the pumped drilling fluid into mechanical energy (speed and torque) that rotates the bit. However, it is an especially-designed multilobed motor that is approximately one fifth the length of oilfield tools. Flowrates range from 150 to 300 gpm, generating 35 to 75 hp at the bit.

Directional drilling is accomplished by placing the motor in an eccentric position in relation to the hole axis by installing stabilizer rings at two points on the motor housing. (Fig. 5). These eccentric stabilizers are positionally matched with the concentric stabilizers in the lowest
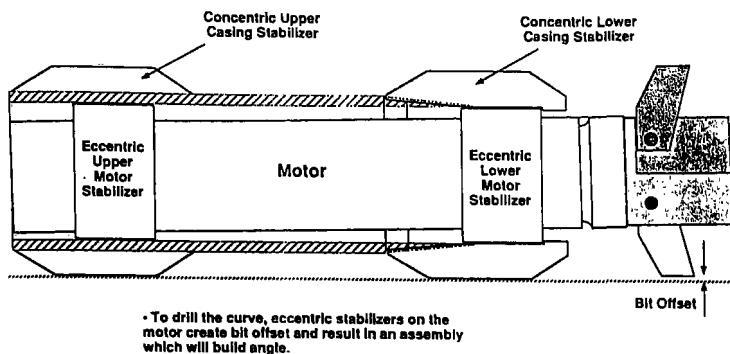
Figure 5
Detail of Lower Drilling Assembly

$$Radius\ (R) = \frac{L_1 + L_2}{2\,Sin\,(\emptyset)}$$

$$Build\text{-}up\ Rate\ (BUR) = \frac{2\emptyset}{L_1 + L_2}$$
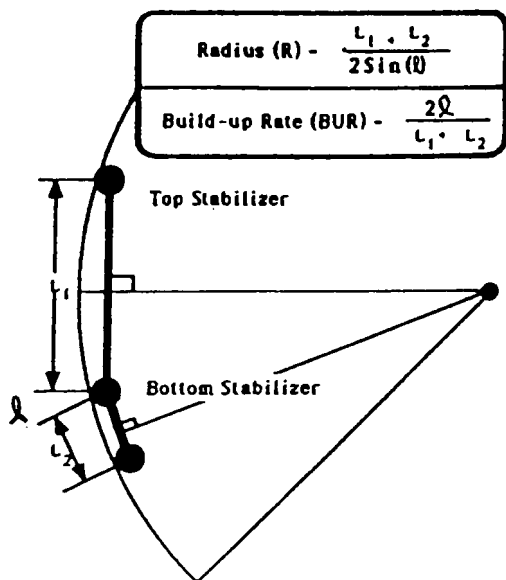
Figure 6
Calculation of Buildup Rates

joint of outer casing. By orienting the direction of the bit offset (also called "toolface"), the hole can be steered. The configuration of the drilling assembly is designed to turn the borehole at a constant rate which can be precisely calculated (Fig. 6). The two stabilizers and the bit gauge serve as tangency points that define a constant radius arc along which the assembly will be drilled. Build rate can be controlled by varying the eccentricity of the inner stabilizers. The system can be used to drill a straight course by regularly adjusting the toolface from side to side.[2]

The downhole drilling system features an expanding drill bit which drills a hole that is large enough to permit the casing to be installed during drilling. The bit used in the curved section drills a 12.25-in. hole for installation of 10.75-in. OD casing, and the bit used in the horizontal section drills an 8.625-in. hole to permit running a 6.625-in. OD casing/ well screen and providing space for gravel packing around the screen. The initial bits used with the system were drag-type bits with hydraulically-spread wings and tungsten carbide cutting surfaces. Other drill bits, in development, will include roller-cone bit technology for drilling harder formations and glacial till.

The toolface indicator system is a mud-pulse telemetry system which measures inclination from vertical and toolface orientation and transmits the measurements to the surface via pressure pulses in the drilling fluid. These pulses are detected at the surface by a pressure transducer, whose readings are interpreted by a surface control computer. The toolface indicator sensors are located just 8 ft above the drill bit, giving system operators the ability to monitor the drill bit's position and wellbore trajectory every 15 sec. The TFI therefore saves a significant amount of time that would be required for single shot surveys, while eliminating the complication and risk associated with electric wireline steering tool devices commonly used in petroleum drilling and river-crossing applications.

DRILLING PROCESS

Before drilling begins, wells are carefully engineered to meet the specific objectives of the project. Site characterization studies, including monitor well data, are reviewed to determine the size and three-dimensional position of the contaminant plume. Groundwater flow and contaminant migration characteristics are analyzed to assure proper well placement. Next, surface location and operational factors are considered. Then, the depth and direction of the horizontal wellbore, screen length, development and pumping methods are determined.

The rig is moved onto location and aligned to drill the horizontal wellbore in the desired direction. The angle of the rig's mast is adjusted to drill the horizontal section at the proper depth.

A 14-in. hole is augered 5 to 10 ft into the soil and a 12.75-in. conductor is set and cemented in place to provide a controlled conduit for the drilling fluid.

A straight drilling assembly is lowered in the hole to drill to the required depth so that the 100-ft radius curve will reach horizontal at the desired vertical depth. Once this depth is reached, the assembly is withdrawn and the curve drilling assembly is picked up and run into the hole.

The curve is drilled in a 12.125-in. hole and case at the same time with 10.75-in. casing. The assembly is oriented in the proper direction using the toolface indicator and by holding orientation at the surface. The same survey tool is used to track the progress of the assembly. After the 20 ft lengths of dual drill string are drilled into the hole, both components of the dual drill string are added simultaneously with the articulated pipe handling system in the rig mast. Once the curve reaches horizontal, the inner assembly is withdrawn leaving the 10.75-in. HDPE in place.

A cementing plug is then run into the hole to seal the end of the casing and to allow the cement grout to be circulated through the drill string to fill the annular space between the casing and the hole wall. Once the desired amount of cement is in place, the drill pipe is withdrawn from the well and the grout is allowed to set. The grout will provide structural support to the casing as well as prevent the migration of contaminants from one zone to another along the outside of the casing.

The plug is drilled out with a special mill on a downhole motor until the formation is encountered. This assembly is then retrieved, and the horizontal drilling assembly is run into the hole.

As mentioned above, the system uses an 8.625-in. bit to drill the horizontal section. A 6.625-in. OD HDPE screen is pulled into the lateral wellbore by the drilling assembly as the well is drilled. The system is steerable for course corrections and fine tuning of the horizontal section. Steering capability is provided by the hydraulic downhole motor, by stabilizers on the casing and by survey instrumentation.

Formation evaluation is accomplished at desired intervals using a core, soil or gas sampler. Drilling is stopped and the inner assembly consisting of the bit, motor and drill pipe is retrieved from inside the slotted liner. The bit and motor are replaced by the sampling tool and run into the hole. The sampling tool is then drilled into the formation the required depth and samples are retrieved. Shelby-tube and soil gas sampling devices also are in a testing phase.

Drilling continues with the horizontal drilling assembly until the desired displacement is achieved. The inner drilling assembly is then retrieved leaving the 6-in. screen in place.

A combination plug running tool, wash sub is run into the ID of the 6.625-in. casing, and a plug is placed at the bottom of the screen. The screen is then washed by circulating fluid through the inner string and out through the nozzles of the wash sub. These nozzles are aimed radially outward to clean the screen to remove any drill cuttings plugging the screen slots or remaining in the wellbore. Once the hole is clean, the wash sub is removed and the string is run back into the hole for the filter packing procedure, should a filter be required between the screen and the wellbore.
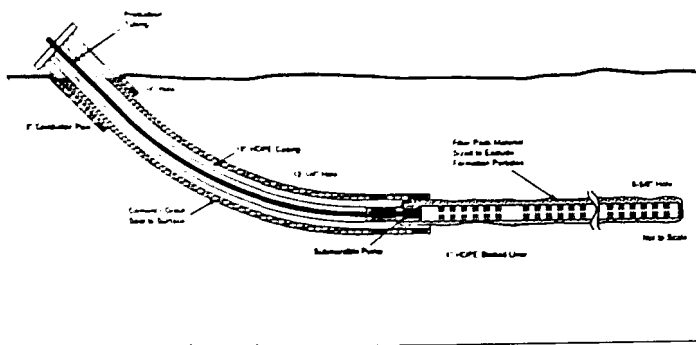
Figure 7
Typical Well Construction

Filter packing is performed using low density materials and a special gravel directing device to assure a uniform layer around the screen. The material is put in place by circulating the packing material suspended in water down through the annulus. As the water passes through the screen to enter the inner string, the filter packing material is screened out, filling the volume between the screen and the wellbore.

Once the filter packing is complete, a submersible pump can be lowered into the well to complete the development. Typical well construction is shown in Figure 7.

An alternative completion method involves using well screen in the horizontal section which has an additional layer of fine mesh well screen to provide sand control, in lieu of the gravel packing. In the right formations, this completion method can cut a day off the well installation process.

A variety of other completion methods are being investigated. In cases where the horizontal section is placed in bedrock, the well can be drilled without the outer casing string, and the desired production hardware, for example stainless steel or wire-wrapped screens, can then be run.

FIELD TEST OBJECTIVES

The prototype horizontal wellbore system underwent its first field trials in the summer of 1990, southeast of Houston, Texas. The objectives of the field test were to:

- Test the functionality of the surface equipment, including rig system components and circulating system.
- Drill a 45-ft vertical hole to demonstrate casing while drilling; to test the functionality of the expanding drill bit; and to gain experience making a hole in the target formation.
- Drill a horizontal hole with approximately 400 ft of departure from the wellhead. This included drilling from a 45-degree slanted rig position and building the hole's inclination along a 100-ft radius. This curved section would be drilled in 12.125-in. hole and cased in 10.75-in HDPE casing, which would then be cemented in place. Then the smaller drilling assembly would be used to drill the horizontal section and install the 6.625-in. liner simultaneously.
- Complete the horizontal section by pumping HDPE gravel packing material into the annulus between the casing and the hole wall.
- During test well drilling, project engineers would monitor the performance of system components, noting areas for improvement.

FIELD TEST PREPARATION

To prepare for the test, a vertical surface hole 12-ft deep was augered and the 12.75-in. conductor was set and cemented in place. A slanted conductor was installed at 45 degrees, close to the vertical hole and positioned so the rig would not have to be moved to drill through it. Once this slanted conductor was cemented in place, an unstabilized rotary assembly with a roller cone bit was used to drill the cement plug and approximately 4 ft of the formation.

VERTICAL HOLE

The vertical hole was drilled with a bottomhole assembly comprised of the 8.625-in expanding bit, a 4.75-in. drilling motor placed con-

centrically in the casing and a 6.625-in. well casing. The hole was drilled to 60 ft in 1 hr, at a flowrate of 150 gpm. The casing easily ran into the hole, demonstrating that the motor/expanding bit concept could successfully be applied.

The formation was a fine, unconsolidated sand, interspersed with clay stringers. Pockets of gravel also were encountered.

When the drilling assembly was pulled out of the hole, the HDPE casing string came with it. Sand had been drawn into the casing causing the motor to jam. Some simple modifications, such as beveling the edges of the eccentric stabilizer rings, were made to facilitate releasing the motor from the lower casing joint.

DIRECTIONAL WELL

The first borehole drilled from a slanted conductor demonstrated the directional drilling capabilities of the downhole system. Drilling parameters and operating procedures were varied to test directional results.

After the vertical hole was drilled, the rig mast was tilted to 45 degrees in preparation for drilling the horizontal hole. Then the 6.75-in. motor assembly was made up and inserted in the plastic casing, and together they were lowered into the conductor.

After orienting toolface to high side (for maximum angle build), drilling circulation was begun at 200 gpm. However, the motor stalled almost immediately. It was surmised that this problem was caused by the condition of the conductor pipe, which still contained some cement which had not been cleaned out. The assembly was retrieved from the hole along with the casing and a stiff assembly, including a 12.125-in. bit and two stabilizers, was used to drill from the conductor (12 ft MD) to 16 ft MD, providing a straight pathway for the curve-drilling assembly to enter the formation.

The curve drilling assembly with casing was run into the hole. The motor was started with a flow rate of 150 gpm, and the assembly was worked up and down until it ran smoothly into the hole. Drilling commenced at 4 ft/min. Because there was no identifiable torque created by the motor, it is likely that the formation was being jetted away ahead of the bit. The formation was an unconsolidated, very fine sand.
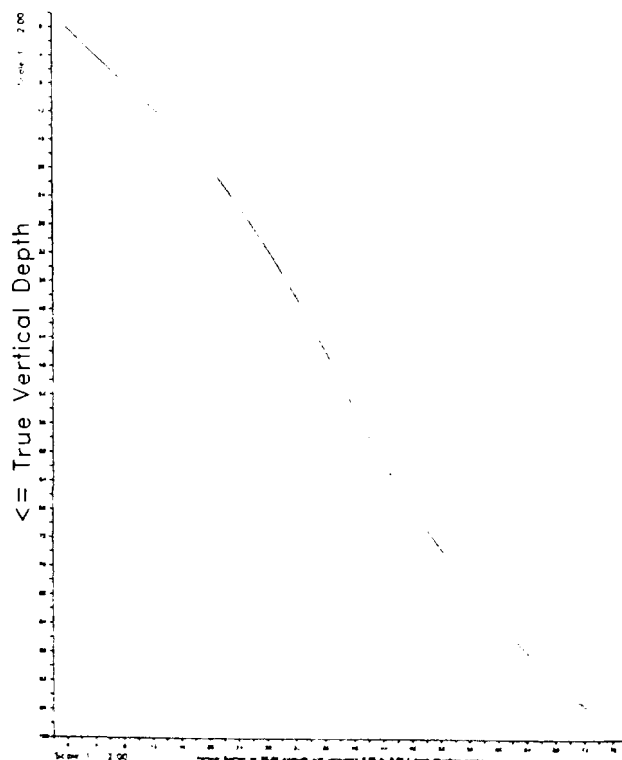
Figure 8
Plot of Directional Test Well

The assembly drilled to 42 ft, but dropped angle at the rate of 0.58 degrees/ft.

Below 42 ft MD, the penetration rate increased to 3.5 ft/min, but the hole continued to drop angle at 0.27 degrees/ft over the next joint to 62 ft MD.

On the next joint, the flow rate was reduced to 150 gpm and the penetration rate dropped to 2.5 ft/min. Over this hole section, the assembly began to build angle at the rate of 0.43 degrees/ft. Some clay was seen for the first time in the return flow of drilling fluid.

Because the reduced flowrate appeared to help regain control over the angle build, it was concluded that the fluid was washing the hole diameter. To reduce these effects, the inner string was tripped out of the hole. The outer-facing bit nozzles (which had been 0.438-in.) were plugged and the forward facing nozzles (previously 0.576-in.) were replaced with 0.625-in. nozzles.

The drilling assembly was placed back inside, and drilling was commenced with 150 gpm of circulation. ROP of 3 to 4 ft/min was achieved. The assembly built angle at 0.36 degrees/ft (159 ft radius).

On the next joint (102 to 122 ft MD), the flowrate was increased to 200 gpm to improve hole cleaning. The penetration rate increased to 4 ft/minute, and the build rate increased to 0.54 degrees/ft. (106-ft radius). At a measured depth of 136 ft (96 ft True Vertical depth TVD), the hole had achieved 52.2 degrees of inclination. (Fig. 8).

Changing the bit nozzles had significantly improved the directional performance of the bottomhole assembly. Armed with this knowledge, the project team decided to start a new well with a newly-installed slanted conductor. Casing from the slanted well would be pulled from the hole for reuse on the second attempt, after installing new threaded HDPE connections using fusion welding techniques.

HORIZONTAL WELLBORE

A second slanted conductor was augered into place approximately 8 ft north of the first one and cemented into place. After moving the rig, the stabilized rotary drilling assembly was used to drill out the cement plug and establish contact with the formation.

The curve-drilling BHA used on this borehole varied from that used on the directional well in that: (1) the outside bit nozzles were plugged and two 0.625-in. nozzles were used at the nose of the bit, resulting in no hydraulic horsepower at the bit and less hole enlargement; and (2) an increased bit deflection (caused by greater eccentricity of the stabilizers on the motor body) was used, resulting in an assembly with a theoretical 90-ft turning radius (compared to the 100-ft radius used on the directional well).

As in the slant well, it was difficult to build angle in the soft formation immediately below the conductor. The well dropped angle slightly as the first joint was drilled, then held angle to approximately 63 ft MD. Then the assembly began building angle steadily, reaching 80 degrees of inclination at 150 ft MD (87 ft TVD), the end of the 10.75-in. casing section.

Due to the low flowrate, pulse heights from the TFI tool had been adjusted to improve the strength of the signal. This system performed impeccably while drilling the curved section.

Some hole drag and compressive buckling of the casing were experienced during the drilling of the curve, possibly due to clay and gravel stringers or to some spiralling of the hole. The drilling assembly was pulled easily from the casing string, and the casing did not move.

The curved casing was cemented into place through the drill pipe by setting a cement plug, dropping a dart and then pumping cement until it came out the annulus. Once the cement had cured, a downhole motor-driven milling assembly was used to mill out the plug and retrieve it. A ring left in the hole was retrieved in one try with a specially-built fishing tool. After a cleanup trip, the project team was ready to drill the horizontal section.

The downhole system comprised of an 8.625-in. expandable bit, 4.75-in. drilling motor, TFI measuring device and 2.875-in. drill pipe was run into the hole along with the 6.625-in. HDPE slotted screen.

Once on the bottom, the drilling assembly began to drill immediately with no stalling or sticking. At a flowrate of 150 gpm, the system drilled at 2 to 3 ft/min. It was found that pump rates have a significant affect

on hole inclination. When flow rate was increased to 250 gpm to improve hole cleaning, inclination dropped by 8 degrees while drilling one 20-ft joint.

By orienting the toolface upwards and holding pump rate steady at 150 to 175 gpm, angle was built to horizontal and maintained until 400 ft of total departure was achieved. (Fig. 9). Some hole sticking was experienced, but these problems were overcome by picking up approximately 6 ft off bottom to ream and circulate. The project team believed they could drill further, but drilling was stopped because all test objectives had been met.
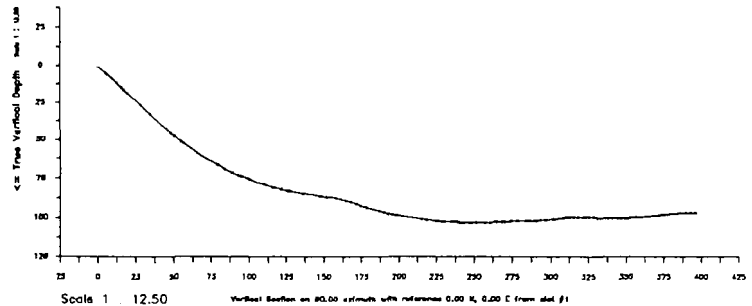
Figure 9
Plot of Horizontal Test Well

Once total depth was reached, the drilling assembly was withdrawn from the hole. Sand drawn into the hole through the open end caused some sticking on this outward trip, but after working the pipe up and down and circulating a little, all tools were successfully pulled from the hole.

COMPLETION

One technical objective of the field test was to prove that a slotted casing could be drilled in—place using the dual string drilling technique. This operation was successfully performed with slotted casing used from surface to total depth.

Several days after drilling was completed, a gravel packing procedure was attempted on the well. First a plug was set in the bottom of the well, and a wash sub, run on the drill pipe, was used to clean the well slots (which were 0.020-in. wide) only in the horizontal section. Pumps and seals were configured to reverse-circulate 0.125-in. HDPE pellets into the annulus between the well screen and the formation. When pumping commenced, it was found that the hole wall had bridged into the casing somewhere in the curve above the horizontal section, preventing gravel packing material from reaching the bottom of the hole. Work continues toward perfecting this gravel packing techniue. Future gravel packing operations, for example, probably will use slotted screen only in the zones of interest.

The project team also has investigated completion techniques that are less complicated than the gravel-packing method. Specifically, a new completion string, incorporating a screen outside the HDPE slotted casing, has been designed and introduced since the initial field test. This system should provide adequate sand control in most situations.

APPLICATIONS

This recently demonstrated horizontal drilling technology has many potential applications in the environmental industry. For example, there are numerous "common sense" applications for horizontal drilling, including recovery of contaminated groundwater or leachate from beneath lagoons, landfills, buildings, storage tanks, refineries and chemical plants. (Fig. 10) In these cases. it is difficult to place vertical wells to perform sampling or remediation.

In other situations, where vertical wells now are used to extract polluted groundwater for treatment, horizontal wells can offer significant advantages. By placing a long horizontal section through the contaminant plume, a single horizontal well may replace many vertical wells, while also reducing clean-up time.[3]
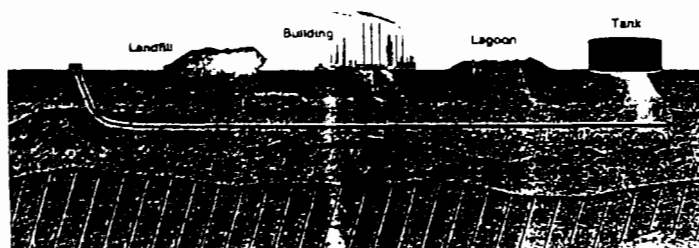
Figure 10
Horizontal Well Used To Sample
and Remediate Beneath Obstacles
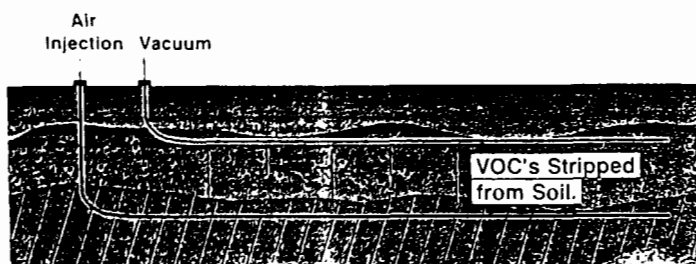
Figure 11
Horizontal Well Used for Soil Gas Extraction

Soil gas extraction is another important potential application for horizontal wells. Figure 11 shows how pairs of horizontal wells can be drilled at different depths. The lower well could be used to inject air, while the upper well could be used to extract the air stream along with VOCs that have been stripped from the soil.[4]

In situ remediation also may benefit from horizontal drilling technology. For example, horizontal wells might be used to convey microbes and/or nutrients for bioremediation of underground contaminants. Likewise, horizontal wells might make it possible to chemically treat heavy metals in-place without incurring the expense and hazards of digging up contaminated soils. Horizontal wells also could be used for in situ vitrification of nuclear waste. In this application, the drilling system would bore a pathway for electrical conductors to turn hazardous waste into glass.

Horizontal wells also could be applied at landfills and other areas where a barrier must be installed to keep pollutants from migrating into the groundwater. A series of horizontal wells beneath a landfill or a lagoon, for example, could be used to place a pressure curtain of pumped air or water, or a floor of grout, epoxy or cement to contain the potentially harmful leachate.

During our technical review, many potential users requested the capability to take samples of soil gas, soil and bedrock from beneath landfills, lagoons, tanks and buildings. In these situations, vertical methods are either impossible, inconvenient or pose a threat to the environment by providing contaminants a pathway into the aquifer. Horizontal drilling systems can be applied to handle the majority of these sampling needs.

In the future, other technologies are likely to be added to the horizontal wellbore system. These innovations could include methods for obtaining undisturbed formation samples and containerized gas samples beneath landfills and buildings; geophysical logging services adapted for horizontal data acquisition; and completion technology to isolate zones along the horizontal well for selective sampling and completion.

CONCLUSION

In conclusion, a new horizontal drilling and sampling system has been designed and built to meet the special requirements of the environmental industry. A prototype system has been successfully field tested and has been refined and introduced for commercial use. We believe there will be many applications for the new system as the environmental industry begins to remediate contaminated groundwater.

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New Technique For Landfill Leachate Well Installation

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INTRODUCTION

Landfilling of industrial wastes has been used extensively as a means of disposal throughout the United States. Prior to RCRA, many landfills were little more than excavated trenches. Although some attention may have been given to engineering concepts and long-term environmental/operational aspects, often they were not fully developed during the construction and filling of such trenches. With the passing of time, one aspect of land management that has been given major emphasis is the concept of water (leachate) management within a landfill. Indeed, leachate treatment has risen to such importance that waste management facilities succeed or fail based on the quality of their leachate management efforts, as judged by groundwater quality around the landfill.

The CECOS International Inc. facility near Livingston, Louisiana, has three pre-RCRA disposal units (landfills) that were designed, constructed and closed by a previous owner. These disposal units were constructed without any type of leachate removal system.

During 1984 and 1985, samples from two nearby monitor wells revealed evidence of groundwater contamination in the area, principally in the shallow (30 foot) zone. A one-year, state-approved groundwater assessment revealed the nature and extent of groundwater contamination. Later, the Louisiana Department of Environmental Quality (LDEQ) approved a remedial action plan (RAP) for this area that included:

- Installation of an engineered slurry wall surrounding the disposal units to isolate the shallow groundwater regime
- Placement of an engineered cap over the units to prevent rainwater infiltration
- Installation of several recovery wells inside the units to facilitate removal of leachate

While efforts are now underway to provide for removal of impacted groundwater in the vicinity of these old wells, the long-term solution is to reduce or, to the greatest extent possible, eliminate the liquid volume inside the cells.

This paper deals with the installation of 16 leachate recovery wells inside the pre-RCRA disposal units.

CONSIDERATIONS

The well installation method selected was required to meet the following criteria:

- Reduced Health and Safety problems: Waste inventories for the pre-RCRA disposal units were given in general terms. Because of the nature of these records, the contents of the disposal units were largely unknown. Costs for personnel protection, if significant amounts of waste material were exhumed, were estimated at $1,000/day.
- Minimized waste generation: Conventional drilling techniques could potentially bring up to the surface substantial volumes of wastes.

Disposal costs were estimated at $1,000 per drum of waste exhumed.
- Reduced risk to the environment during installation: Exhumed wastes could pose a threat to human health and the immediate environment and contaminate the newly placed composite cap.
- Assured uniform sandpack: An effective recovery system required installation of a uniform sandpack in the loosely compacted fill material, which could have collapsed into an open hole. Since it was known that a substantial portion of the inventory was drummed, placement of a conventional sandpack might have been very difficult.

Drillers proposed several approaches for achieving the requirements stated above:

- Conventional hollow stem auger as the sole means
- Hollow stem auger as the primary technique, with a driving technique as a secondary means
- A driving technique to be used as the sole means.

Bids from prospective drillers ranged from $100,000 to $125,000 for the entire job, exclusive of additional personnel protection or monitoring.

AWD Technologies, Inc., a wholly owned subsidiary of The Dow Chemical Company, proposed to install the entire system using an innovative method of driving pipe. CECOS was led to this technique through a conversation about the project with the Louisiana Department of Environmental Quality. The Dow Chemical Company plant in Plaquemine, Louisiana, had used the method to install 236 recovery wells in contaminated soils.

SELECTION

The "driving" technique for well installation was chosen for the following reasons:

- Time: This method was estimated to take 16 days (conservatively) in contrast to a minimum of 30 days using conventional drilling techniques.
- Waste reduction: AWD's previous experience had shown the method capable of substantial reductions in volumes of waste generated.
- Health/Safety: Due to minimal waste production, the method greatly reduces the need for extensive Health and Safety equipment and monitoring.
- Obstructions: The method works even where obstacles, such as drums, are encountered.
- Sandpack: The method would allow the installation of a prepacked well screen, thus providing some assurance of a functional pack.
- Cost: All of the above factors have the potential to keep the cost of installation to an acceptable level.

SAFETY

The entire area immediately around the landfills was secured and

designated as a restricted work area. Further, a 40-foot diameter "exclusion" area was established around each borehole. Anyone working in this area had to wear all personal protective equipment (PPE) recommended by the Health and Safety Officer. Areas were designated for decontaminating PPE as well as for rest breaks.

A preconstruction meeting was held to fully brief all crew members on the project objective, Health and Safety requirements, management structure and communications procedures.

The work was started in modified level C protection; i.e., Sanarex suits, steel-toed rubber boots, rubber gloves taped to the suits and full-face cartridge respirators. A large portable fan placed approximately 20 feet from the borehole provided air movement across the work area.

When the first casing was set in clay at the bottom of the landfill, the Health and Safety officer removed the push cap, sampled the air, detected no appreciable volatile organic carbons (VOCs), and approved the use of level D protection for the remaining wells. Careful monitoring was continued to detect any need to upgrade the personal protection.

The entire project was coordinated by CECOS.

EQUIPMENT AND MATERIALS

Three pieces of equipment were required during the installation process: a back-hoe (CAT 245 or equivalent), a 50-ton crane and a manlift.

Several specialized tools were developed by Ray Frankson and Charles Oliver of The Dow Chemical Company to implement this procedure. The key components were a thread-jointed casing that allows installation to various depths and an internal thread-jointed driving tool that could be removed once the casing reaches the desired depth. Shackling facilitates extracting the casing and driving tool from the ground and moving the apparatus to a new location (Fig. 1).

Figure 1
Well Installation Tool

INSTALLATION

Prior to beginning work, all equipment was positioned to maximize use of time and effort.

Well installation began with assembling the outer casing pipe. The inner "insert" with the driving point was assembled next. The back-hoe held the casing in a vertical position while the driving insert was slowly lowered into the casing using the crane. Once this was accomplished, a flat, threaded pressure plate was attached to the outer pipe and the back-hoe then pushed both pipes into the ground at the same time (Fig. 2). When the desired depth was reached, the insert with the point was removed and replaced by another insert which had a hollow sampling tube at the bottom (Fig. 3). When this sample tube was positioned inside the casing pipe, both pipes were again pushed approximately one foot to obtain a sample to verify that the well was seated in clay at the bottom of the landfill. The sampling tube was

Figure 2
Back-Hoe Pushes Pipes Into Ground

removed from the insert and transported in a 55-gallon drum to an extruder in order to push the sample out, monitor organic vapors and perform visual classification of the material.

At this point, only the outer drive pipe remained in the ground (Fig. 4). The fiberglass reinforced epoxy (FRE) well casing with a presanded screen was then assembled and lowered in sections using a detachable grommet at the top of each section (Fig. 5). Once the complete well was installed, the outer pipe was slowly pulled out of the ground. As this casing was removed, crew members scraped residual materials from the outside surface using special tools. These scrapings (waste material and clay) generally amounted to no more than 1 gallon of material per well. Scrapings and coring samples were containerized as the work progressed.

Since the outer pipe was somewhat larger than the presanded well casing, the annular space was filled with sand. Because the entire depths of waste (20 to 25 feet) were screened, the bentonite seal was placed on the lower level of the engineered cap. Water was added to the pellets, and the bentonite was allowed to hydrate at least overnight. The grout plug was completed the next day (Fig. 6).

Leachate was pumped from each well. An average of one well volume of liquid was removed per well. All wells produced water. As expected, recovery rates varied because of the heterogeneity of landfill materials.

To complete the installation and comply with state regulations, a 12-inch diameter steel protective pipe was driven into the ground, and later the final well shroud and concrete slab were placed around it.
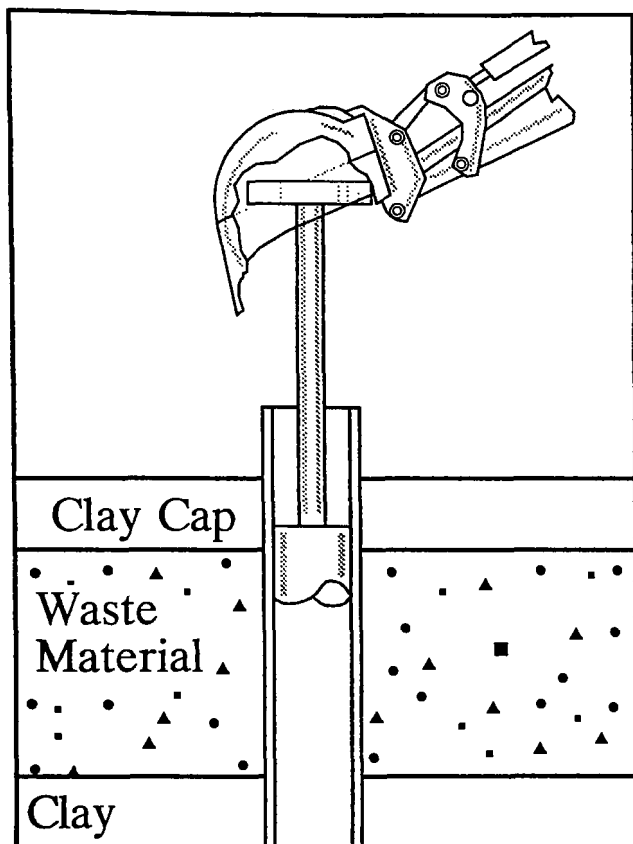
Figure 3
Hollow Sampling Tube
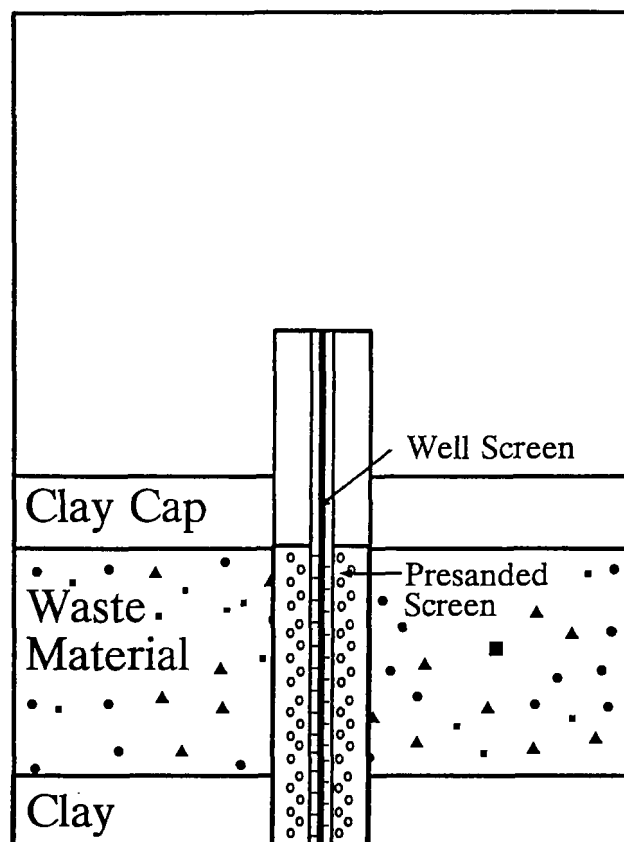
Figure 5
Fiberglass Reinforced Epoxy Well Casing
with Presanded Screen
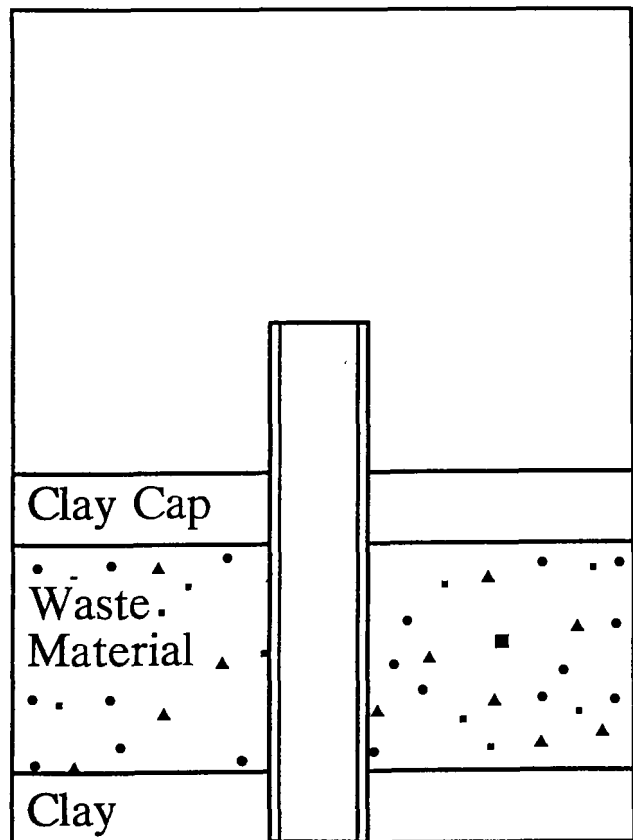
Figure 4
Only the Outer Drive Point Remains in the Ground
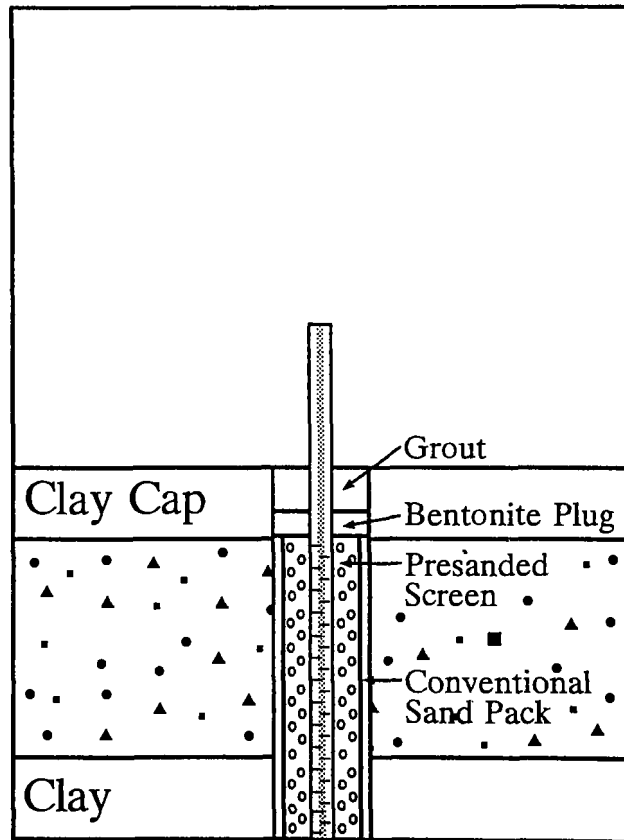
Figure 6
Completed, Grouted Well

CONTAMINATED GROUNDWATER CONTROL & WELL TYPES 365

DECONTAMINATION

During breaks and at the close of each day, all working personnel removed soiled personal protective equipment (PPE) prior to leaving the work area. Their boots were washed and stored for reuse. All PPE waste, including decontamination water, was containerized and stored on-site awaiting disposal.

After well installations were completed, the drive pipe and tools were cleaned using a pressure steam cleaner in a secure containment area on-site. All the water generated in this manner was containerized.

CONCLUSIONS

Overall, the installation method fulfilled our expectations. The entire well installation took 8 working days to complete, for an average of two wells per day. It met our Health and Safety, waste volume, environmental risk and uniform sandpack expectations.

- Health and Safety concerns were minimal. We found that, with few exceptions, virtually all work could be completed using Level D protection.
- The volume of waste produced by the well installation was extremely low. The core samples and casing scrapings were the only well installation wastes directly produced. The waste containers which required sampling prior to disposal were:

Decontaminated water	330 gallons
Personnel protective equipment & water	715 gallons
Soil cores	25 gallons
Leachate	440 gallons

Each waste type was sampled and submitted to a laboratory for analyses of full Appendix 3 plus EP-tox parameters. The results verified that all of the wastes generated could be disposed of on-site.

- The environmental risk was very low. Since the only drilling waste was the clay core samples and the very small amount of material adhering to the casing, contamination of the new clay cap did not occur.
- A uniform sandpack was guaranteed through the use of a presanded well screen. The loose sand added when the casing was removed served only to fill any voids.

All the leachate wells have water in them, and it appears that they will function adequately. We are in the process of constructing a treatment and storage facility to manage the liquids to be extracted for off-site disposal. Once this system is in service, the long-term effectiveness of the wells can be quantified.

This well installation method should be considered in situations requiring the following:

- Expedited installation
- Greatly reduced Health and Safety concerns
- Reduced disposal costs
- Reduced potential for adverse environmental impact
- Comparable installation costs.

The choice of this method must also include considerations of the subsurface geology and the nature of any man-made materials which could be encountered.

Use of Modified Hydropunch For Cost-Effective Groundwater Sampling

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ABSTRACT

During field investigations at the Naval Supply Center (NSC) Oakland, in Oakland, California, PRC Environmental Management, Inc., (PRC) used a modified Hydropunch to obtain groundwater samples. This sampling method was chosen to maximize the amount of data collected while minimizing costs associated with traditional groundwater sampling methods. The modified Hydropunch allows the collection of a discrete, chemically-representative groundwater sample without incurring the costs associated with the installation, maintenance and sampling of groundwater monitoring wells.

The purpose of field investigations at the NSC Oakland site was to determine the presence of contamination at two sites. By providing a rapid, cost-effective means for collecting groundwater samples, the modified Hydropunch effectively achieved this goal. For each site under investigation, little specific information existed concerning storage and disposal of hazardous materials. Therefore, sufficient information did not exist to determine efficient placement of monitoring wells. By using the modified Hydropunch, PRC was able to effectively assess the areas of concern without the need to install monitoring wells. This sampling device allowed a sufficient number of representative samples to be obtained at costs significantly less than those associated with traditional sampling methods.

During field investigations at NSC Oakland, 20 shallow soil borings were performed, each drilled to the top of the water table approximately 10 feet below land surface. By placing the modified Hydropunch inside the hollow stem augers and pushing it into the aquifer, 18 representative groundwater samples were collected from the 20 soil borings performed. Water samples were extracted from the modified Hydropunch using a standard bottom filling bailer. In all cases where water samples were not collected, the limiting factor was the availability of water in the aquifer, not the sampling tool. Because the modified Hydropunch places a 3-foot section of Teflon screen within the aquifer, the volume of water extracted is sufficient to perform a full suite of chemical analyses.

INTRODUCTION

PRC Environmental Management, Inc. (PRC) performed a site inspection (SI) at the Naval Supply Center (NSC) Oakland, in Oakland, California. As part of the SI, groundwater was sampled using a modified Hydropunch (MHP). This approach allowed PRC to collect an adequate number of representative groundwater samples without incurring the costs associated with the installation and sampling of monitoring wells. This paper describes the approach taken for the NSC Oakland SI and the advantages of the MHP.

The NSC Oakland SI was performed as part of the preliminary assessment/site inspection (PA/SI) requirements as outlined in the NCP. Based on information gathered during the PA, two sites suspected of being contaminated, due to inappropriate hazardous materials handling, were studied under this SI. The objective of the SI was to determine the presence of contamination at the sites. After evaluating potential sampling methods, the MHP was chosen for groundwater sampling. PRC chose this sampling device because it allowed a sufficient number of representative groundwater samples to be obtained at costs significantly less than those associated with traditional sampling methods. Specific site factors that contributed to choosing the MHP as a means of determining the presence of groundwater contamination included:

- Large area to investigate
- Unknown subsurface conditions
- Unknown depth to groundwater
- Limited background information on possible contaminants
- Short schedule for project completion
- Budget limitations

Typically, SIs are conducted using standard investigative methods such as exploratory borings to determine subsurface geology and the monitoring wells to provide information on groundwater contaminant levels. Additional information can be obtained using a variety of nonintrusive methods that include geophysics and soil gas analysis.

At NSC Oakland, the SI focused on the collection of soil and groundwater samples to determine the presence of contamination. Monitoring wells were not proposed for the SI because the areas potentially affected by contamination were very large and sufficient background information was not available for determining effective placement of monitoring wells to detect releases from poorly defined sources. Costs associated with installing the number of monitoring wells needed to study the sites would have been. By using the MHP, however, a sufficient number of groundwater samples could be obtained, providing large area coverage at a significantly lower cost than that associated with installation of monitoring wells. Based on groundwater data gathered using the MHP, areas of significant contamination could then be identified, thus satisfying the objectives of the SI. These data could then be used to determine the effective placement of a limited number of monitoring wells if further studies or remedial investigations are deemed necessary.

DESCRIPTION

The MHP (Fig. 1) is composed of a 30-inch long by 1.5-inch diameter Teflon screen attached to a standard steel well point. The screen and well point are placed inside a 5-foot section of 2-inch inside diameter stainless steel pipe and secured with Teflon tape. This apparatus is then lowered into the hollow-stem augers and driven ahead of the lead auger with the drill rig hammer, in the same manner as a split-spoon sampler. As necessary, 5-foot lengths of pipe are added to place the MHP at

the desired location within the saturated zone. After reaching the appropriate depth, the stainless steel pipe is pulled back, leaving the well point in place and exposing the bottom 20-inches of the Teflon screen (Fig. 2).
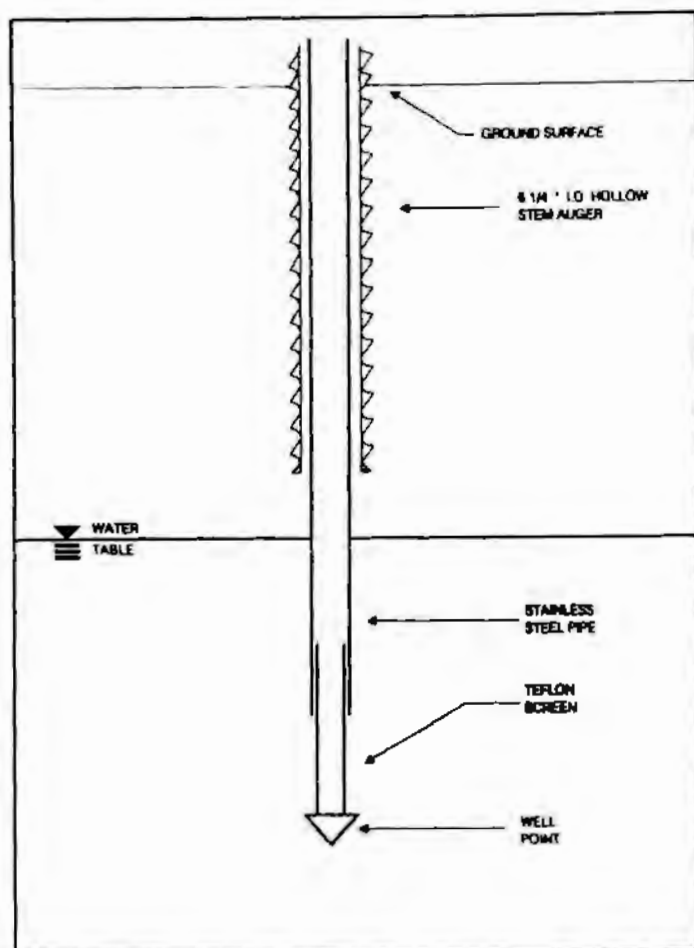
Figure 1
Modified Hydropunch

Under its own hydrostatic head, groundwater enters the screen and fills the MHP. Groundwater samples can then be collected using a 1-inch diameter bottom filling bailer. The bailer is lowered through the stainless steel pipe and down into the Teflon screen. After sampling, the stainless steel pipe is removed and the Teflon screen and well point are left in the ground.

By driving the MHP ahead of the lead auger, groundwater samples can be collected from a section of the aquifer unaffected by the drilling process. In addition, a seal is created between the piping and the aquifer formation. This seal allows the collection of a sample that is undisturbed and representative of true subsurface conditions.

In the past, an inexpensive method for obtaining groundwater samples was to drill into the aquifer and sample directly from the hollow-stem auger. This method is technically unsound because of the many drilling processes that can obscure groundwater contamination. (The MHP is a patented instrument and is a derivative of the standard Hydropunch sold by QED.)

INVESTIGATION

During this study, two sites were investigated to confirm or deny the presence of contamination: a hazardous waste storage lot and an area surrounding two large buildings.

At the hazardous waste storage lot (Fig. 3) the primary areas of concern are eight uncovered storage bins and a staging area adjacent to

the bins. Each storage bin is approximately 20 by 20 feet. The staging area is approximately 75 feet wide and 250 feet long. The entire area is paved except for the exposed surface along the railroad tracks that lie adjacent to the storage bins. Prior to 1981, this area was used to store drummed hazardous materials from numerous military installations in the San Francisco Bay Area. The storage bins at the site are now used for storage and redrumming of hazardous wastes generated at the facility prior to shipment off-site. The floors of all storage bins have significant cracking and exposure of the soils below. Soil staining is evident within the storage bays. The asphalt in the staging area, however, is intact and has very little visible signs of staining. The staging area was no longer in use at the time of the SI.

Figure 2
Well Point, Teflon Screen and Stainless Steel Pipe of the MHP
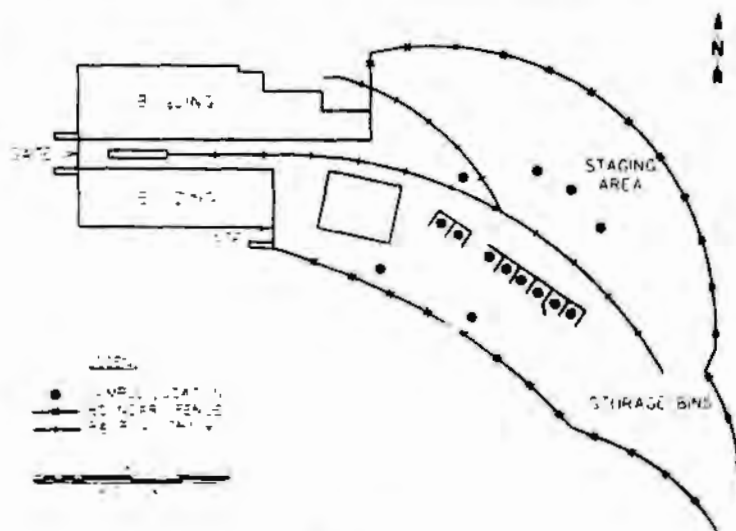
Figure 3
Hazardous Waste Storage Lot

At this site, many possible sources of contamination exist, including each of the eight storage bins and the staging area. By using the MHP, each possible source was evaluated without the need to install monitoring wells. To determine if contamination was present, 14 borings were performed, with a groundwater sample collected from each boring. One boring was performed within each of the storage bins, two were performed in an area believed to be downgradient from the storage bins and four borings were performed in the staging area adjacent to the storage bins. Borings were performed with 6.25-inch inside diameter

hollow stem augers. Soil samples were collected at 5-foot intervals for both stratigraphic control and chemical analysis. Upon reaching the top of the water table, approximately 10 feet below land surface, drilling was stopped and the MHP was placed inside the augers. The MHP was then advanced 3 feet ahead of the augers and opened to allow water to accumulate inside the sampler.

The MHP worked very well in the conditions found at this area. The top 7 to 10 feet of each boring consisted of fine sand fill and bay muds. Below this, clean to clayey medium grain sands were encountered. Depth to groundwater was approximately 10 feet below land surface. The aquifer at this area had a flowrate large enough to allow the collection of a large volume of water. Also, the medium grained sands were coarse enough so as not to flow into the Teflon screen and clog the sampling device. These conditions proved to be ideal for application of the MHP.

Results of chemical analyses of groundwater and soil samples collected at this area indicate that significant contamination is not present. Only low concentrations of toluene and diesel were detected in each sample matrix.

The area surrounding Buildings A and B (Fig. 4) is located on the southwest side of NSC Oakland and consists of two large buildings and a paved parking area between them. The paved parking area between each of the buildings slopes slightly downward to a low lying depression. Cracks are visible in the low lying paved area as are stains from standing water. Two other features of interest behind Building A are a large Imhoff tank and a suspected underground storage tank. The surface around the Imhoff tank is not paved. Railroad tracks lie along the west side of each building.

The western side of Building B and the eastern side of Building A were used in the past to stage drummed materials such as lubricants, solvents, paints and motor oils. No visible signs of spills or disposal

Figure 4
Buildings A and B

Table 1
Cost Comparison: Installation of the Monitoring Wells Compared to Installation of the Modified Hydropunch Process

MONITORING WELLS

Time and materials needed to install 5 monitoring wells:

Drillers costs		
17 hours at $130/hour		$2,210.00
Materials		
25 feet slotted casing	$7/foot	175.00
75 feet blank casing	$5/foot	375.00
15 sacks sand	$6/sack	90.00
5 buckets bentonite	$50/bucket	250.00
35 sacks cement	$10/sack	350.00
5 cristy boxes	$50/each	250.00
5 locking caps	$25/each	125.00
Develop and purge wells		
15 hours	$95/hour	1,425.00
	TOTAL	$5,250.00

MODIFIED HYDROPUNCH

Time and materials needed to collect 5 ground-water samples:

Drillers costs		
10 hours	$130/hour	$1,300.00
Equipment Rental (MHP)		
1 day	$200/day	200.00
Materials		
5 Teflon screens and well points	$35/each	175.00
35 sacks cement	$10/sack	350.00
	TOTAL	$2,025.00

activities are present in these areas. The area surrounding the Imhoff tank was used for personal automobile repair and hobby activities. Waste materials included sandblasting grit, lubricants, solvents, paints and motor oil. There are also signs of tar and creosote.

This area is very large and although handling and disposal of hazardous material was known to have occurred, point sources of contamination could not be identified. PRC, therefore, decided it was necessary to evaluate the entire site. The cost of installing the number of monitoring wells needed to do this would have been excessive. By providing a means of collecting many groundwater samples in a cost-effective manner, the MHP proved to be a valuable tool. To determine if contamination was present at this area, seven soil borings were performed. Because conditions found at this area were less than ideal, groundwater samples were collected from only five of the seven proposed sample locations.

The top 3 to 4 feet of each boring consisted of fine sand fill material. Below this, interbedded clayey medium grained sands and silty clays (bay muds) were encountered. Groundwater generally was found in a large sand bed approximately 8 to 10 feet below land surface. Because of the large amount of fine grained material present in subsurface soils, the quality of water samples collected at this area was less than that of the samples collected at the hazardous material storage lot. At two boring locations, insufficient water was available for the collection of groundwater samples. At one boring location, during sample collection, the Teflon screen filled with flowing fine grained sands so that only one half the required volume of water could be collected.

Soil samples at this area typically were collected 2 feet, 5 feet and 10 feet below land surface. Soil samples collected at the 2-foot and 5-foot intervals from the borings between Buildings A and B were contaminated with a family of semivolatile organic compounds known as Polycyclic Aromatic Hydrocarbons (PAH), toluene and diesel fuel. Only diesel and toluene were detected in the 10 foot samples. PAH compounds
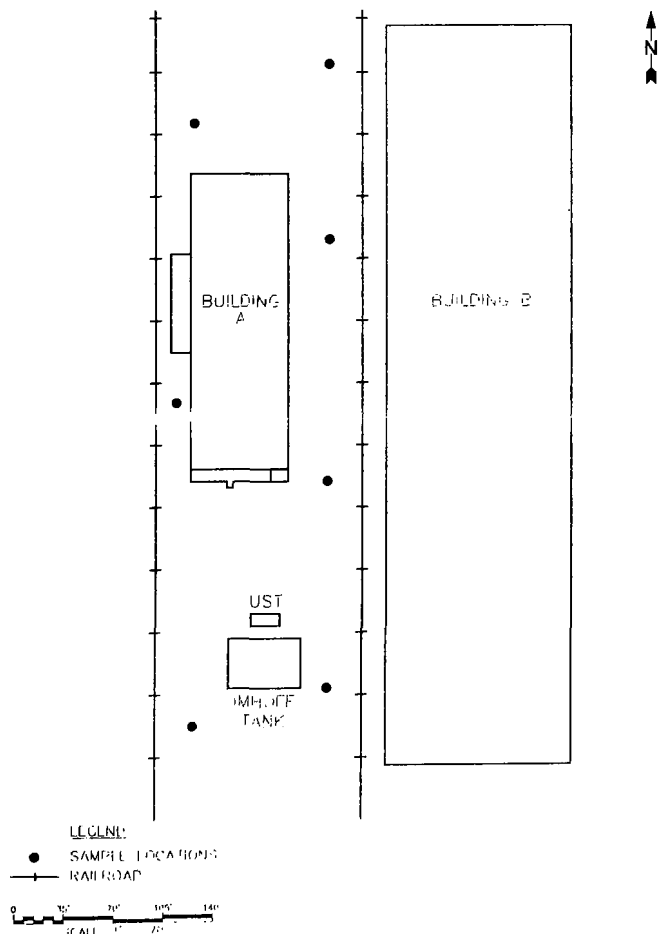
detected in soil samples included benzo(a)pyrene, fluoranthene, chrysene and pyrene. These compounds typically are found as a mixture in the products of incomplete combustion. PAHs are believed to be the main, if not only, carcinogenic ingredients in mixtures such as soot, coal, tar and heavy fuel oil. PAHs are known to attach to organic matter and to accumulate in fine grain sediments such as those found at this area. They are immobile, insoluble in water and will not partition into the water column. Groundwater samples collected at this area did not contain detectable levels of PAH compounds, but did contain low levels of toluene and diesel fuel. Because of the known chemical characteristic, PAH compounds would not be expected in groundwater samples. PRC was able to use the MHP to confirm the immobility of the PAHs and to determine that they were not an immediate threat to groundwater.

COST

One of the primary reasons for choosing the MHP as a sampling method is that a large number of representatives samples can be collected for a relatively low cost as compared with standard sampling methods. This cost savings is particularly obvious when compared with the costs necessary for the installation and sampling of monitoring wells. During a single 10 hour work day, five MHP groundwater samples were collected at NSC Oakland. This sampling included collection of 2 to 3 soil samples per boring and assumed a water table depth of 10 feet below land surface. By comparison only three monitoring wells could typically be installed during this same time frame. Also, additional time is needed to develop and purge monitoring wells. These tasks are not necessary for the collection of groundwater samples from the MHP.

Table 1 presents a cost break down comparing the MHP to standard 2-inch schedule 40 PVC monitoring wells. Costs are based on time needed to acquire an equal number of groundwater samples from the same aquifer.

Based on this comparison, groundwater samples can be collected using the MHP at cost savings of approximately 60% as compared to monitoring wells. Additional costs not shown above are associated with monitoring wells, including 55-gallon drums for water storage, disposal of purge and development water and eventual abandonment of monitoring wells. By adding these costs to those already presented for monitoring wells, the advantage to using the MHP in site inspections becomes greater.

CONCLUSION

At both sites of the NSC Oakland SI, there were many variables with respect to possible sources of contamination. These variables prevented the effective placement of monitoring wells. At the hazardous waste storage lot, there were many possible sources; each of the eight storage bins and the staging area. At the Building A and B site, no known point sources existed and because of the lack of specific background information, a large area needed to be investigated. At each of these sites, the MHP was an effective tool for determining the presence of contamination.

Although, the author would recommend this sampling method for SIs, several drawbacks do exist. The large mesh size of the Teflon screen meant that a water sample could not be collected in the presence of fine grained aquifer material. Also, the MHP can only be used for one time sampling, whereas a monitoring well can be sampled repeatedly, thus precluding the MHP's use for detailed site characterizations. Because the steel well point and Teflon screen are left in the ground, drilling beyond the initial sampling point may be difficult.

Nevertheless, by using the MHP for the NSC Oakland SI, PRC was able to collect a large number of representatives soil and groundwater samples. As a result, greater coverage was provided for soil and groundwater sampling and more data were available for studying the sites without increasing field costs.

Baird & McGuire Superfund Site:
Investigation of Arsenic and Lead Removal From Groundwater

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ABSTRACT

As part of the design effort for the Baird & McGuire Superfund Site Groundwater Treatment Plant, Metcalf & Eddy conducted a series of treatability tests. Since the State of Massachusetts Department of Environmental Protection regulations require that any discharge to groundwater meet drinking water standards, the goal of the tests was to remove metals and organics from the groundwater to federal Safe Drinking Water Act Maximum Contaminant Levels (MCLs). The ROD called for on-site groundwater treatment by metals precipitation, biological treatment using activated sludge, filtration and activated carbon adsorption. Therefore, treatability tests were designed to optimize these processes to meet regulatory requirements.

The topic of this paper is the removal of metals from the groundwater. The metals of concern included arsenic, lead and iron. Tests were run on a groundwater sample collected from a recirculation system installed in the most highly contaminated part of the site during a previous remedial action.[1] Precipitation and coagulation tests were conducted at various Ph values and chemical dosages. Lime and sodium hydroxide were tested for Ph adjustment, and ferric sulfate and ferric chloride were tested as coagulants. Single and two-stage precipitation were investigated. Two-stage precipitation involved adjusting the Ph to the optimum levels for arsenic and iron removal and adding coagulants in one step, settling, removing the supernatant and readjusting the Ph for the removal of lead in a second step. Only by optimizing chemical dosages in the two-stage tests were the MCLs met for all three metals of concern. Water pretreated by single-stage precipitation was used to study the downstream activated sludge and carbon adsorption processes. Following biological treatment and carbon adsorption, samples were analyzed for metals to determine whether additional metals removal could be achieved in these unit operations. No removal was achieved in either process.

INTRODUCTION

The Baird & McGuire Superfund site currently ranks 14th out of 989 sites on the NPL. Baird & McGuire, Inc., operated a chemical mixing and batching facility in Holbrook, Massachusetts, for more than seventy years. Operations at the facility included production of household and industrial products such as floor waxes, wood preservatives, pesticides and solvents,[2] and resulted in widespread contamination of the Baird & McGuire property, as well as the surrounding property, by numerous toxic organic and inorganic compounds. In September 1986, following a number of investigations, the U.S. EPA issued the ROD for the Remedial Alternative for the site. Included in the ROD was remediation of contaminated groundwater by metals precipitation, biological treatment and carbon adsorption and remediation of soil by incineration.

Investigations conducted at the Baird & McGuire site by several groups including consultants for Baird & McGuire, Inc., the town of Holbrook, the U.S. EPA, the Massachusetts Department of Environmental Quality Engineering, Goldberg-Zoino Associates and GHR Engineering Associates have shown arsenic and lead to be present in concentrations above the MCLs. Most recently, Metcalf & Eddy conducted a comprehensive groundwater sampling effort to provide support for design activities. The analytical data from this sampling round documented extensive groundwater contamination by metals, semivolatile organics, volatile organics and pesticides. Of the metals detected in the groundwater, arsenic was found throughout the site in concentrations up to 4.4 mg/L. Lead was detected less frequently, but exceed the MCL in several samples. In addition, iron was detected at concentrations up to 70 mg/L.

For the Baird & McGuire site, the MCL for arsenic and lead in the groundwater discharge is set at 0.05 mg/L (ppm) and for iron, the MCL contaminant level is set at 0.3 mg/L.

TREATABILITY STUDIES

As part of the remedial design effort, Metcalf & Eddy conducted treatability studies on the groundwater in order to confirm the ability of the proposed technologies to meet the discharge criteria and to develop design data. To evaluate metals precipitation, a series of jar tests was conducted at different Ph values and chemical dosages.

Both lime and sodium hydroxide were investigated for Ph adjustment. Review of the literature[4] indicated that arsenic is not removed as a hydroxide but can be removed by coprecipitation with ferric hydroxide floc. Therefore, two ferric salts, ferric chloride and ferric sulfate were tested to enhance formation of the heavy ferric floc. In addition, due to the high concentrations of iron found in the groundwater, tests were run without the iron salts to determine whether arsenic removal would occur with the naturally occurring iron concentrations.

Solubility curves[5] and the literature indicated that minimum solubility of ferric hydroxide and coprecipitation of arsenic occurs near a neutral Ph, while the minimum solubility of lead hydroxide occurs in the 10 to 11 Ph range. Therefore, tests were conducted over a Ph range of 7 to 10. In addition, two-stage tests were conducted in which precipitation was conducted at the Ph value found to be optimum for iron and arsenic removal; then the supernatant from the first precipitation step was adjusted to the optimum Ph for lead removal.

Test conditions are given in Table 1. All precipitation tests were conducted on samples collected from an on-site recirculation system that was installed in the most contaminated part of the site as an interim measure. Arsenic and lead spikes were added to several of the test samples to ensure the presence of these contaminants, since influent sample analysis and groundwater sampling analysis results would not

be available prior to testing. Metals concentrations and groundwater quality parameters concentrations found in the test samples collected from the recirculation system are presented in Table 2.

Test Procedure

A sample of groundwater taken in August 1988 best characterized the nature of metals contamination of the site groundwater. Table 1 shows that the groundwater had an initial total solids content of 134 mg/L, an initial elemental iron content of 56 mg/L and an initial elemental arsenic content of 2.6 mg/L. Lead had been detected in at least one monitoring well, having a groundwater concentration of 4 mg/L.

Based on MCL levels, the groundwater treatment technology chosen for metals removal is required to remove 98% of the elemental arsenic and lead and 99.5% of the elemental iron contained in the recirculation well groundwater.

The first jar test study of the site groundwater used ferric sulfate to

enhance arsenic removal, with limited success.[6] Reagent grade ferric sulfate was added to the contaminated groundwater at a dose of 55 mg/L resulting in 97% removal of arsenic at a final treatment Ph of 10.5. The final concentration of arsenic in the sample was 0.1 mg/L.

The ferric sulfate reagent used was difficult to put into solution with deionized water; also, it was found that ferric sulfate was not readily available in bulk quantity.

Testing sodium hydroxide as a substitute for lime produced an effluent which did not meet the MCLs. Using sodium hydroxide would produce less sludge, but the discharge criteria could not be met.

After we reviewed the data obtained with ferric sulfate in conjunction with both sodium hydroxide and lime conditioning, we decided to test ferric chloride with lime only. To set a basis for ferric chloride dosing quantities, a Taiwanese study on arsenic removal from drinking water was used.[7] In this study, the authors found that a ferric chloride addition of 30 mg/L would remove 92% of arsenic from a well water

Table 1
Baird & Mcguire Treatability Study -
Modification #5 - Metals Treatment Analytical Results

Chemicals	Units	Raw Groundwater Sample	1	1A	2	2A	3 Spike	3A Spike	4 Spike	4A Spike	5	5A
Ferric Chloride	mg/l			25	25				25	25	100	100
Lead in dilute Nitric Acid	mg/l						4	4	4	4		
Lime (CaOH₂)	mg/l		380	360	380	364	370	370	340	328	400	400
American Cyanamid Magnafloc 1827	mg/l											
pH	mg/l	6.14	10.59	10.60	10.45	10.52	10.52	10.52	0.60	10.45	10.50	

Parameters	Units											
Arsenic (Total)	mg/l	2.6	.1	.13	.087	.080	.087	.096	.056	.058	.039	.038
Barium (Total)	mg/l	0.11	.01	ND	ND	.010	.01	.010	.010	.01	.02	.020
Cadmium (Total)	mg/l	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iron (Total)	mg/l	56	.98	2.1	1.5	1.1	.90	1.1	.75	.72	.70	.66
Lead (Total)	mg/l	ND	ND	ND	ND	ND	.23	.14	.073	.096	ND	ND
Nickel (Total)	mg/l	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Chemicals	Units	6 Polymer	6A Polymer	7 First Stage	7 Second Stage	7A First Stage	7A Second Stage	8 First Stage	8 Second Stage	8A First Stage	8A Second Stage
Ferric Chloride	mg/l	25	25					25		25	-
Lead in dilute Nitric Acid	mg/l										
Lime (CaOH₂)	mg/l	268	88		272		284		288		288
American Cyanamid Magnafloc 1827	mg/l	2.5	2.5								
pH	mg/l	10.12	7.95	6.14	10.45	6.14	10.55	6.14	10.55	6.14	10.55

Parameters	Units	6 Polymer	6A Polymer	7 First Stage	7 Second Stage	7A First Stage	7A Second Stage	8 First Stage	8 Second Stage	8A First Stage	8A Second Stage
Arsenic (Total)	mg/l	.043	.070		.140		.094		.039		.035
Barium (Total)	mg/l	.017	.075		.011		.012		.021		.023
Cadmium (Total)	mg/l	ND	ND		ND		ND		ND		ND
Iron (Total)	mg/l	.60	1.4		2.20		1.3		.59		.53
Lead (Total)	mg/l	ND	ND		ND		ND		ND		ND
Nickel (Total)	mg/l	ND	ND		ND		ND		ND		ND

Chemicals	Units	9 First Stage	9 Second Stage	9A First Stage	9A Second Stage	10 First Stage	10 Second Stage	10A First Stage	10A Second Stage
Ferric Chloride	mg/l					25		25	
Lead in dilute Nitric Acid	mg/l								
Lime (CaOH$_2$)	mg/l	96	220	112	212	90	200	100	164
American Cyanamid Magnafloc 1827	mg/l								
pH	mg/l	7.15	10.55	7.03	10.50	7.0	10.51	7.30	10.60
Parameter	**Units**								
Arsenic (Total)	mg/l		.051		.051		.025		.025
Barium (Total)	mg/l		.015		.016		.029		.017
Cadmium (Total)	mg/l		ND		ND		ND		ND
Iron (Total)	mg/l		.070		.060		ND		ND
Lead (Total)	mg/l		ND		ND		ND		ND
Nickel (Total)	mg/l		ND		ND		ND		ND

Chemicals	Units	11 First Stage	11 Second Stage	11A First Stage	11A Second Stage	12 First Stage	12 Second Stage	12A First Stage	12A Second Stage	M-1 Laboratory Duplicate	M-2 Laboratory Duplicate
Ferric Chloride	mg/l					25		25		25	25
Lead in dilute Nitric Acid	mg/l	132									
Lime (CaOH$_2$)	mg/l		150	130	144	104	124	N/A	102	NA	NA
American Cyanamid Magnafloc 1827	mg/l	8.14									
pH	mg/l		10.57	8.01	10.51	8.10	10.64	8.24	10.62	9.30	9.30
Parameter	**Units**										
Arsenic (Total)	mg/l		0.34		0.43		.022		.021	.084	.081
Barium (Total)	mg/l		.024		.020		.026		.024	.053	.053
Cadmium (Total)	mg/l		ND		ND		ND		ND	ND	ND
Iron (Total)	mg/l		.06		.24		.05		ND	2.9	2.9
Lead (Total)	mg/l		ND		ND		ND		ND	ND	ND
Nickel (Total)	mg/l		ND		ND		ND		ND	ND	ND

sample containing 1.72 mg/L total arsenic and 0.8 mg/L total iron at a natural groundwater Ph of 7.4.

The advantage that ferric chloride has for arsenic removal by coprecipitation over ferric sulfate is its solubility. Ferric chloride is readily soluble in either hot or cold makeup water and does not have to be added to a waste stream as a slurry.

PRECIPITATION TESTING RESULTS

Results of the metals precipitation in the jar tests are given in Table 1 along with test conditions. Also found in Table 1, are the MCLs for the metals of concern.

Treatment chemicals and spike concentrations added to the samples are indicated at the top of Table 1. Jar testing was performed using ASTM Method D2080. Lead spike was added to the raw groundwater at concentrations of 4 mg/L for metals jar test samples 3, 3A, 4 and 4A, in order to indicate a worst-case condition of lead concentrations experienced in the groundwater at the site. Arsenic spikes were not added to any of the test samples, as arsenic concentrations in the raw groundwater sample represented average-to-worst case site conditions. Removal efficiencies of arsenic, lead and iron were determined for both the single-stage and two-stage precipitation processes.

Ferric Chloride Addition Results

Ferric chloride addition was evaluated by running sets of duplicate jar tests, subjecting one set of jars to lime (Ca(OH)$_2$) addition only to a selected Ph and adding ferric chloride to an alternate set of jars prior to adding lime, then adjusting to the same Ph.

The analytical results given in Table 1 show reductions in total iron and total arsenic concentrations in each test using ferric chloride as compared to its analogous test without using ferric chloride. These reductions are largely evident in the two-stage removal tests. In cases (7 and 7A) vs (8 and 8A) and (9 and 9A) vs. (10 and 10A), the reductions in the arsenic concentrations by using ferric chloride were sufficient to bring arsenic level to below the MCL drinking water standards.

Tests 5 and 5A show the effect of coagulant ferric chloride added in larger quantities than those used in the Taiwanese Study (100 mg/L).

Chemicals	Units	Reporting Limit	MCL(b)
Ferric Chloride	mg/l		
Lead in dilute Nitric Acid	mg/l		
Lime (CaOH$_2$)	mg/l		
American Cyanamid Magnafloc 1827	mg/l		
pH	mg/l		

Parameter	Units		
Arsenic (Total)	mg/l	.003(a)	.05
Barium (Total)	mg/l	.010	1.0
Cadmium (Total)	mg/l	.005	.01
Iron (Total)	mg/l	.05	.30
Lead (Total)	mg/l	.005	.050
Nickel (Total)	mg/l	.04	N/A

ND = Not Detected.
NA Not Applicable.
b   MCL refers to the Maximum Contaminant Levels according to the EPA Safe Drinking Water Act Standards.
c   These are the threshold concentration of substances inhibitory to the activated sludge process.

Table 2
Baird & Mcguire Recirculation Data Summary for Test Samples

Groundwater Quality Parameters Analysis (mg/l)

Total Suspended Solids	134
Total Volatile Solids	104
Total Kjeldahl Nitrogen	2.6
Total Phosphorus	1.8
Chemical Oxygen Demand	267
Total Organic Carbon	42
Biochemical Oxygen Demand	72
pH	6.24

Groundwater Metals Analysis (mg/l)

Antimony	ND	0.05
Arsenic	3.4	0.1
Barium	0.14	0.005
Beryllium	ND	0.001
Cadmium	ND	0.005
Chromium	ND	0.01
Copper	ND	0.006
Iron	76	0.05
Lead	ND	0.005
Mercury	ND	0.0002
Nickel	ND	0.04
Selenium	ND	0.005
Silver	ND	0.005
Thallium	ND	0.008
Zinc	ND	0.01

Greater reductions in arsenic and iron treatment concentrations are evident with the increased coagulant addition; however, the reduction induced by increased addition is not substantial as compared to the lower level of ferric chloride dosage (Tests 2 and 2A).

Two-Stage Metals Precipitation Results

The two-stage metals precipitation process was compared to the single-stage process, also by using a series of analogous tests. Tests number 1 and 2 represent analogous single-stage metals treatability tests and test 7 through 12A present two-stage treatability test, related to single-stage numbers 1 and 2. The final target pH for all tests mentioned was 10.5.

Single-stage test (1 and 1A) did not use ferric chloride. Analogous two-stage tests to (1 and 1A) were test (7 and 7A), test (9 and 9A) and test (11 and 11A). First-stage treatment pH values were varied in each of these two-stage tests.

Test (11 and 11A) showed the greatest removal of arsenic in a two-stage system not utilizing ferric chloride, as compared to test (1 and 1A). Iron removal efficiency was adequate in test (11 and 11A). Total lime (Ca(OH)$_2$) consumption for tests (11 and 11A) was averaged at 278 mg/L as compared to 370 mg/L for tests (1 and 1A).

Single-stage test (2 and 2A) used ferric chloride to enhance arsenic removal. Analogous two-stage systems reported were tests (8 and 8A), (10 and 10A) and (12 and 12A). First stage pH values were varied in each of these two-stage tests, along with ferric chloride at 25 mg/L at the first stage.

Test (10 and 10A) showed optimal removal capabilities in arsenic contamination when compared to all two-stage testing performed and also removed iron to concentrations below the analytical detectable limit. Total lime consumption in tests 10 and 10A was an average of 277 mg/L, as compared to 372 mg/L in test 2.

Lead Spike Analytical Results

Tests 3, 3A, 4 and 4A were spiked with 4 mg/L of lead in dissolved nitric acid to simulate worst-case site condition for this metal. The test results show a 50% or better reduction in dissolved lead concentration in tests 4 and 4A in which ferric chloride was added.

CONCLUSIONS

Adjusting the pH to 7 in the first stage and 10 in the second stage by lime addition then ferric chloride at a concentration of 25 mg/L to form a ferric hydroxide floc in the groundwater in the first stage mixing, effectively removed arsenic from the Baird & McGuire site groundwater to the MCL. The removal of arsenic in jar test number 10 and 10A, a two-stage process using ferric chloride at a pH of 7 and pH

adjusting to 10 using lime in the second stage, is shown to be 99%, from an initial arsenic concentration of 2.6 mg/L.

Iron was removed from an initial concentration of 56 mg/L to nondetectable levels using the same set of jar test conditions.

Ferric chloride was also shown to enhance lead removal. Although the two-stage system was not screened for lead removal in comparison with MCLs, it is believed that the two-stage system will be able to appropriately remove any groundwater lead contamination to at or below MCL values.

The two-stage system was also effectively in reduced hazardous metals concentrations below activated sludge MCL limits. The two-stage metals removal process also was shown to reduce lime consumption by 20% or greater over single-stage removal efficiencies as reported in Table 1.

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Computer Modeling in the Site Assessment Process:
A Case History

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ABSTRACT

A 250-acre island in the Mississippi River was identified as an uncontrolled municipal and industrial waste landfill. This facility, which served a city of 64,000, received various wastes for approximately 35 years before ceasing operation in 1976. The island lies within 2,000 feet of the city's shallow water well gallery. The likelihood that hazardous wastes were deposited at this site, and its proximity to a major municipal well gallery, prompted the Region VII Superfund Branch of the U.S. Environmental Protection Agency (EPA) to investigate the facility.

A Preliminary Assessment (PA) revealed significant exposure potentials in four migration pathways: soil, air, groundwater and surface water. Before field work for the Screening Site Inspection (SSI) commenced, groundwater modeling was employed to allow a thorough evaluation of the potential risk posed by site conditions. Information obtained during the SSI showed significant releases of heavy metals from the landfill to area groundwater. These contaminants were detected in the raw municipal water. Preliminary modeling results applied to field analytical data indicated that the site was a likely source of this municipal well contamination.

The modeling results were used to design the most effective sampling scheme for the final stage of the site assessment process, the Listing Site Inspection (LSI). Well locations were determined, and an aquifer test was designed to allow an empirical check of parameters used in the groundwater model. The LSI delineated the vertical extent of the groundwater plume and identified several alternative potential contamination sources. The aquifer test provided the data necessary to verify the accuracy of the model. The groundwater model effectively assessed the complex hydrogeological environment in the site vicinity and provided information required to design an appropriate sampling scheme. The groundwater model also facilitated interpretation of the field data acquired during the SSI and LSI. An additional benefit of this site assessment approach is that it may provide the city some guidelines for pumping the shallow well gallery in order to minimize the impact of local groundwater contamination on the municipal water supply.

INTRODUCTION

This paper presents a case study of a Superfund Site Assessment in which computer groundwater modeling was employed to aid in designing an effective sampling scheme and interpreting field data acquired from the field work. The modeling results also can be used to manage aquifer pump rates in order to minimize potential contamination of the shallow municipal well gallery. The Superfund Site Assessment process is divided into three parts. The initial site assessment is carried out under the Preliminary Assessment (PA) phase. In the PA phase, no samples are taken, the investigation is limited to on-site reconnaissance,

background file review and interviews. If evidence is acquired during the PA indicating actual or potential contamination of the air, soil, groundwater or surface water pathways, and if significant environmental or human target groups exist, then the site is moved to the Screening Site Inspection (SSI) phase. This second phase involves environmental sampling and continued background data collection. If data from the SSI confirm the presence of contamination and indicate a significant threat via one or more of the exposure pathways, the site is advanced to the third and final phase of the Site Assessment process, the Listing Site Inspection (LSI). The purpose of the LSI is to gather sufficient site-specific data to support the proposal of a site to the National Priorities List (NPL). Within this overall objective, LSIs are designed specifically for the data and information needs at a particular site.

SITE BACKGROUND

The site is located on an island in the Mississippi River. Between the mid-1940s and 1976, the southern three-fourths of the island served as an industrial and municipal waste landfill for a city of 64,000 residents. The landfill operation was used to fill low areas on the island (sloughs) and to raise its overall elevation. On-site borings indicate that the former landfill area has 5 to 30 feet of waste fill; fill may be deeper in former sloughs. The hazardous substances present, identified through on-site groundwater and soil sampling, are listed in Table 1.

Table 1
Hazardous Substances Identified in Soil and Groundwater Samples

Methylene Chloride	Barium	Mercury	Cyanide	DDD
	Cadmium	Nickel	Silver	DDT
Acetone	Chromium	Polychlorinated	Polycyclic	Dieldrin
Toluene	Copper	Biphenyls	Aromatic	Zinc
Arsenic	Lead	Selenium	Hydrocarbons	Xylene
Benzene	Endosulfan	Dibenzofurans		

Sometime after landfill operations ceased, a sand cover was placed over fill areas to produce a more level grade; it was not a formal closure procedure. Currently, the former landfill area is used as a city recreational area. The center of the former landfill is situated 3,200 feet south of the shallow well gallery for the city. The deep municipal wells are located approximately 4,800 feet north of the center of the former landfill (Figure 1).

Past erosion and scouring from the Mississippi River have modified the local bedrock topography. The bedrock surface in the general site vicinity appears to slope eastward from the limestone bluffs which define the floodplain to the main river channel. The bluffs are composed of
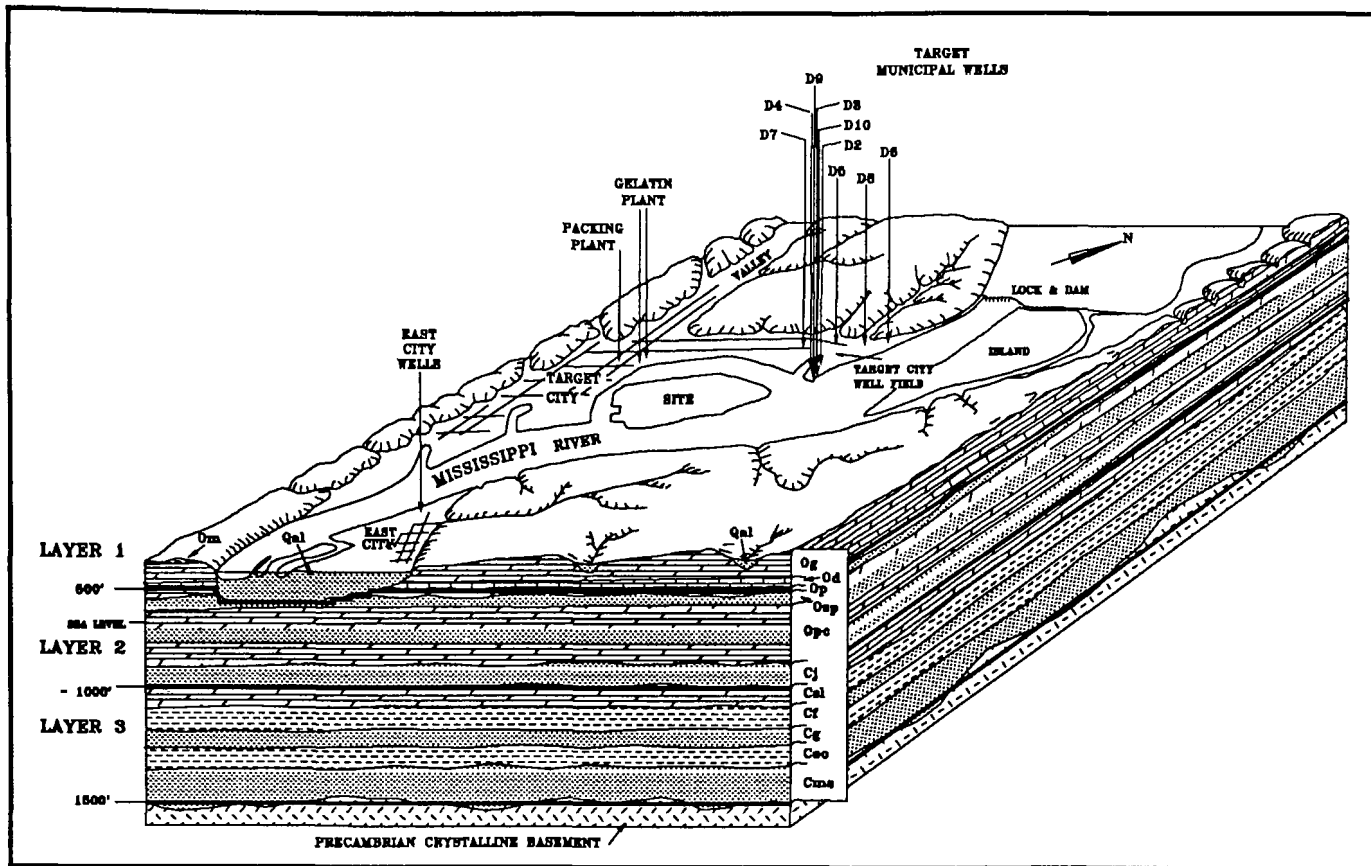
Figure 1
Site Map: Major Pumping Wells
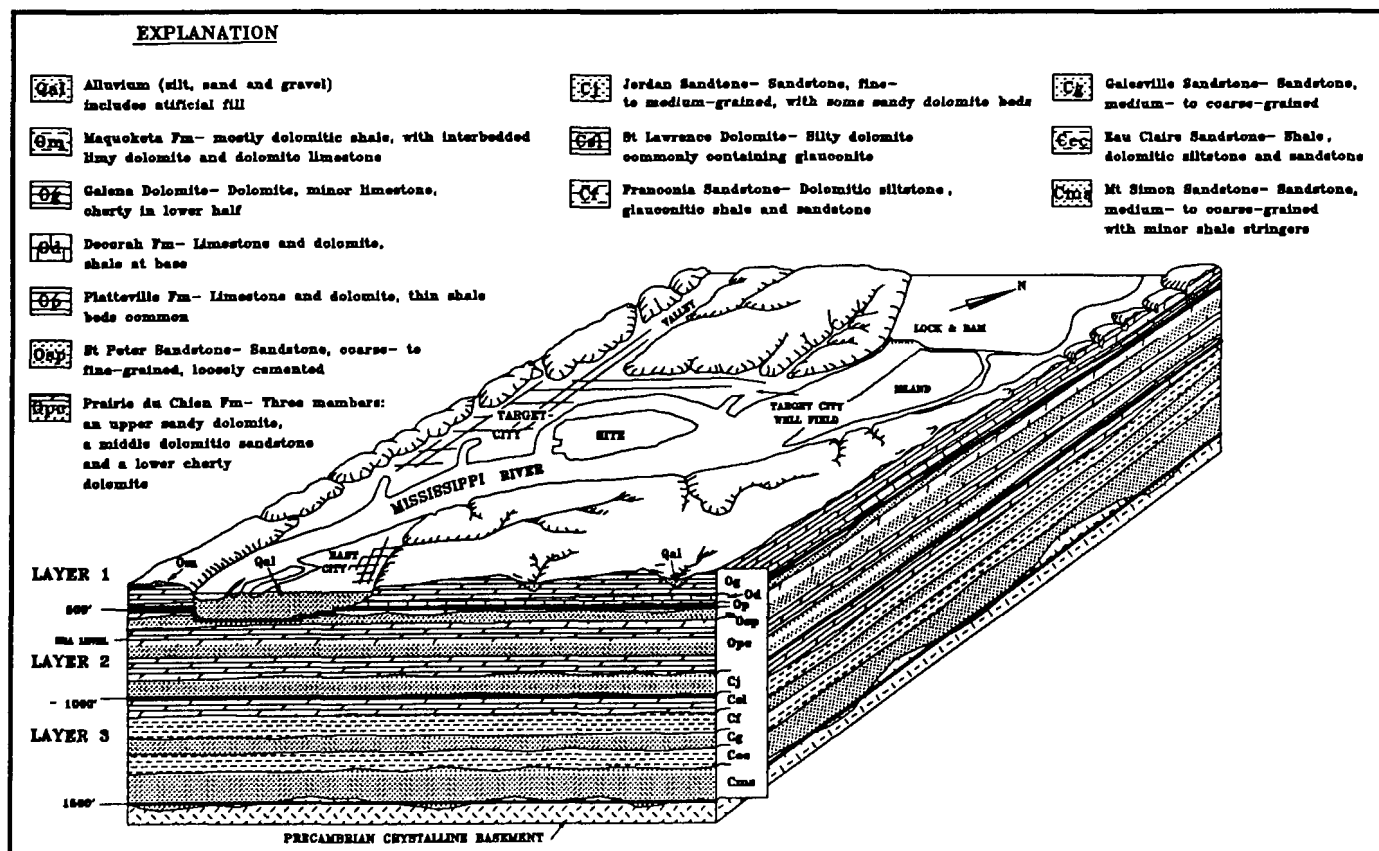
Figure 2
Geology of Study Area

Ordovician limestones, dolomites and shales of the Champlainian Series. Moving toward the main river channel, the sandstone members of the Ancell Group found at the bottom of the Champlainian Series are increasingly eroded, eventually exposing the St. Peter Sandstone, which is the bottom formation in the Ancell Group. In the main river channel, the St. Peter is sufficiently eroded to expose the Shakopee dolomites of the Prairie du Chein Group in the Canadian Series. Alluvial sands and gravels ranging in thickness from 0 to at least 350 feet provide the major overburden for the bedrock between the bluffs (Figure 2). These erosional features are caused by the geomorphic processes associated with the flow and meandering of large rivers during past interglacial periods.

The site is located on and within the surficial alluvial aquifer. The upper 30 feet of this aquifer are isolated from the main aquifer body by the presence of the Mississippi River and a side channel which surround the site (Figure 3). This surficial aquifer extends down to the upper bedrock units. The eastern and western boundaries of this aquifer are defined by the Ordovician-aged limestone bluffs. The boundaries of this aquifer are recharge areas for the alluvium, while the alluvium in turn discharges into the Mississippi River.

Seismic Interpretation

Nine water supply wells are used by this city. Five wells make up the shallow gallery and draw from the alluvial aquifer at 80 to 200 feet (Figure 1). The remaining four wells are deep wells which draw from the lower Ordovician and Cambrian units at 300 to 1,800 feet. The city withdraws 6 to 9 million gallons of water per day from its well galleries, approximately two-thirds of which is taken from the alluvial aquifer. To produce this magnitude of water withdrawal, generally two deep and two to three shallow wells are pumped concurrently.

SITE ASSESSMENT

Based on the information generated at the PA, and the proximity of the site to the city's municipal well field, this site was deemed to be a potential threat to human health and the environment and warranted

further Superfund investigation. The site was moved to the SSI phase.

Planning for the SSI was complicated by the site's location on an island and the unknown influence of the Mississippi River on contaminant migration. In order to better define the local hydrogeology, U.S. EPA Region VII Superfund subcontracted HydroGeologic, Inc. to conduct preliminary groundwater modeling at this site. The objectives of this modeling were as follows:

- Determine the zones of influence for the deep and shallow municipal well fields, both separately and together, for normal, peak and maximum pumping rates
- Assess the impact of water infiltration through river bed sediments during the pumping of the shallow municipal wells
- Evaluate the likelihood that water from under the land-fill could be drawn into the shallow or deep municipal wells
- Quantify the impact of smaller water wells, situated around the site, on the capture zones for the municipal well gallery
- Identify input parameters that have the greatest impact on the ground-water flow system
- Provide input on the development of a sampling plan if the site were to move into the LSI phase

To accomplish these objectives, the modeling effort arranged into the following six elements:

- Formulation of an initial conceptual model which was continuously tested and refined throughout the modeling process
- Identification of input parameters likely to have a controlling effect on the groundwater flow
- Determination of high and low bounds of the input parameters
- Investigation of the effects of key input parameters on the ground-water flow system, both individually and collectively, through a sensitivity analysis
- Simulation of scenarios to predict the effect that alternative pumping procedures would have on the groundwater flow system
- Comparison of aquifer test data obtained from LSI field work with the hydraulic conductivity range used in the modeling
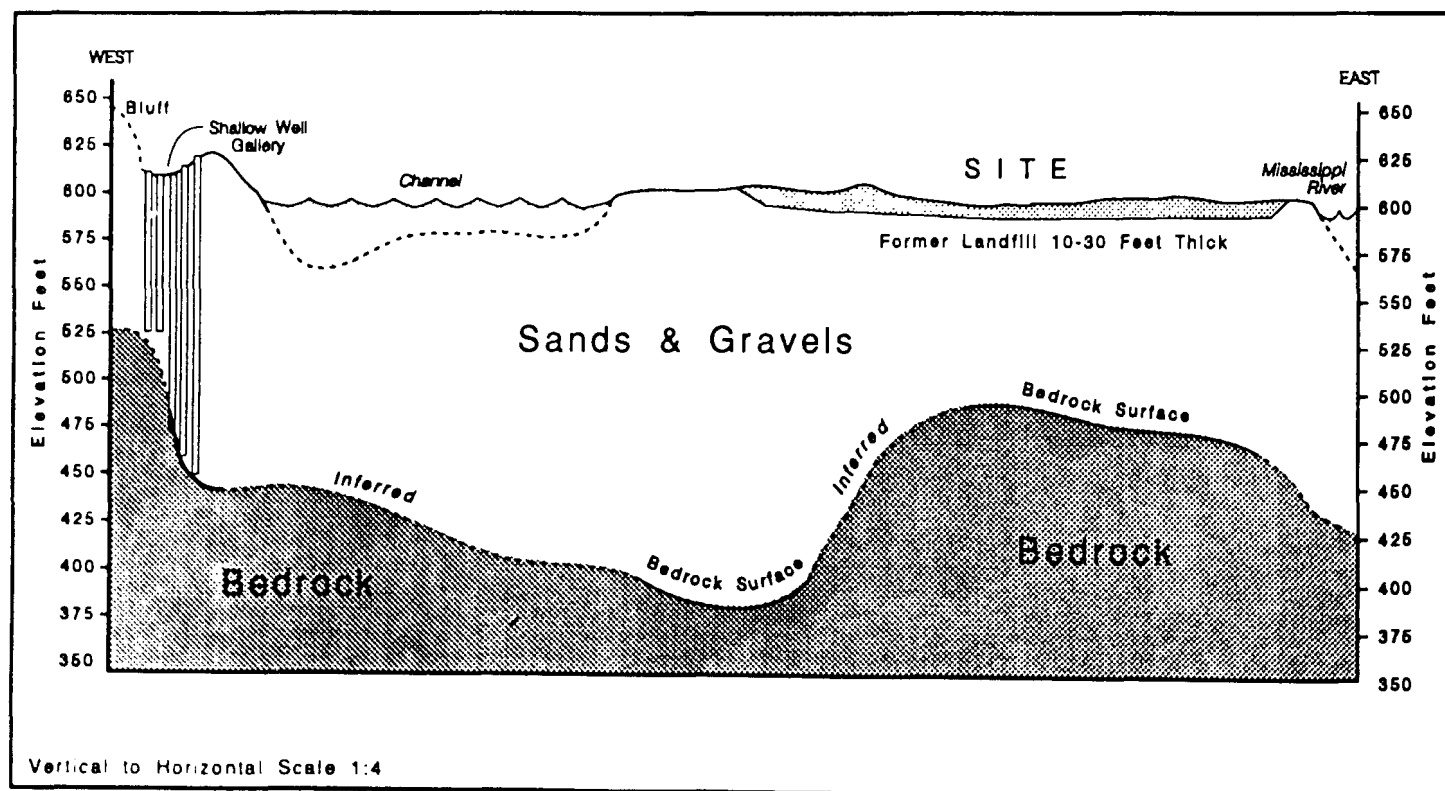
Figure 3
Shallow Well Gallery to Site: Cross-section
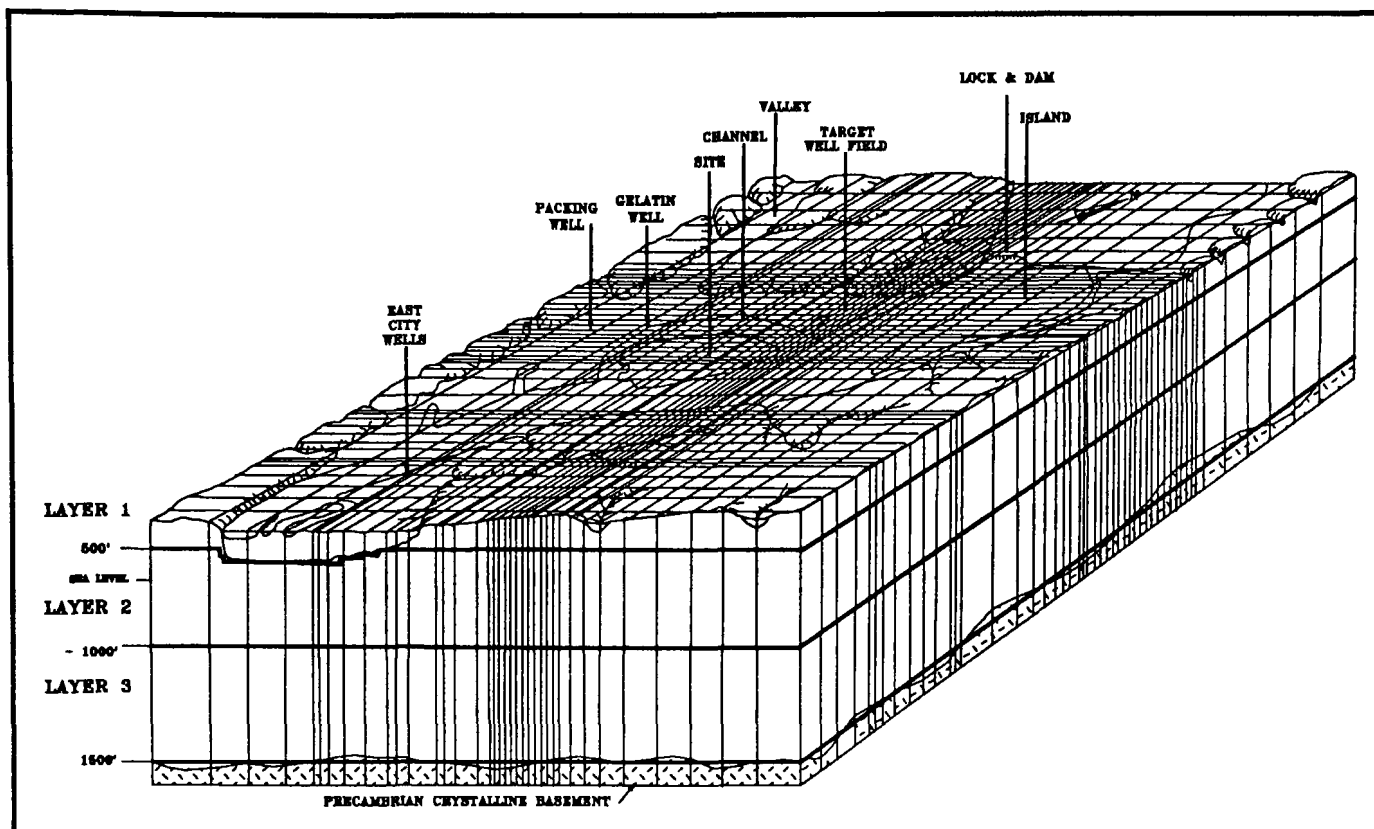
Figure 4
Layer Classification and Gridding

The conceptual model of the hydrogeologic flow system was developed using data that included published reports, well logs, laboratory permeability studies, geologic maps river stage and seepage measurements, geophysical information, regional potentiometric surface maps, and well pumpage data. In essence, the hydrogeologic environment beneath the site comprises a series of interbedded aquifers and lower permeability confining units that extend to a depth of approximately 3,000 feet. Groundwater flow is dominated by the Mississippi River, which acts as a regional drain causing strong vertical upward gradients, allowing groundwater to move from the lower aquifers and discharge into the River.

The parameters and processes most likely to influence groundwater flow in the area of interest were identified to be: vertical and horizontal hydraulic conductivity contrasts between hydrogeologic units, pumping rates, depths and locations of the municipal wells, stage of the Mississippi River, conductance of the Mississippi River Bed and areal recharge. A detailed literature search provided the expected high and low values of the input parameters which allowed a bounding approach to be taken during the sensitivity analysis.

Once the conceptual model was formulated, it was quantified by implementing the numerical code MODFLO (Modular Three-Dimensional Finite-Difference Ground-Water Flow Model).

The modeling required that the site be divided into a grid composed of almost 2,000 nodes. A variable grid spacing was used and, in areas requiring greater definition (area of the municipal well field), grid spacings were set to 200 feet and graded to a maximum of 2,000 feet at the model boundaries (Figure 4).

The aquifer system was divided vertically into three distinct hydrogeologic units (Figure 1). The intermediate range model parameters for each layer are presented in Table 2. Within each layer, the hydraulic characteristics, aquifer thickness and other location-specific data were varied over the representative nodal area.

Table 2
Aquifer Parameters

	Layer #1	Layer #2	Layer #3
Unit Thickness (ft)	100–400	1,300–1,500	1,000
$^\wedge$h (ft/day)	65–268	35–70	35–70
^{K}v (ft/day)	0.01	0.1–0.01	0.1–0.01
Composition	Alluvium	Lower Ordovician Upper Cambrian	Lower Cambrian Precambrian
No. of Active Well	6	5	2

Before the LSI, there were no actual field measurements of the parameters and processes which were expected to control groundwater flow in the area of interest. Therefore, the majority of the modeling focused on estimating the probable range of these parameters and conducting a detailed sensitivity analysis.

The sensitivity analysis involved evaluating the groundwater-flow field that resulted from multiple combinations of the various parameters within their expected ranges. In this manner, an approach was undertaken to predict if a potential exists for the migration of contaminants from beneath the landfill to the well field. This approach included both conservative as well as more probable estimates for the expected ranges of parameters.

The parameters exhibiting the greatest sensitivity were vertical and horizontal conductivity, riverbed conductance and pumping rates. Groundwater flow appears to be less sensitive to precipitation (recharge) and river stage.

Confining layers between the aquifers were not explicitly simulated with the model; however, the equivalent effects were obtained using a vertical conductance term between each layer. This design is com-

monly referred to as a quasi-three-dimensional approach. To simulate the long-term effect of the well field on groundwater flow, all simulations were run to steady-state. After completion of the sensitivity analysis, simulation scenarios were performed to evaluate the effect that alternative pumping schemes would have on the groundwater flow system.

Modeling results indicated that even under nonconservative conditions (e.g., low pumping rates and high hydraulic conductivities), the capture zones created by the well field would extend under the landfill, creating the potential for contaminants to move with the groundwater into the well field. Furthermore, with the exception of the immediate area of the well field, a strong upward gradient appears to exist between Layer 1 and Layer 2 as predicted by the conceptual model.

The only wells that appeared to have a significant impact on the regional groundwater gradients were the municipal wells. (Accurate pumping rates for other wells in the area are unknown and were estimated.) As expected, the wells in the deeper, more confined systems had large capture zones. However, the strong upward flow gradients would tend to isolate them from the contamination potentially leaking downward from the alluvial aquifer.

The SSI also had the primary objectives of identifying on-site contaminants, assessing the potential contamination of the shallow municipal wells, documenting contamination in any of the four pathways, creating a geologic cross-section between the site and the bluffs and measuring riverbed seepage. Temporary monitoring wells installed with a Geoprobe unit showed significant total and dissolved metals contamination in the top of the alluvial aquifer. Minor amounts of volatile and semi-volatile organics also were detected. Arsenic, barium, cadmium, selenium and benzene levels were detected above Maximum Contaminant Levels (MCLs). These metals also were detected in the shallow municipal well samples, but at lower concentrations.

The analytical data supported the attribution of the shallow groundwater contamination on the island to the former landfill area. However, this sampling did not provide sufficient data to show attribution for the contamination detected in the shallow municipal wells. The SSI also called for shallow (0 to 2 feet) soil sampling in high use recreational areas. Elevated metals and pesticide concentrations were detected in soils collected from areas of exposed fill. Sediment samples from off-site drainageways showed no contamination. It is likely that the surface water is being contaminated through a groundwater release.

The geological cross-section was developed through a seismic survey and interpretation of well logs (Figure 3). This cross-section provided alluvium thickness data essential to the model. Seepage meter sampling was conducted to evaluate the impact of pumping or alluvial aquifer recharge on the river. Seepage meter sampling indicated that 50 feet off the shore from the pumping wells the flow is upward into the river, and in side channels off the main river channel, a near zero flow condition exists.

The gross contamination of the top of the alluvial aquifer on the island and the contamination detected in the shallow well gallery were sufficient to advance this site to the LSI. The main objectives of the LSI were to measure alluvial aquifer characteristics, allowing the preliminary modeling results to be checked against actual field data, enhancing the validity of the model; another project goal was to define the source of the contamination in the shallow well gallery.

The first project objective was addressed by conducting an aquifer test on the north tip of the island, approximately 1,000 feet south of the shallow well gallery. The second objective was met by installing four well nests composed of three wells each. Each nest had a monitoring well screened at the top (10 to 20 feet), middle (90 to 100 feet) and bottom (160 to 180 feet) of the alluvial aquifer. The vertical spacing was intended to define the vertical extent of contaminant plumes.

The well nests were placed around the municipal well gallery in such a manner to identify the source of the municipal water contamination. The well nests were distributed approximately 1,000 feet south (1 nest), west (2 nests) and north (1 nest) of the shallow municipal well gallery. The preliminary modeling results obtained during the SSI were used to locate possible migration routes and source locations. The well nest

installed on the north tip of the island was also used to conduct the aquifer test. Due to the high water table and noncohesive matrix, special drilling techniques were required for the deep wells. The shallow and medium depth wells were installed with a conventional auger technique, while the deep wells were installed through dual-tube reverse air rotary drilling. Field analytical screening and fast turn-around laboratory analysis were used to determine if drilling wastes and well development wastes were hazardous.

The aquifer test was run on the mid-level well that was installed with a cable tool rig and screened from 100 to 120 feet below grade. This well differed from other monitoring wells in that it was constructed of 6-inch ID PVC casing. During the aquifer test, this well was pumped at a constant 224 gpm. The drawdown phase of the test was run for 1.65 days. Within 13 hours, the pressure transducers recorded steady-state water elevations in the three monitoring points (top, middle and bottom of the alluvial aquifer) around the pumping well. The bottom and middle monitoring points were 29 feet from the center of the pumping well. The top monitoring point was located 13.75 feet from the center of the pumping well. This steady-state condition indicated that the drawdown had intercepted the river boundary.

The city maintained a steady withdrawal rate from the shallow and deep wells for four weeks before the aquifer test to allow the system to approach equilibrium. Approximately 4 days after the aquifer test pump was stopped, the shallow municipal wells were shut off. Within 5 minutes, all monitoring points showed between a 0.2- and 0.5-foot recovery. A similar but reversed response was recorded when the wells were restarted. This rapid aquifer response is indicative of a semiconfined system. Using the Theis solution, the aquifer test data were analyzed. Table 3 shows the results of this aquifer test.

Table 3
Aquifer Test Data

Transmissivity (gpd/ft^2)	10^5 to 10^6
Storativities (dimensionless)	10^{-1} to 10^{-3}
Horizontal Hydraulic Conductivities (ft/day) (assuming 40 feet saturated thickness)	65 268

Measurements taken from river piezometers before and after the municipal well shutdown showed that during pumping, river seepage is into the alluvial aquifer, within 50 feet of shore in the main channel. Once the wells were restarted, the gradient reversed, drawing water through the riverbed into the alluvial aquifer.

To confirm assumed alluvial aquifer porosities and stratigraphy, downhole geophysics was conducted in two monitoring wells. EM and natural gamma logging were conducted at each location. Both logging techniques detected a clay-rich zone from 0 to 7 feet below grade. Porosities in this zone ranged from 54 to 69% range, and natural gamma counts averaged 105 cps. Between 7 and 175 feet, both measurements indicated a relatively homogenous sandy matrix with porosities in the 16 to 34% range and natural gamma counts of 30 to 50 cps. Drilling logs were in agreement with these findings.

The results of the aquifer test indicated that the actual hydraulic conductivities were in the intermediate range used during the modeling sensitivity analysis. If hydraulic conductivities were substantially higher than the highest range assumed during the modeling, it is likely that the capture zones created by the well field would not have reached the landfill.

The LSI groundwater sampling indicated that under current pumping rates the former landfill is an unlikely or minor contributor to the contamination detected in the shallow municipal wells. This conclusion is based on current withdrawal rates. Sampling data suggest that the contamination is attributable to a source south of the municipal well gallery. Two nearby plating facilities, located within 1,600 feet of the shallow well gallery, are potential sources of this contamination. These

facilities have been in operation for fewer than 20 years.

An additional potential contaminant source was identified almost 5,000 feet south of the well gallery. This source is the location of buried foundry wastes. The foundry wastes have been in place for more than 30 years. They were disposed of in a swamp and they are, therefore, likely to be in contact with the water table. Natural groundwater flow into the river creates strong easterly gradients in the vicinity of the plating facilities which may transport contaminants into the capture zone of the shallow well gallery. These gradients also may carry the foundry contamination under the site. It is possible that these contaminants could then intersect with the capture zone of the shallow well gallery.

The groundwater sampling identified two distinct groundwater plumes: one plume occurs in the top of the alluvial aquifer and a second plume was detected in the deep monitoring wells at the bottom of the alluvial aquifer. This plume disparity could be caused by different contributing sources. The nearby plating facilities could be responsible for the shallow plume. The proximity of this source(s) may not allow the metals plume sufficient distance to sink below the top of the alluvial aquifer. The more distant potential source, the foundry wastes, may have a sufficient travel distance to allow the bulk of the plume to sink to the bottom of the alluvial aquifer. For this scenario to occur, the capture zones for the well gallery would have to extend out to the foundry waste area and be stronger than the natural gradients. Only one midlevel monitoring well detected metals contamination. This well is situated directly between the plating facilities and the shallow gallery; it may have detected mixing between the two plumes.

The groundwater modeling showed that the shallow municipal well capture zones in Layer 1 extended under the island and south, close to the foundry waste burial area under low, moderate (current) and high (doubled current) pumping rates. This pattern was held true for all three layers. Layers 2 and 3 were not considered potential targets due to the strong upward gradient between Layers 1 and 2.

The modeling parameters exhibiting the greatest sensitivity were vertical and horizontal conductivity, riverbed conductance and pumping rate. Groundwater flow appears to be less sensitive to precipitation (recharge) and river stage. Limiting the pumping from Layer 1 and increasing the pumping from Layer 3 could greatly reduce the potential for contamination in the alluvial aquifer to migrate into the shallow well gallery.

The results from this modeling are based on relatively broad parameter ranges applied at semiregional scale. Although the parameters were checked against empirical data and found to be representative of actual conditions, a finer mesh model would be required to produce a more detailed analysis of the physical flow or transport process. This additional modeling could be developed into a wellhead protection program, design of alternate pumping schemes or the selection of an alternative well field.

CONCLUSIONS

The field investigation and modeling were implemented using an integrated approach. At the PA phase, a set of questions was developed concerning the potential threat that this site posed to human health and the environment. The SSI was designed to answer these questions. Due to the complexity of the hydrogeological system around the site, groundwater modeling was deemed necessary to fully interpret the potential risks posed by this site. The conceptual model was designed and the data gaps were filled through data acquisition at the SSI phase. The conceptual model and field sampling plan were developed concurrently.

Information produced at the SSI confirmed contamination of the alluvial aquifer and allowed completion of the preliminary modeling. This information indicated that the site was a possible source of observed contamination of the shallow municipal well gallery. Attribution of this contamination was still incomplete.

This site was then advanced to the LSI phase, which focused on contaminant attribution and confirmation of modeling parameters. The preliminary modeling results were used to guide the design of the LSI field work. Well placements and the location of an aquifer test site were based on modeling data. The empirical data produced at the LSI phase allowed confirmation of the parameters used in the conceptual model and identification of the likely sources of the shallow municipal water well contamination. Additionally, based on the findings of this study, the city may be able to greatly reduce the impact of the alluvial aquifer contamination on its municipal water supply. Although not a permanent solution, it allows risk reduction while the appropriate authorities take whatever action is deemed necessary regarding the groundwater contamination. The city was also planning to add an additional well in the shallow gallery; this study shows that this is not a desirable option.

Modeling not supported by field verification is based on assumptions; sampling in a complex environment without first modeling the system may lead to missed or over-emphasized data. The integrated approach of this site assessment, developing sampling plans in conjunction with groundwater modeling, assured the most effective use of resources and the most representative or accurate data interpretation. Implementing this strategy in a phased approach allows for alteration and refinement of the model and sampling plan as information is developed.

Extraction/Interception Trenches by the Bio-Polymer Slurry Drainage Trench Technique

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ABSTRACT

Groundwater extraction and interception trenches are often an integral part of contaminated groundwater remediation projects. Deep drainage trenches can provide a means for contaminate extraction for treatment and interception for containment. The construction of these trenches may be costly and risk-filled if conventional methods are employed which require shoring, dewatering, over excavation and personnel working in the trench.

The Bio-Polymer Slurry Drainage Trench Technique (B-P Drain) is a relatively new method, based on the slurry trench technique, which permits the installation of trenches without the problems associated with conventional construction. The B-P Drain method permits the installation of perforated pipes, filter fabrics, free-draining aggregates, sumps and/or wells in relatively narrow trenches under conditions which minimize health risks to workers and costs to the owner.

The design of extraction/interception trenches constructed by the B-P Drain technique requires an understanding of the project requirements as well as an appreciation of the technique. The quality control demands for B-P Drain construction require trained, experienced field personnel capable of determining the actions necessary to preserve the biodegradable slurry during construction and then the destruction of the slurry when the drain is activated.

This paper presents an overview of the B-P Drain technique as it is presently used on waste remediation projects. Case studies of four projects are used to illustrate the various design concepts and field installation procedures.

INTRODUCTION

The installation of deep drainage trenches has long been a risk-filled and costly endeavor. Conventional installation techniques involve dewatering, sheeting and shoring and danger to personnel working in the trench, from trench collapse. Recently, due to the public's concern for the environment and the need to preserve groundwater resources, there has been an increased demand for deeper and more sophisticated groundwater extraction and interception trenches. These trenches are even more difficult to construct because of the volatilization of toxins and increased groundwater and trench spoil disposal restrictions and costs.

The introduction of a new construction method, the Bio-Polymer Slurry Drainage Trench (B-P Drain), now provides a quicker, safer, more cost-effective method to install deep drainage trenches. This new method is a modification of the well-known slurry trench method which uses a biodegradable trenching slurry to temporarily support the trench walls and control trench width. Using the B-P Drain method, the usual drainage structures (e.g., wells, perforated pipes and free-draining aggregates) can be placed without dewatering, sheeting or shoring, or men

working in the trench. Experienced personnel and quality control are especially critical in constructing B-P Drains. This paper provides an overview of the technique and illustrations of a few example projects.

CONSTRUCTION METHODS

Trench Excavation and Support

Slurry trench construction is a well-established technique for installing groundwater control and/or deep foundation systems to great depths at a minimum cost. Generally, a bentonite-clay slurry fills the excavation to support the side walls and permit the creation of a narrow, vertical trench. In the typical slurry trench, the bentonite-clay slurry cakes on the trench walls and plugs porous formations creating a hydraulic barrier. A slurry wall is formed by replacing the slurry with a permanent, engineered backfill. Trench stability is maintained during construction by controlling slurry properties (e.g., density, viscosity, etc.) and by keeping the level of slurry in the trench above the groundwater table.

With the B-P Drain method, a biodegradable slurry is used in a similar manner to bentonite-clay slurry except that the B-P slurry does not form a cake or permanently impede groundwater flow. After excavation and backfilling are complete, the B-P slurry can be treated with additives to convert it to water and a very small amount of natural carbohydrate.

Compared to more traditional trenching methods, B-P Drain construction is far simpler, safer, faster and usually less costly. Trench support is provided by the slurry eliminating sheeting and shoring, trench shields and bracing. Since the trench is filled with slurry, no workers can enter the trench. The slurry trench method also eliminates dewatering and the treatment of dewatering liquids. Usually B-P Drains can be constructed much narrower than trenches constructed by traditional methods since internal supports are unnecessary, thus providing an additional savings in excavation, disposal and backfill material volumes and costs.

B-P Drains usually are excavated with a hydraulic excavator. Depths up to 70 ft are possible using custom-built hydraulic excavators with extended reach capabilities (Fig. 1). The design width of the trench (usually 18 to 36 inches) is ensured by using a back hoe bucket of the same width. An earthen pad (working platform) is created prior to trenching by leveling the trench alignment to provide room for the temporary storage and drainage of trench spoil removed during excavation. A level working platform is required to maintain the slurry level in the trench at an acceptable elevation. In the case of highly contaminated soils, the working platform may be lined to prevent additional contamination. All excavation is carried out under slurry so continuity, depth and soil conditions are determined by observations of the construction process and soils as discharged from the excavator bucket.

Figure 1
Long-Stick hydraulic Excavator Digging Bio-Polymer Drain

Drain Backfill and Structures

Depending on the purpose and design of the drainage trench, different materials and structures can be placed through slurry into the trench. The simplest systems involve the placement of a coarse aggregate (pea gravel) around well casings spaced in the trench (Fig. 2). Well casings are lowered vertically into the trench, through the slurry, with the pea gravel tremie-placed around the well to maintain the alignment of the casing. The trench between wells is also filled with pea gravel by end-dumping backfill down the backfill slope to ensure proper displacement of the slurry. If a finer or graded aggregate (sand or gravel) is used, it must be wetted first with slurry to permit tremie placement. Filter fabrics and geomembranes (geofabrics) also can be placed through the slurry into the trench to line the trench walls (Fig. 3). The placement of geofabrics is facilitated by attaching weights to the geofabric to provide ballast. Continuity of the geofabrics is provided by overlapping the geofabric sheets by at least 5 ft.
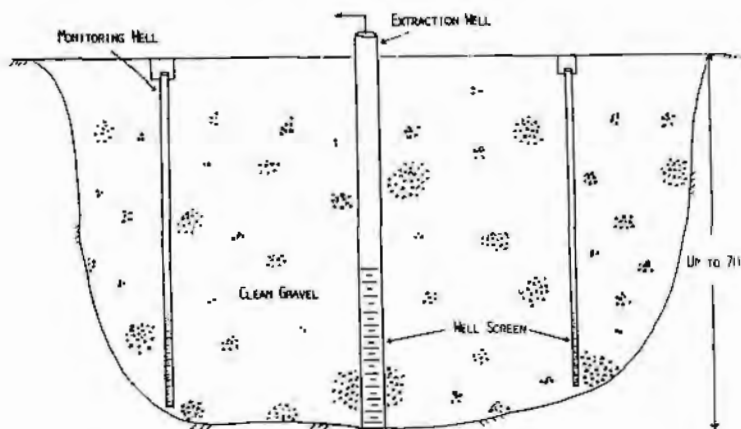
Figure 2
Profile of Typical B-P Drainage Trench

When design considerations dictate that a horizontal drain pipe be used along the bottom of the trench, it can be installed by the B-P Drain method. Using a flexible pipe, corrugated for strength, a separate pipe laying machine travels behind the hydraulic excavator laying the pipe through the slurry while simultaneously bedding and backfilling around the pipe (Fig. 4). Additional backfill can be placed by end loader to bring the backfill to grade. Small diameter sumps or wells (4 to 24 inch diameter) are either attached directly to the drain pipe or placed directly beside the drain pipe perforations for continuity.

Figure 3
Installation of Geofabric in Bio-Polymer Trench
Tremie Pipe in Foreground

Figure 4
Pipelaying Machine Placing Flexible Perforated
Pipe in Bio-Polymer Trench

Since the backfill is placed through slurry, the aggregate must extend to near the surface to displace the slurry and maintain trench stability. The top 3 to 5 ft of the drainage trench usually are backfilled with excess trench spoil or other soil to cap the trench. This zone may also support buried vaults, discharge piping and pump controls so that all drainage structures are buried and hidden from view.

DESIGN AND QUALITY CONTROL

Design Considerations

The design of a B-P Drain should combine the project requirements, soil conditions, pollutant characteristics and installation procedure into a reasonable solution. A B-P Drain can serve as a groundwater cutoff, plume extraction trench, groundwater interceptor trench, injection trench and/or shallow groundwater skimmer. In some cases, well points or conventional deep wells may not function effectively or efficiently. Often a B-P Drain with a single well can replace an entire array of conventional wells.

The continuity provided by a B-P Drain can be especially advantageous in the design. Soils that typically produce poor groundwater yield can be effectively drained by B-P Drains. Preferential groundwater conduits such as sand seams, buried conduits and root holes that are difficult to intercept with other methods can be effectively intercepted and collected.

Groundwater conditions and pollutant characteristics may dictate the depth of the drainage trench. A high groundwater table and a floating pollutant (e.g., petroleum) may permit the design of a relatively shallow drainage trench which intercepts the groundwater table at an elevation sufficiently deep to overcome seasonal groundwater fluctuations. A deep groundwater table or a pollutant which is heavier than water may require a much deeper trench.

Soil conditions affect both the type of drainage structures and the backfill requirements. Silty soils can migrate to a drain and plug the backfill, thus limiting the drain's effectiveness or fouling pumps. A filter fabric can be used to protect an open graded backfill, or a backfill with an engineered gradation can be designed for the trench based on filter criteria.

When the drainage trench is designed to provide a positive groundwater cutoff in highly permeable soils, a perforated pipe on the bottom of the trench may be necessary or the drain can be installed deeper to allow a lower operating head. In many cases, a slurry cutoff wall can be economically combined with the B-P Drain for a positive cutoff and more efficient groundwater collection (Fig. 5).

In general, conventional manholes or lift stations are not recommended for a number of reasons. First, conventional manholes typically used for sanitary sewers constitute a confined space which can allow unintentioned access. The presence of contaminated groundwater makes entry into such an environment potentially hazardous even for the well-trained worker. Second, pumps, control facilities and access to same can be provided through conventional well equipment at a much lower installation cost. Duplex systems can be provided using multiple well casings for backup pumps. Third, conventional manholes must be constructed by conventional means (sheeting, shoring and dewatering) negating a significant portion of the savings and time provided by the B-P Drain installation. Finally, concrete manholes are sealed structures which are only attached to the drain field through the perforated pipe. A much larger radius of influence can be provided by using a perforated sump or well and in the case of failure of the drainage pipe, the perforated sump or well provides a safety factor for ensuring the continued service of the drainage trench.

Quality Control

The control and monitoring of construction quality for a B-P Drain installation focus on the properties of the bio-polymer slurry. Adequate control of the slurry is required to support the trench and permit the proper placement of the backfill during construction. In addition, the safe and effective treatment of the slurry after construction is necessary to ensure that the drain is activated and fully functional.

The bio-polymer slurry consists of ground guar beans, water and proprietary degradable additives. A suspension of the guar and water at very low percentages (approximately 1%) creates a viscous, pseudoplastic slurry capable of supporting an earthen trench. Additives are used to control and extend the life of the slurry. Without additives, enzymes in the soil will quickly cause the slurry to "break" or degrade and become ineffective in approximately one day.

Primary quality control parameters for the slurry are viscosity, density, filtrate loss and pH. All monitoring and testing should be performed by an experienced Bio-Polymer Slurry Engineer. Chemical adjustments to the slurry are made to both fresh and trench slurry to extend the working life. Depending on the grade of guar, a target viscosity of 40 cP is typically used to ensure adequate guar content. Titrations of the slurry are performed as needed to calculate additive requirements. The slurry pH is maintained at 8.0 or higher to limit enzyme action during excavation. Tests on the filtrate properties of the slurry indicate that the slurry does temporarily seal off the trench wall, but instead of a filter cake (as with bentonite slurry), a very thin, slimy, gelatin-like substance bridges over porous formations to support the trench with its high gel strength.

Once construction is complete, the slurry must be broken and the drain developed much like a water well is developed. First, the pH of the slurry is reduced to below 7 to initiate enzyme action, then a proprietary enzyme breaker solution is added to ensure biodegradation. The drain is now functional, but residue from the guar can degrade slowly or incompletely due to toxins in the groundwater causing anaerobic digestion in the trench and/or an unpleasant odor. To alleviate this problem and to ensure that the drain is fully functional, the drain is continuously pumped and recirculated while metering in additives to inhibit anaerobic digestion. Chlorine, typically used in water well development, can be used to help develop a B-P drain but only under the strictest controls since an untimely or over-application of chlorine can produce toxic byproducts. Pumping and flushing continue for one day or several days depending on the size of the drain and the permeability of the native soils.

When the drain is fully developed, the flush water should be clear and free of slurry and the trench continuity obvious. Excess waters usually have been disposed of through a municipal wastewater treatment plant or held for priority pollutant testing and flushed into the storm water sewer system.

Evidence from past projects has shown that construction creates a small groundwater mound around the trench which temporarily limits the inflow of contaminated water. Usually, pollutants in the groundwater are absent in the recovered B-P slurry. With continued pumping, the drain installation results in a line sink and pollutants are again collected in the groundwater.

APPLICATIONS

Over the past decade there have been several dozen B-P Drains con-
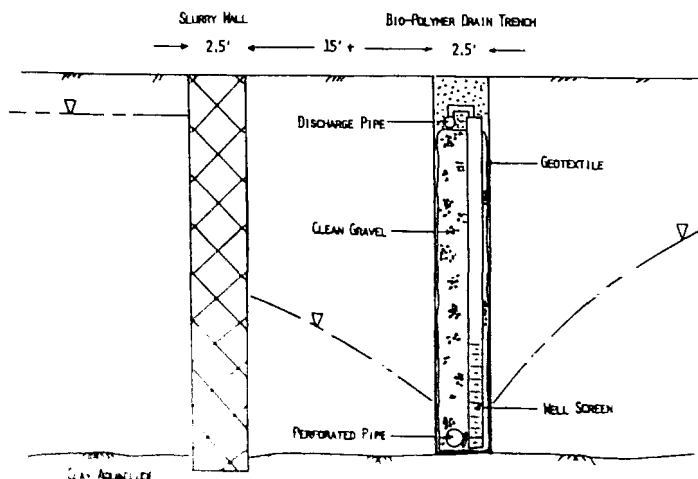
Figure 5
Cross-Section of Groundwater Contaminant and Extraction System

structed in the United States and Europe. Most applications in Europe were intended for the interception of groundwater to stabilize and dewater slopes along highways, while applications in this country have concentrated on contaminated groundwater remediation. The following recently completed projects illustrate recent applications in the United States and the variety and magnitude of projects now being pursued.

PILOT PROJECT IN NEW JERSEY

An older pharmaceutical manufacturing plant in a highly developed urban area discovered that it had leaked vinyl chloride, trichloroethylene (TCE), PCBs and other toxins into the groundwater. The congestion of the site and cost of conventional construction provided encouragement for the engineers to seek a solution to the groundwater extraction problem by using a B-P Drain. The pilot project design called for a 100-foot long trench, 2 to 3 ft wide and 27 ft deep constructed through silts, peat and a groundwater table within 2 ft from the surface. Since TCE is heavier than water, the drain used a 6 inch perforated, corrugated pipe along the bottom of the trench which terminated in an 18 inch diameter polyethylene sump. The B-P Drain was installed in approximately one week, flushed, developed and ready for pumping into an on-site treatment plant. Monitoring wells were placed inside the trench and alongside the trench perimeter.

Over a year of monitoring and testing have proven the success of this drainage trench. Pumping rates of 3 to 10 gpm are currently used. The pea gravel backfill used has shown no plugging or fouling problems to date. Due to the success of the pilot project, 10 more short, deep B-P Drains are planned to fully remediate the hot spots on the two square block area at the site.

One of the most significant advantages of the installation was the complete lack of toxic volatilization. Monitoring wells within 4 ft of the trench alignment gave consistently high readings of volatiles. The B-P slurry temporarily blocked these toxins during construction and permitted the safety level of the work to be down graded from Level B (supplied air respirators) to Level D (street clothes).

Interceptor Trench in Missouri

A munitions plant in Missouri found that solvents used in the manufacturing process, including TCE, had escaped the property and the plume was traveling toward a nearby river. Soils at the site consisted of clay over gravel over bedrock with the plume traveling on top of the bedrock. Conventional well spacing design was found to be so close that a deep drainage trench became a practical necessity. The trench was 250 ft long, 3 ft wide and 30 ft deep with a woven geotextile envelope around a pea gravel backfill. A six inch diameter stainless steel well casing was placed in the center of the trench for pumping with six inch diameter PVC monitoring wells on each end of the trench. The trench was installed in approximately one week. The B-P slurry was broken and the drainage trench developed by pumping. Prior to completion, the continuity of the installation was demonstrated by pumping the central well and observing the immediate response of the monitoring wells.

Extraction Trench in Central California

An oil company in central California owned a service station which was found to be leaking gasoline into two aquifers under the site. Silty sands and cemented sands limited the effectiveness and continuity of conventional extraction well systems. In addition, the groundwater gradients in the two aquifers flowed in different directions making two deep trenches with different alignments a distinct advantage. Two trenches were constructed with 18-in diameter stainless steel wells placed in a graded filter backfill. The deeper trench was 65 ft deep and 170 ft long and had an impervious backfill material placed over the graded filter backfill zone to maintain the separation between the aquifers. The second trench was 35 ft deep and 240 ft long. Total construction time for both, trenches including earthwork to level the site topography, was approximately three weeks.

Collection Trench in Northern California

A major manufacturing plant feared that past spills of processing chemicals might have leaked into the groundwater and affected the pending sale of the property. An on-site treatment and containment system was designed which called for 2,000 ft of B-P Drain and a soil-bentonite slurry wall to provide a downgradient groundwater recovery system. A soil-bentonite slurry cutoff wall and a B-P Drain were selected as the most cost-effective method for this project.

The B-P Drain was constructed through clays and silts approximately 15 ft upgradient and parallel to the cutoff wall. The trench was constructed 3 ft wide and approximately 30 ft deep and lined with a woven geotextile. The pipe laying machine laid and bedded a 6 inch diameter perforated pipe through the slurry. Pumping wells 12 inches in diameter and 4 inch diameter monitoring wells were placed in the trench alongside the perforated pipe. Construction time for the entire project was less than two months.

CONCLUSION

The Bio-Polymer Slurry Drainage Trench method represents a significantly improved method for the construction of deep drainage trenches. The primary advantages are in safety, cost and the ability to employ deep trench applications in problem soils and polluted groundwater. The quality control requirements of the B-P slurry demand that all projects be supervised by experienced, competent experts.

The design of deep drainage trenches by the B-P method should recognize the advantages and limitations of the B-P Drain method in design. Most conventional drainage structures and systems can be employed, except large diameter manholes and rigid piping are impractical. The most critical aspects of quality control are in extending the slurry's life during construction and then eliminating the residues of the slurry when the drain is developed.

The B-P Drain projects illustrated in this paper show the method to be practical in a variety of soil types, applications, project sizes and with different pollutants. Construction is generally rapid and quite cost-effective. The number of new applications for the B-P Drain technology continues to grow as more engineers and owners become familiar with the real advantages offered by this new technology.

Evaluation of Groundwater Extraction and Treatment Scenarios Using Quasi-Three-Dimensional Transport Model

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ABSTRACT

A Remedial Investigation (RI) was conducted for trichloroethylene (TCE) contamination of the groundwater underlying the Northeast (NE) Disposal Area at George Air Force Base (GAFB), San Bernardino, California. A Feasibility Study (FS) was performed to select a preferred alternative selected previously for the remediation of the TCE contamination in the Upper Aquifer underlying the NE Disposal Area. One of the primary objectives of this RI for the NE Disposal Area was to reassess the effectiveness of the preferred alternative developed in the previous FS for remediation of the Upper Aquifer. To accomplish this objective, a three-dimension numerical model of the groundwater flow within the Upper Aquifer was refined with the hydrogeologic parameters calculated from the aquifer pump test conducted within the NE Disposal Area. The refined model was then incorporated into a solute transport model used to assess the extent and rate of TCE plume movement, as well as to reevaluate the groundwater extraction and disposal components of the preferred alternative.

RI activities focused on an evaluation of TCE contamination within the Regional Aquifer to the center, north, east and southeast of the TCE plume identified within the Upper Aquifer. Water quality sampling results suggest that the Regional Aquifer is not contaminated to the east of this plume where the Upper and Regional Aquifers merge. Contamination to the east currently does not present an immediate threat to any potential receptor and can be addressed as part of the Upper Aquifer TCE remediation efforts. TCE was also detected in the Regional Aquifer to the southeast of the Upper Aquifer TCE plume at concentrations below the 5 ug/L State Action Level (SAL) and Federal Maximum Contaminant Level (MCL). This contamination is believed to be unrelated to the TCE plume observed within the Upper Aquifer.

The five Upper Aquifer monitoring wells installed during this RI indicated the presence of a TCE plume covering approximately 500 ac, in comparison with the previous estimate in the FS of approximately 400 ac. When measured through the center, the TCE plume having concentrations greater than 5 ug/L is approximately 7,000 ft long and 4,000 ft wide, extending approximately 5,000 ft from the northern GAFB boundary. The mass of the TCE present within this plume located in the Upper Aquifer is estimated to be approximately 430 lb.

The preferred alternative selected previously included nine on-base and off-base extraction wells, two packed-column air stripping towers operated in series and two deep wells for injection of treated groundwater into the Regional Aquifer. The quasi-three-dimensional solute transport model results suggested that the

groundwater extraction component of the preferred alternative would not successfully remove the TCE from the Upper Aquifer. The reasons on which this conclusion was based included the restricted pumping rate per extraction well due to lower transmissivities calculated for the area and the larger plume extent to the northeast.

Six detailed alternative groundwater extraction and disposal scenarios were developed and modeled. All six scenarios incorporated a 19-well groundwater extraction component to expedite remediation. The additional extraction wells were placed primarily to address the larger plume extent observed within the merged Upper and Regional Aquifers located to the east and northeast. Three of the scenarios modeled include a component which recharges the Upper Aquifer with the extracted and treated groundwater in order to create a circulation zone within which the TCE would be trapped. Recharging of the Upper Aquifer emerged as an applicable control measure primarily because of the limited availability of the groundwater (due to lower aquifer thickness) for high rate extraction. In addition, recharging the Upper Aquifer will have advantages of minimum resultant drawdowns and flushing of any contaminants remaining in the soil.

Following a detailed technical evaluation, the extraction and disposal component of the preferred alternatives for the remediation of the Upper Aquifer TCE plume was selected as Scenario 7. This scenario would consist of extraction of the contaminated groundwater with 19 wells and percolation of a portion of the treated water back into the aquifer via the former Sewage Treatment Plant (STP) Percolation Ponds.

THREE-DIMENSIONAL GROUNDWATER FLOW MODEL

The three-dimensional finite difference groundwater flow model of the NE Disposal Area and its surroundings is based on the code developed by the U.S. Geological Survey.[1] This code has been applied to groundwater studies throughout the United States and has been extensively tested and verified. Minor changes to the code have been made by James M. Montgomery, Consulting Engineers, Inc. (JMM) to enable its execution on an IBM Personal Computer and to handle specific input-output requirements of the solute transport model.

MODEL GEOMETRY

To model the three-dimensional groundwater flow system around the George AFB site, the natural system was simplified. The area modeled covers approximately 54 mi² of Victorville fan deposits and includes a portion of the Mojave River deposits (Fig. 1). The modeled area extends well beyond the base boundaries so
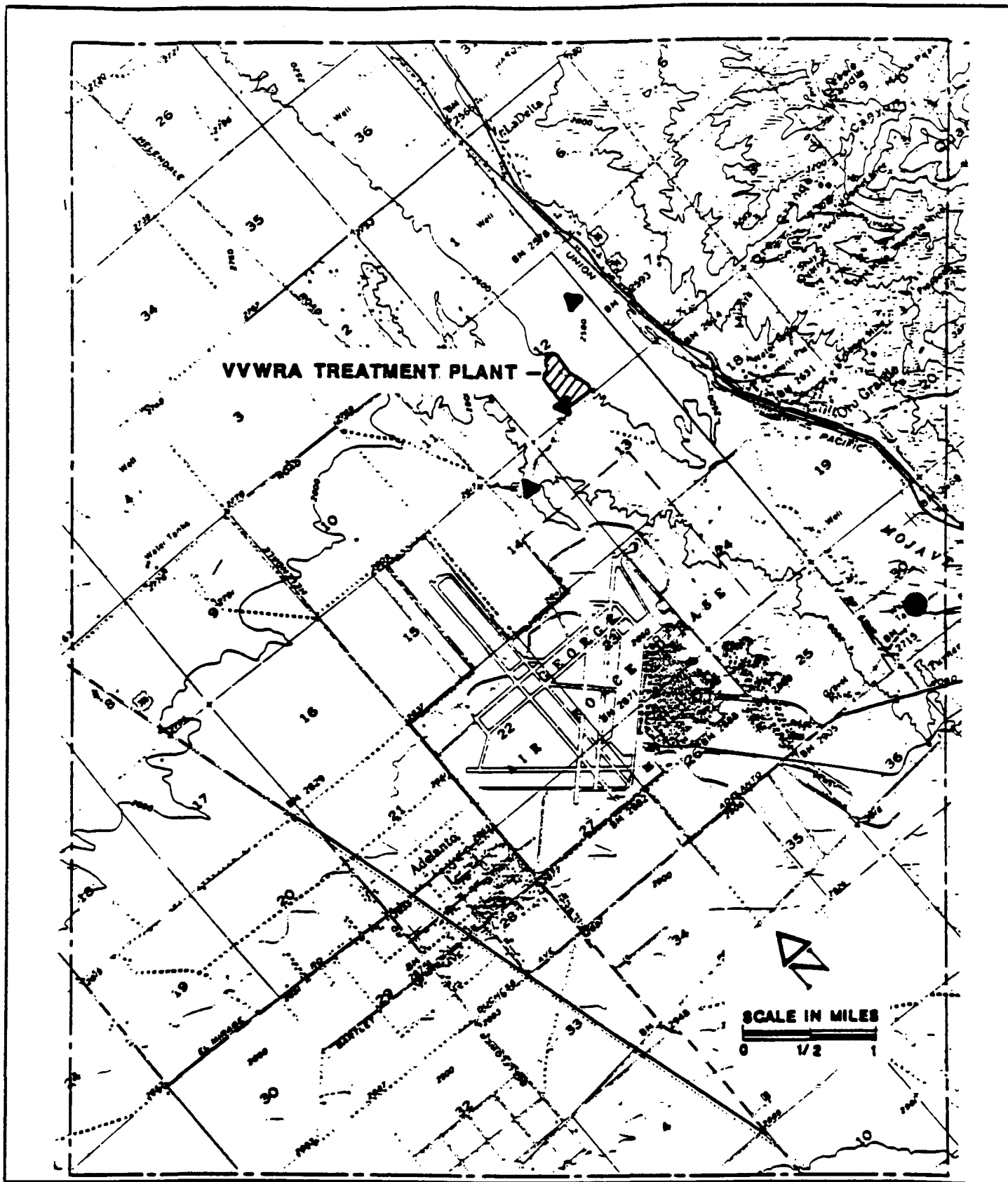
LEGEND

● GEORGE AFB AND CITY OF
  ADELANTO SUPPLY WELLS

▲ GROUND WATER OBSERVATION
  LOCATIONS FOR MODEL

—··— MODEL BOUNDARY

Figure 1
Base Map Showing Boundaries of Model

that the extraction wells on or near the base are not affected by the boundary flows.

The aquifer system is modeled in three layers. The top layer simulates the conditions in the Upper Aquifer (above elevation 2,600 ft) and the portions of the sandy and gravelly Mojave River deposits. The two lower layers represent upper and lower portions of the Regional Aquifer and are separated to simulate the three-dimensional flow effects near the river. Each layer is divided into 2,040 blocks (34 columns and 60 rows). Smaller blocks are used in the vicinity of the NE Disposal Area so that flows can be modeled in more detail. Figure 2 shows the boundaries of the modeled area and the finite difference grid specified to represent those areas where the TCE plume shows the highest concentrations.

Boundary Conditions

To calculate the flows in and out of each block within the model area, the flow and/or head conditions at the boundaries of the modeled area must be specified. Model boundaries to the north and southwest of the base are defined by controlled flux. These boundary conditions simulate flux of groundwater to and from the modeled area at a rate proportional to the head difference between either side of the boundary. The heads outside the model boundary are based on the observed values. The heads inside the model boundary are calculated during each iteration. The resulting controlled flux is simulated for groundwater discharge from the model area along the northeast boundary, above the river, and for groundwater inflow along the southwest boundary. A no-flow boundary is specified west of the base where the non-water-bearing bedrock crops out or is located very near the surface. Northwest and southeast of the base, flow in the aquifer is approximately parallel to the model boundary, and thus, no-flow conditions also are specified for these boundaries. The top model layer (layer 1) is simulated as a dynamic boundary represented by the water table conditions. The lower boundary in the third model layer is simulated as no-flow at the bottom of the Regional Aquifer where the alluvial sediments intersect the basement complex.

Additional inflows and outflows to the aquifer system include artificial recharge, community production wells and the Mojave River (Fig. 1). The Victor Valley Wastewater Reclamation Authority (VVWRA) facility, located northeast of the base on the west bank of the Mojave River, percolates approximately 0.7 mgd to the Upper Aquifer. Seven production wells, located southeast of the base, supply potable water to the George AFB and the City of Adelanto. The groundwater at this location is extracted from the Regional Aquifer at an approximate rate of 3.6 mgd. Within the modeled area, the Mojave River causes a net discharge from the Upper and Regional Aquifers (base flow). The boundary conditions for the river involve input of constant head in the river, the elevation of the bottom of the riverbed and the vertical hydraulic conductivity of the riverbed deposits. The flux is calculated by the model based on the rate of leakage between the river and aquifer nodes adjacent to the river. The net flow due
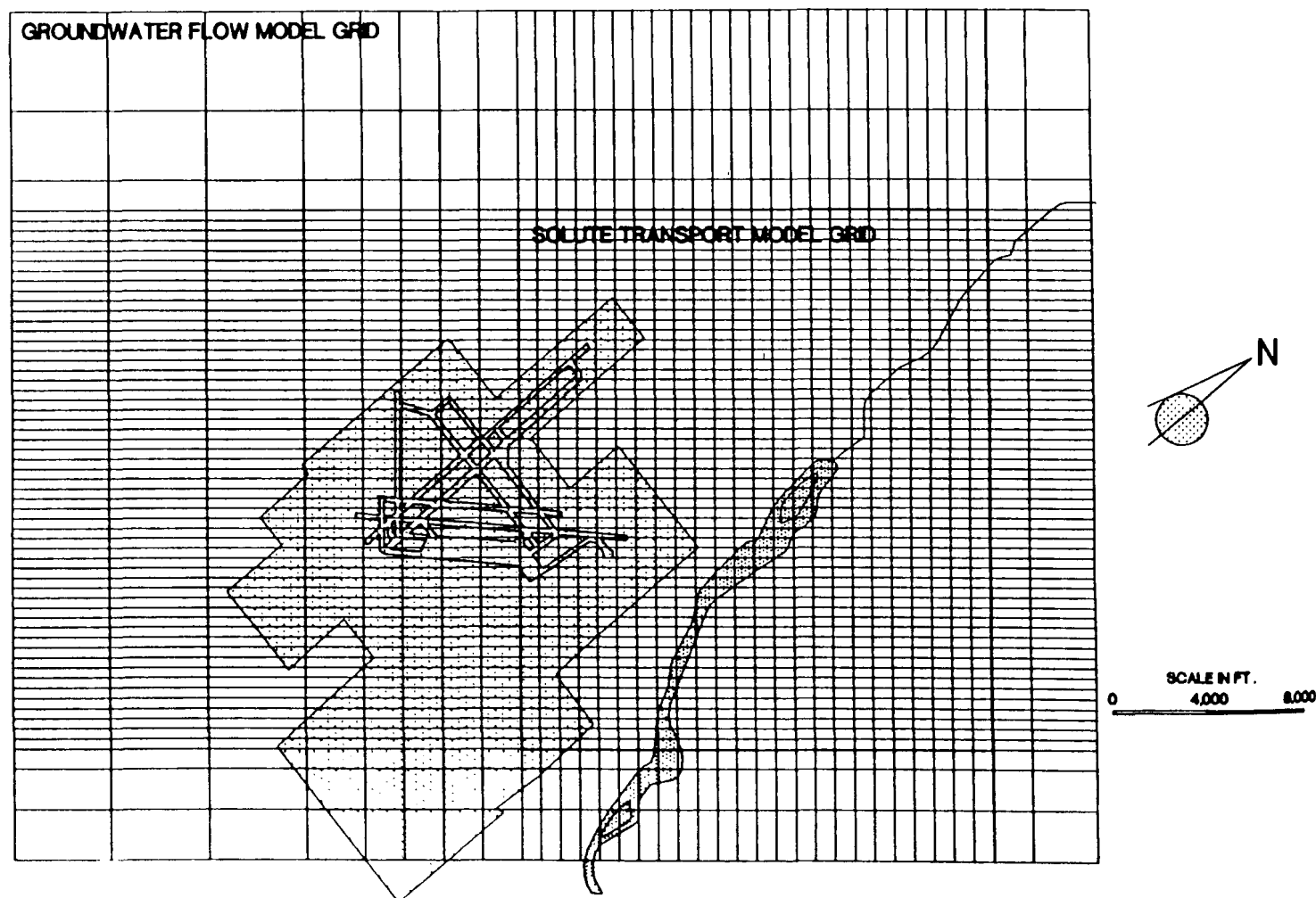
Figure 2
Two-Dimensional Solute Transport Model Grid Integrated into
Three-Dimensional Groundwater Flow Model Grid

Table 1
Aquifer Parameters

Parameter	Initial Estimate	Similar Aquifer	Values From Literature(1)	Aquifer Tests	Calibrated Values
Transmissivity (sq ft/d)					
Upper Aquifer alluvium	5,400 to 270		5,000 to 5	1,650 to 144	9,000 to 50
Regional Aquifer	7,800 to 650	2,800 to 5,700 1,800 to 2,500	15,000 to 25		4,990 to 700
River Deposits	70,000 to 2,500	8,500 to 11,400	100,000 to 5	279,000 to 33,000	
Storage Coefficient (dimension-less)					
Upper Aquifer	0.02 to 0.10	1.5 to 5.7×10^{-4}	0.01 to 0.3	1.4×10^{-2} to 9.5×10^{-4}	0.1
Regional Aquifer	2.6×10^{-4}		5×10^{-3} to 5×10^{-5}	0.003	0.001
River Deposits	0.20		0.01 to 0.3		0.1 to 0.001
Vertical Hydraulic Conductivity					
Between Upper and Regional Aquifers	0.05	0.05	1.0 to 1×10^{-5}		0.0001 to 0.03
Within Regional Aquifer	0.05		1.0 to 1×10^{-5}		0.01 to 0.02
Within River Deposits	20		50 to 0.1		0.09

(1) Freeze and Cherry, 1979.

to precipitation and evapotranspiration is considered negligible for the aquifer system. The average annual precipitation for the Victorville area is less than 5 in., which is exceeded by the potential evapotranspiration estimated at more than 82 in. annually. Evapotranspiration along the river is incorporated into the model input of river elevations.

Aquifer Parameters

Aquifer parameters of transmissivity, vertical hydraulic conductivity and storage were initially set at values estimated by JMM. These parameters were adjusted within an acceptable range during the calibration process. Three sources were used to delineate this range of reasonable values: (1) parameter values for similar aquifers estimated for other sites in the vicinity of George AFB, (2) parameter values measures for similar soil types,[2] and (3) parameter values calculated from aquifer tests conducted at GAFB. Table 1 lists the initial parameters, the range of parameters given by each source and the range of final parameters used in the model.

Calibration

Calibration of the model was achieved by simulating long-term average conditions of the aquifer. The initial input heads to the model were those observed in the natural system. The aquifer parameters, boundary fluxes and the interaction of the aquifer with the Mojave River were adjusted until the simulated steady-state heads matched the observed heads. The anisotropy of the natural aquifer material was simulated to match observed gradients.

The three-dimensional groundwater flow model was calibrated by first setting the thickness of the first model layer to the actual values observed during drilling of new monitoring wells which are believed to have penetrated through the total thickness of the Upper Aquifer. In areas south of the NE Disposal Area, the first model layer thickness was set at 60 ft. The thickness was then gradually reduced toward the north where the Upper and Regional Aquifers merge. Reduced aquifer thickness resulted in reduced transmissivity of the Upper Aquifer, which, in turn, resulted in higher than observed hydraulic gradients near the TCE plume. A number of simulations were conducted to obtain a reasonable match. These calculations included several simulations of the aquifer test performed at the northeast portion of the base. Although direct comparison to observed drawdowns was difficult due to the relatively large size of the model grid (400 ft by 800 ft), the calibration efforts resulted in model transmissivities (1,450 ft²/day or 10,922 gpd/ft, near pumped well) that matched reasonably well to those calculated analytically from aquifer test data.

The adjusted transmissivities resulted in a reasonable match (+ 10 ft/mi) of the Upper Aquifer hydraulic gradients observed near the NE Disposal Area. However, simulated Upper Aquifer piezometric heads were 30 to 50 ft higher, and the head differences between the Upper and Regional Aquifers were 20 to 40 ft lower than those observed. To overcome simulated high water level conditions, inflow from the southern model boundary was reduced by lowering the prescribed head outside the model area. To overcome the low head differential between the Upper and Regional Aquifers, the vertical hydraulic conductivity of the silty clay layer underlying the Upper Aquifer was reduced until a reasonable match (± 20 ft) was obtained. The final calibrated verti-

cal hydraulic conductivity values for this aquitard ranged from a low to 1.5×10^{-9} cm/sec to a high of 6×10^{-7} cm/sec, with an average value of 2×10^{-8} cm/sec near the NE Disposal Area TCE plume. Such low vertical hydraulic conductivity values are verified in the field by presence of a thick (more than 100 ft) unsaturated zone separating the Upper and Regional Aquifers and by no TCE contamination in the Regional Aquifer measured from deep monitoring wells.

The model calibrated piezometric surface and water levels of the Upper Aquifer are shown in Figure 3. Comparison of model-predicted water levels to observed water levels suggest a very good match within the area of interest (i.e., the TCE plume). For example, the predicted and measured water levels in wells NZ28 and 43 are within less than 0.5 ft of each other. The piezometric water levels of the second and third model layers are shown in Figure 4. The Upper Aquifer water levels shown are assumed to represent the long-term average conditions in the vicinity of the NE Disposal Area and therefore are used as initial conditions for calibration simulations of the transient solute transport model.

SOLUTE TRANSPORT MODEL

The solute transport model of the NE Disposal Area and its surroundings was developed to simulate the rate and the extent of contaminant movement as well as to evaluate groundwater extraction and/or recharge scenarios. Although the flow model is developed as a three-dimensional model, only a two-dimensional solute

transport model is used to simulate the transport of TCE in groundwater. This change is primarily due to the results of the field investigations suggesting: (1) presence of TCE contamination only in the Upper Aquifer (where the two aquifers are separate units) and (2) shallow depth of TCE contamination in the Upper Aquifer (less than 60 ft). The observed shallow depth of the TCE contamination makes the two-dimensional approximation a valid one.

The two-dimensional solute transport and dispersion model code (known commonly as the MOC Model) developed and subsequently modified by the U.S. Geological Survey is used to simulated the transport of TCE and to evaluate the effectiveness of various groundwater extraction and/or recharge alternatives. The computer program solves two simultaneous partial differential equations; one equation describes the head distribution (the groundwater flow equation), and the second equation describes the concentrations of chemical species (the solute transport equation) in the aquifer. The solution to the groundwater flow equation is computed by an iterative alternative direction implicit (ADI) procedure, while the solution to the solute transport equation is computed by the method of characteristics (MOC, and

Model-Predicted Piezometric Groundwater Levels of Middle Aquifer

Model-Predicted Piezometric Groundwater Levels of Upper Aquifer

Model-Predicted Piezometric Surface of Upper Aquifer; All 30000
Node. Area View S3000 ft from North of Primary Instrument Runway
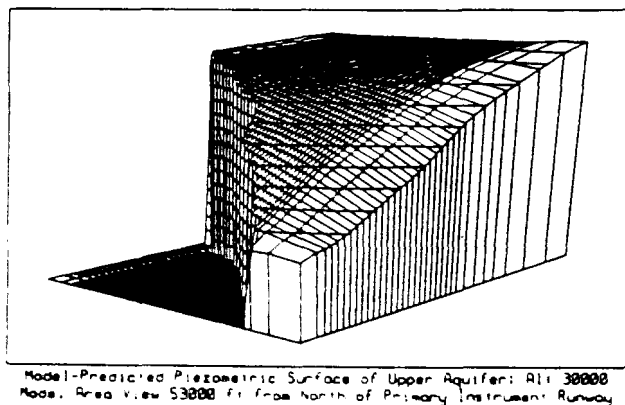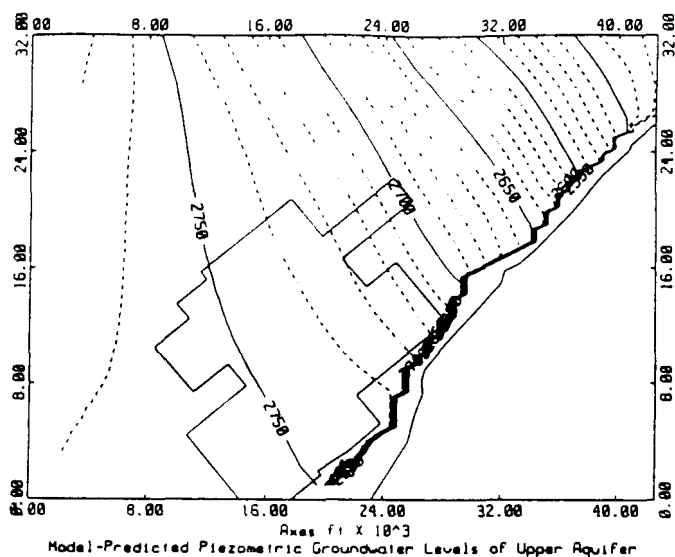
Figure 3
3-D Groundwater Model Steady-State Groundwater Levels in
Upper Aquifer

Model-Predicted Piezometric Groundwater Levels of Lower Aquifer
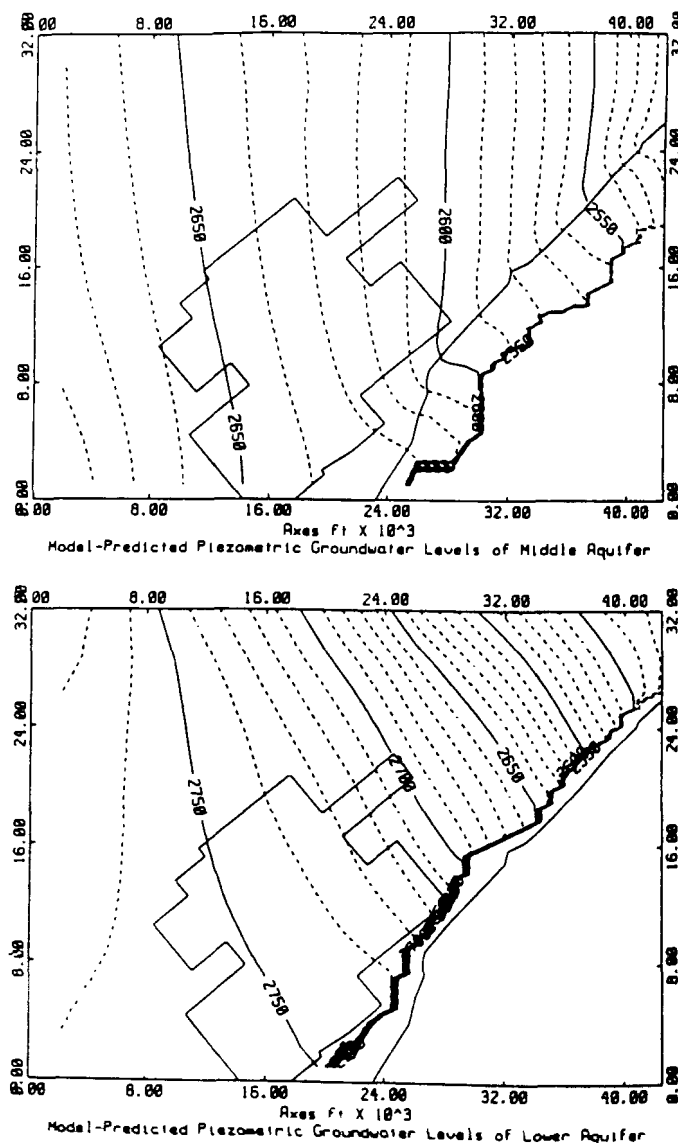
Figure 4
3-D Groundwater Model Steady-State Groundwater Levels in
Middle and Lower Aquifer

hence the nickname of the Code). The coupled flow and transport equations can simulate both the steady-state and transient flow problems.

The objective of the solute transport model is to compute the concentration of a dissolved species in an aquifer at any specified place and time. Changes in chemical concentration occur within a dynamic groundwater system primarily due to four distinct processes:

- Convective transport, in which the dissolved chemicals are moving with the flowing groundwater
- Hydrodynamic dispersion, in which molecular and ionic diffusion and small-scale variations in the velocity of flow through the porous media cause the paths of dissolved molecules and ions to diverge or spread from the average direction of groundwater flow
- Fluid sources, where water of one composition is introduced into water of a different composition
- Reactions, in which some amount of a particular dissolved chemical species may be added to or removed from the groundwater due to chemical and physical reactions in the water or between the water and the solid aquifer materials.

Model Setup

The solute transport model developed for the NE Disposal Area is an integral extension of the three-dimensional groundwater flow model. The two-dimensional solute transport model is arranged to function under the groundwater flow conditions prescribed by the first model layer of the three-dimensional model. This layer depicts the flow conditions in the Upper Aquifer only, where the Upper and Regional Aquifers are separated, and in the upper part of the Regional Aquifer (approximately 60 ft thick) where the two aquifers are merged. As shown in Figure 2, the solute transport model is set up within a subgrid area of the three-dimensional model. It consists of 48 model rows 400 ft wide and of 26 model columns 800 ft long. The model covers an area of approximately 14.3 mi^2 within and around the NE Disposal Area. The modeled area is surrounded by the constant head boundaries on all four sides.

The solute transport model first solves the flow equation to calculate groundwater velocities, which are then used in the solute transport equation. The boundary conditions to the flow equation are prescribed by the three-dimensional flow model. A postprocessor is developed for the three-dimensional model to calculate the appropriate flow boundary conditions to the two dimensional model. The simulation process for the models is as follows:

- The three-dimensional groundwater flow model is set up with appropriate boundary conditions and executed. Appropriate fluxes are included in those simulations involving extraction and/or recharge wells.
- The post-processor is executed which reads the output file from the three-dimensional model and creates an input file for the two-dimensional model. Calculated by the post-processor are the groundwater elevations, including those along constant head coundaries, and vertical leakage to the Regional Aquifer, as well as vertical groundwater discharge from the upper to lower part of the Regional Aquifer. These values are then input to the two-dimensional model as initial head and recharge (or discharge) to each model grid.
- The two-dimensional solute transport model is then executed, which calculates groundwater velocities and TCE concentrations throughout the aquifer.

The process of utilizing three-dimensional groundwater flow models to generate boundary conditions to the solute transport model has several advantages. First, the assumption of "no vertical flow component" associates with two-dimensional models is eliminated since vertical fluxes are calculated from the three-di-

mensional model. Second, the change in vertical and/or horizontal flux can always be accounted for by simulating the three-dimensional model each time the aquifer stresses are changed. Third, since the initial conditions are precalculated by the three-dimensional model, the flow part of the two-dimensional model is unconditionally stable and uses computing time at fractions of seconds to calculate velocities. Finally, for conditions which may be justified in the future by field monitoring of plume progress, three-dimensional solute transport conditions can be simulated at lower Regional Aquifer layers. This can be accomplished by simply creating a second post-processor which links the output files of the two models described above to generate an input file to a second two-dimensional solute transport model. This model would then simulate the solute transport in the second model layer of the three-dimensional model.

The disadvantage of the above-described approach to solute transport modeling is that for simulations involving transient conditions with small time steps (e.g., less than 6 mo), the process of calculating fluxes from a three- to two-dimensional model becomes time-consuming. However, for simulations involving large time steps, the solution to groundwater flow equation approaches steady-state, and hence, no recalculation of fluxes is required.

Model Calibration

The input conditions for the groundwater flow part of the two-dimensional solute transport model are calculated from the three-dimensional groundwater flow model. Hence, no calibration of flow conditions is required. Solute transport calibrations were accomplished by back-calculating from the location(s) of potential sources of assumed magnitude which would create the currently known extent and mass of the TCE plume.

A longitudinal dispersivity value of 90 ft was selected based on experience in modeling solute transport within similar aquifers in southern California. Although values ranging from 70 to 150 ft were tested during model calibration runs, 90 ft for longitudinal dispersivity appeared to result in the most reasonable predictions. This value is also within the range reported in the literature for similar geologic formations. The transverse dispersivity value of 72 ft (80% of the longitudinal dispersivity value) was used since the width of the currently known TCE plume appears to be approximately 80% of the length of the plume. Simulation with several ratios of transverse to longitudinal dispersivity suggested 80% to be the most appropriate value.

In contrast to the dispersivities, which increase the distance any dissolved compound would travel within a given time period, adsorption will slow the movement of a particular compound. This is accounted for by estimating retardation factors. The retardation factor depends on several parameters, including: chemical compound specific octonal/water partitioning coefficient (K_{ow}); and aquifer specific bulk density (K_d) and fraction of soil organic carbon (f_{oc}). The K_{ow} value of 195 for TCE is reported in the literature.[3] A soil density of 2.65 g/cm^3 for typical sand and silt material would result in a K_d value of 1.99 g/cm^3 at an assumed soil porosity of 25%. The f_{oc} values reported in the literature for similar geologic formations in southern California range from a low of 0.0001 (0.01%) to a high of 0.005 (0.5%). Several model calibration simulations suggest that a f_{oc} value of 0.001 is representative of conditions in the Upper Aquifer. Using the values given above, the retardation factor for the TCE is calculated to be 2.63 for these conditions. In simple terms, this means that TCE moves at an average velocity which is 2.63 times slower than average groundwater velocity.

To calibrate the solute transport model, each potential source was assumed as a source and a resultant TCE plume was simulated for the start of the operational period through 1988. Model simulations had suggested that none of the 12 potential source sites alone would result in forming the currently known TCE plume. Alternative simulations were performed whereby contri-

butions from one or more of the sources were considered. To formulate the potential source combination, the sites were separated into two groups; one that would form the western limits of the plume; and one to form the majority and the eastern portion of the plume. The final calibrated model simulation involved percolation of TCE into the groundwater from the arroyo during the period from 1945 through 1975 (when most of the operations believed to have contributed to contamination ceased) as the first potential source.

A secondary source of TCE to the groundwater, from Site S-5, was then added for the period from 1970 to 1985. The resultant TCE plume formation is shown in Figure 5. Source concentrations of 500 ug/L for the arroyo and 1700 ug/L for Site S-5 were back-calculated to form the 1.95×10^{11} ug (or 430 lb) of TCE mass currently believed to be present in the groundwater. The resultant plume at the end of 40 yr of simulation is assumed to represent the current conditions and, therefore, is used as initial concentration distributions to subsequent model runs.

SIMULATION OF GROUNDWATER REMEDIATION SCENARIOS

An evaluation of the rate and extent of TCE plume movement
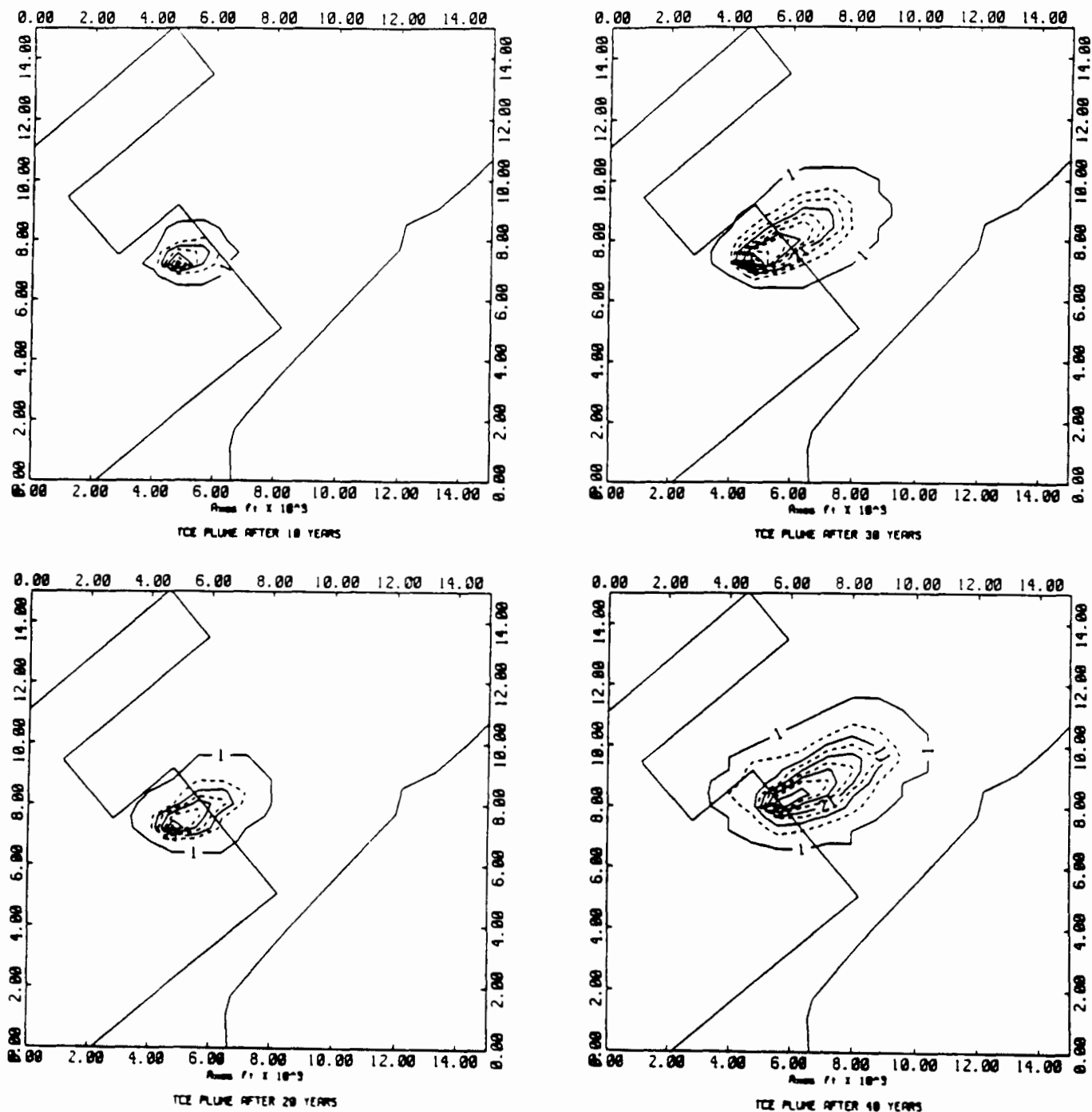
ALL CONCENTRATIONS IN ug/L

Figure 5
Transient Calibration 30-Year Injection at Old Fire Training Area and
10-Year Injection at New Fire Training Area

under the no-action alternative has been made by simulating conditions expected under a no-action alternative. Figure 6 shows the migration of the TCE plume during the next 30 yr at 5-yr intervals. As shown in Figure 6, the center of the TCE plume moves approximately 1 mi from the northern GAFB boundary in 30 yr. Model results suggest that the average peak effective transport velocity within the TCE plume over a 30-yr period would be approximately 236 ft/yr. This 236 ft/yr velocity would translate into a TCE displacement of approximately 90 ft/yr (plus some additional displacement due to dispersion) based on a retardation factor of 2.63. It should be noted that, for the purpose of the modeling discussion presented here, the "peak effective transport velocity" is defined as the highest velocity calculated by the model in any direction within the aquifer domain bounded by the TCE plume at any given time. TCE mass balance calculations done by the model suggest that, of the 430 lb total mass of TCE currently in the aquifer, 364 lb are associated with the soil matrix during the 30-yr period due to the soil adsorption process. The remaining 66 lb of TCE remain in solution. This portion would continue to adsorb to soil surfaces and move until all mass is discharged to the

ALL CONCENTRATIONS IN ug/L
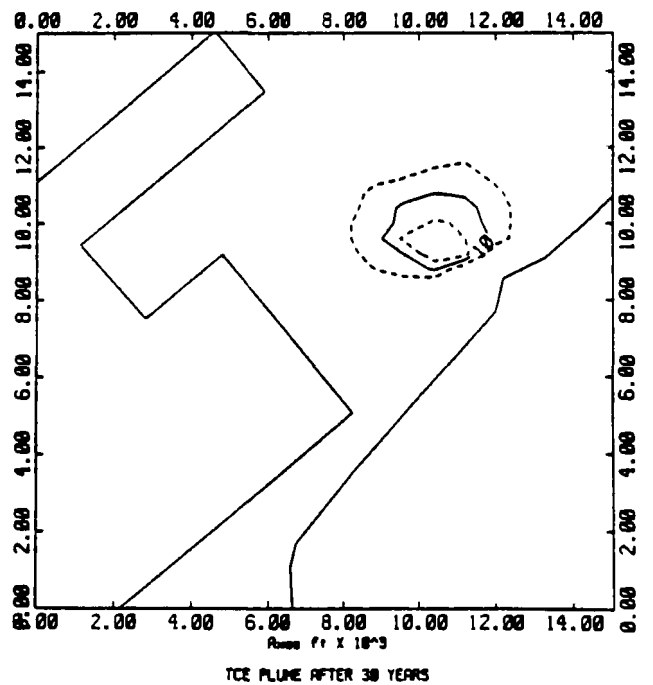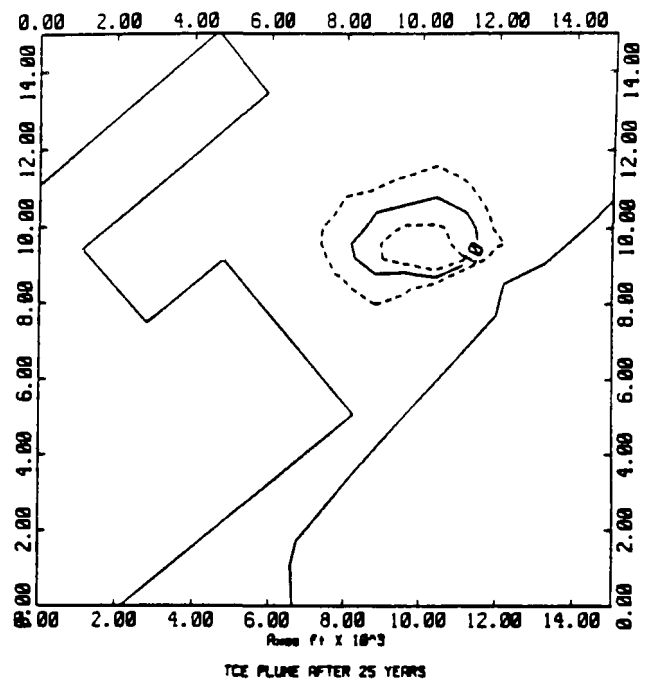
Figure 6
GAFB Plume Extraction Scenarios
No Active Alternative
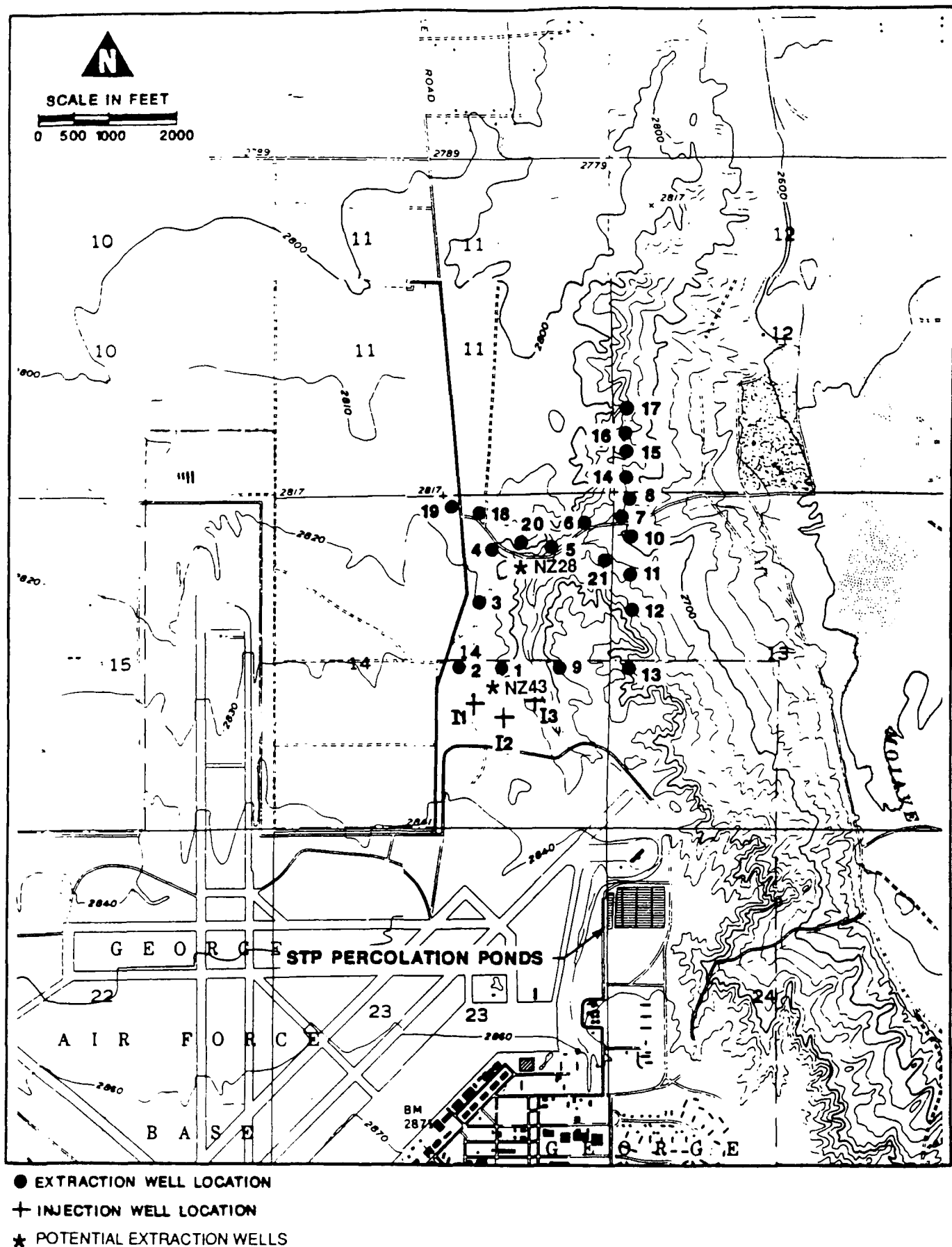
Figure 7
Locations of Simulated Potential Groundwater
Extraction and Disposal Wells

Table 2
Summary of Groundwater Extraction and Disposal Scenarios

Scenario	Description	Extraction Well Nos.	Rate gpm
1	9 wells extracting 360 gpm; reuse, surface discharge or groundwater injection to Regional Aquifer	1-9	40 each
2	19 wells extracting 500 gpm; reuse, surface discharge or groundwater injection to Regional Aquifer Option 1	1-9 10-19	40 each 14 each
3	19 wells extracting 500 gpm; reuse, surface discharge or groundwater injection to Regional Aquifer Option 2	1, 2, 9, 11 12, 14-18 3-8, 10, 13, 19	14 each 14 each 40 each 40 each
4	19 wells extracting 500 gpm; reuse, surface discharge or groundwater injection to Regional Aquifer Option 3	1, 2, 9, 11 12, 15, 17 18, 20, 21 3-8, 10, 13, 19	14 each 14 each 14 each 40 each 40 each
5	19 wells extracting 500 gpm; groundwater injection to Upper Aquifer	Same as Scenario 3	
6	19 wells extracting 500 gpm; groundwater recharge at STP Percolation Ponds	Same as Scenario 3	
7	19 wells extracting 500 gpm; 340 gpm groundwater recharge at STP Percolation Ponds; 160 gpm Reuse	Same as Scenario 3	

Table 3
Model Predicted Piezometric Head and Drawdown at TWP
Existing Monitoring Well Locations

Scenario	Monitoring Well NZ43		Monitoring Well NZ28	
	Head (ft)	Drawdown (ft)	Head (ft)	Drawdown (ft)
Measured Water Level (9/87)	2716.51	0	2710.96	
Steady State	2716.9	0	2710.5	0
1	2696.8	20.1	2687.5	23.0
2	2690.0	26.9	2679.6	30.9
3	2691.8	25.1	2679.8	30.7
4	2691.4	25.5	2679.3	31.2
5	2720.2	-3.3	2706.8	3.7
6	2710.8	6.1	2696.6	13.9
7	2704.7	12.2	2691.2	19.3

Table 4
Technical Performance Summary of Groundwater
Extraction and Disposal Scenarios

Scenario	Peak Effective Transport Velocity (ft/yr)	Simulation Duration (yr)	Maximum TCE Concentration Remaining (μg/l)	TCE Mass Remaining (lbs)	% Removal
1	216	30	10	24	94
2	238	30	5	9.6	98
3	243	30	7	7.2	98
4	253	30	<5	5.6	99
5	382	30	5	18	96
6	492	30	5	9.6	98
7	360	30	5	8.1	98

Mojave River.

To develop the groundwater extraction scenarios, some combinations of 21 potential extraction well locations have been selected based on: (1) minimum distance required between extraction wells to minimize drawdown effects on each other (estimated at 400 ft from the aquifer test conducted at well NZ43), (2) known or predicted available saturated thickness and (3) site access to avoid areas of steep slopes. Locations of these potential extraction wells are shown in Figure 7.

A number of groundwater extraction and disposal scenarios have been formulated. Of these, only seven scenarios have been modeled and evaluated in detail since they represent a unique combination of control measures. The description of each modeled scenario is tabulated in Table 2 together with the number (referenced in Fig. 7) and rate of the extraction wells.

Tables 3 and 4 are developed to aid in comparison of the technical performance of each scenario. Model predicted piezometric water levels and the drawdowns at two existing monitoring well locations are tabulated in Table 3. Also shown in this table are the model calibrated steady-state piezometric water levels and the actual water levels measured in the field during September 1987 from monitoring wells NZ43 and NX28. As shown in the table,

ALL CONCENTRATIONS IN ug/L

Figure 8
Upper Aquifer Groundwater Levels—Scenario 7
19 Wells Pumping 500 GPM Total and 340 Recharge at Percolation Ponds

Model-Predicted Piezometric Groundwater Levels of Upper Aquifer

Model-Predicted Piezometric Surface of Upper Aquifer; Alt 30000
Model Area View 53000 ft from North of Primary Instrument Runway

Figure 9
GAFB Plume Extraction Scenarios—Scenario 7
19 Wells Pumping 500 GPM Total and 340 Recharge at Percolation Ponds

the measured and model calibrated water levels are in agreement (less than 0.5 ft difference). The calculated drawdowns are relative to the model steady-state calibrated heads.

Table 4 shows the technical performance summary of the simulated groundwater extraction and disposal scenarios, reduced from the lengthy computer output from each model run. Shown

in the table are the peak effective transport velocities, as well as the TCE mass and concentration remaining in the groundwater after approximately 30 yr of simulation. The significance of peak effective transport velocities is that higher velocities result in faster contaminant removal, up to a certain limit. The extraction system needs to be able to extract the contaminant before the higher velocities transport it past the wells. This is clearly evident in comparing Scenario 5 with Scenarios 1 through 4, where higher velocities do not necessarily result in better contaminant removal. The percent removal values reported in the table are calculated as percent removal in comparison with the initial 430 lb of TCE in the aquifer.

DESCRIPTION OF THE PREFERRED ALTERNATIVE

Following detailed evaluation of groundwater extraction and/or recharge scenarios, Scenario 7 was selected as the preferred alternative for groundwater remediation at NE Disposal Area. This scenario involves extraction of 500 gpm groundwater from 19 wells located throughout the known extent of the plume. The existing unused STP Percolation Ponds would be utilized to percolate the extracted and treated groundwater. It is assumed that 160 gpm of the 500 gpm extracted groundwater would be utilized for irrigation (domestic and/or golf course) or would evaporate during the percolation process. The objective of Scenario 7 is to reduce the high effective transport velocity calculated for Scenario 6, while increasing TCE capture efficiency and providing a beneficial use of the extracted water.

The predicted piezometric groundwater levels and the surface of the Upper Aquifer for this groundwater extraction and percolation scenario are shown in Figure 8. The predicted TCE concentrations for the 20-yr period from the start of remediation are shown in Figure 9. The three-dimensional groundwater flow model results suggest that reducing the percolated amount by 160 gpm forms a smaller groundwater mound beneath the percolation ponds, with a resultant 132 ft/yr lower peak effective transport velocity. The solute transport model, on the other hand, suggests that the lower velocities would result in better TCE removal efficiency. In fact, the reduced velocities result in all of the plume remaining in the capture zone of the extraction system.

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Hydraulic Performance of Horizontal Wells

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INTRODUCTION

Environmental applications for horizontal wells, a technology developed for and routinely used in the petroleum recovery industry, are being recognized and explored with increasing frequency in other applications. For contaminated groundwater recovery operations, horizontal wells have clear technical advantages over vertical wells in situations involving fractured rock aquifers; dense nonaqueous phase liquid recovery; and recovery from below landfills, lagoons, buildings, wetlands, lakes or other surface obstructions.

Bedrock contamination is being encountered with increasing frequency at contaminated sites, and traditional vertical well recovery systems frequently do not provide effective recovery. As already demonstrated in the oil and gas industry, the ability to cross multiple bedrock fractures at a high angle will provide enhanced product or contaminant recovery where traditional vertical extraction methods have proven ineffective.

Horizontal wells are also ideally suited for recovering dense non-aqueous phase liquids (DNAPLs) in groundwater. DNAPLs, such as chlorinated solvents, tend to sink through porous media, regardless of water table gradients, until they encounter a low hydraulic conductivity layer. At this point, the DNAPLs spread out along the boundary, which in most cases will be horizontal to subhorizontal. Since the horizontal wells can be easily oriented parallel to horizontal bedding planes, the cleanup can be much more effectively accomplished than with vertical wells, which typically perform poorly in such situations.

Horizontal wells, unlike vertical wells, do not have to be drilled directly above a contaminant source to effectively remove contaminants. Rather, the bore hole can be advanced in the direction of contaminants for a distance of up to 500 feet. This advantage has obvious implications for remediating obstructed areas such as under buildings, lagoons, landfills and wetlands in terms of monitoring capability, cleanup rates and overall effectiveness. In addition, horizontal wells have hydraulic characteristics that may prove advantageous for groundwater recovery in numerous unobstructed situations.

Other environmental applications are related to activities such as vadose zone soil gas vacuum extraction, steam injection remediation, bioremediation and grouting. Remedial applications for unsaturated conditions, such as gas extraction or steam injection, may benefit from the enhanced exposure within the contaminant zone available through a continuous well screen of up to 500 feet in length. By combining an injection and recovery dual horizontal system, significant progress may be realized in cleanup effectiveness. Bioremediation applications may benefit from increased exposure to the contaminant for injection of both nutrients and nonindigenous organisms in either saturated or unsaturated conditions.

Horizontal wells may also be useful for grouting for remedial systems. Horizontal wells can provide direct grout access below, above and along

any side of an existing contaminant plume or a potential threat to ground-water quality. In this capacity, horizontal wells can function as a preventative or remedial measure to isolate contaminants.

Significant progress has already been made towards applying horizontal well extraction to remediation of contaminated soil at the Savannah River Laboratory located in Aiken, South Carolina. Two horizontal wells were installed by Eastman Christensen along a leaking sewer line to test a new method of in situ remediation. Additionally, during fiscal year 1990, the Department of Energy (DOE) plans to conduct further studies of horizontal well applications at the Savannah River Station. Current DOE plans for this program include: (1) in situ bioremediation of groundwater, (2) in situ characterization techniques, (3) remote monitoring techniques and (4) innovative technologies for soil cleanup. The DOE recognizes the limitations of vertical wells for stabilizing contaminants and the previous untapped capability of horizontal wells to succeed in stabilizing migrating contaminants.

Recent updates in the capability to sample through horizontal drilling will provide a means for effective lateral characterization of dispersed waste for both chemical sampling purposes and geologic logging. Horizontal wells will also offer the unique ability for remote characterization, sampling and extraction in areas characterized by either high toxicity or radioactivity. This capability is not only technically attractive, but also will likely produce overall cost savings due to decreased levels of safety requirements for drilling and sampling crews.

In summary, horizontal wells show potential for providing both significantly better performance and lower total remediation costs than systems relying on only vertical wells for a large number of situations. These situations include not only areas where surface obstructions interfere with vertical access, but also areas where hydrogeologic or contaminant distribution conditions render vertical wells ineffective; situations where continuous horizontal exposure to the subsurface materials is advantageous; and areas where human health and safety concerns are of unusual severity.

The purpose of this study is to compare, through the use of computer modeling, the technical performance of horizontal and vertical well contaminant removal systems and, subsequently, to evaluate cost-effectiveness of those systems when combined with typical groundwater treatment systems. The scope of work includes; (1) developing of a hypothetical model to evaluate horizontal and vertical well contaminant recovery performance under a variety of conditions, (2) performing a numerical model evaluation based on real site hydrogeology in order to compare horizontal and vertical well performance under specific real world conditions and (3) evaluating the relative cost-effectiveness of horizontal and vertical well contaminant recovery systems when coupled with typical groundwater treatment systems.

The hypothetical modeling study of horizontal wells and vertical wells

was designed to evaluate contaminant removal effectiveness under a variety of controlled conditions. We used numerical models of groundwater flow and contaminant transport to evaluate the performance of several different well arrays for a variety of contaminant plumes and hydrogeologic parameters. We presented the results principally in terms of contaminant recovery rates and total contaminant recovery, but we also developed a variety of other information such as streamlines and flow velocities to help develop a more thorough understanding of horizontal well hydraulics. The results from this hypothetical phase of the study were used to design the horizontal well system used for the real site modeling effort.

The case study modeling was based on hydrogeology at a contaminated site. We developed a numerical model of groundwater flow and contaminant transport for this site and selected vertical and horizontal well systems. The vertical well system design was taken from a previous proposal by others for remediating the site. The strategy for maximizing effectiveness of the horizontal well system was based on principles developed during the hypothetical modeling study. The two systems are roughly equivalent in pumping rate and well location, using eight vertical wells and four horizontal wells. The two systems were compared on the basis of total contaminant recovery rates.

Subsequent to the contaminant recovery modeling we estimated groundwater treatment costs for three commonly used groundwater treatment systems; air stripping, air stripping with vapor phase carbon adsorption and air stripping with liquid phase carbon adsorption. We then combined the treatment costs and groundwater recovery costs and performed a comparative economic analysis, accounting for the faster contaminant recovery achieved by the horizontal well system.

HYPOTHETICAL MODELING STUDY

Background

Horizontal wells work on the same theoretical principles as vertical wells. Both are governed by Darcy's Law for groundwater flow. Direct analytical solutions numerical approximations for the hydraulic performance of vertical wells are widely known and used. Bear[2] provides a good discussion of many of these solutions and a list of references where further information can be found. In addition, the scientific/technical community that works with the hydrogeology of contaminated sites is generally very familiar with the theory of vertical well hydraulics and actual vertical well performance data.

Horizontal well hydraulics, however, while theoretically similar to vertical well hydraulics, are not as well known. Hantush[3] and Hantush and Papadopulos[4] present solutions for flow to horizontal wells, but these solutions are not widely known or used in the environmental restoration business. Further, since horizontal wells are not widely used for environmental restoration, there are minimal field data documenting their performance for this purpose. The extensive horizontal well performance data developed by the petroleum industry are not widely known in the environmental field. Also, much of the information developed in the petroleum industry, while useful for developing a general understanding of horizontal well performance, is not directly relevant to the problems faced during groundwater contamination recovery.

In theory, horizontal well performance can be approximated by a series of closely spaced vertical wells with short screens, and vertical well performance can be approximated by a series of closely spaced (vertically) horizontal wells with short screens. Both practical and cost considerations, however, frequently dictate against either of these options.

This hypothetical modeling study is a first step towards developing a base of knowledge about horizontal well performance for the environmental restoration business.

Approach

Our approach to this hypothetical modeling uses numerical models of groundwater flow and contaminant transport to simulate the performance of horizontal and vertical wells. For the numerical model development, we used the MODFLOW[5] code to simulate the groundwater hydraulics and the MODPATH[6] code to simulate contaminant transport. MODFLOW is a finite difference solution for fluid flow in porous media. MODPATH is a particle tracking model designed as a companion to MODFLOW.

The general scope of this hypothetical modeling effort includes the following elements:

- Selection of representative contaminant scenarios
- Development of three-dimensional groundwater flow and contaminant transport numerical models for hypothetical scenarios
- Selection and optimization of representative horizontal and vertical recovery well arrays
- Assessment of relative contaminant capture effectiveness for the various well arrays and contamination scenarios
- Assessment of the effects of hydrogeologic and contaminant plume variations on contaminant capture effectiveness of vertical and horizontal wells

We selected three contaminant scenarios for evaluation in this work. Two of the scenarios represented hypothetical existing contaminant plumes, and the third scenario represented active leachate from a landfill or lagoon. The two existing plume scenarios had the same lateral dimension, but different thicknesses. This selection allowed us to evaluate the relative performance of horizontal and vertical wells with respect to plume geometry. The thick plume also allowed us to more easily evaluate the horizontal well hydraulic performance at larger vertical distances from the well and for multiple wells separated vertically. The active leachate plume was selected to allow us to evaluate the performance of horizontal wells placed directly under leachate sources and compare that to vertical wells surrounding the sources.

In selecting and optimizing representative horizontal and vertical extraction well arrays, we first developed a wide variety of well configurations and then selected a group from among these for further evaluation. As part of this process, we optimized the well placement within each configuration. For example, for the single horizontal well perpendicular to the groundwater flow direction, we optimized the location of that well prior to developing the results shown here.

We assessed the relative contaminant capture effectiveness principally by evaluating the contaminant mass captured as a function of time. In addition, for selected scenarios we also developed graphic displays of contaminant streamlines, time of travel contours, contaminants not captured and contaminant particle velocities. ADL[1] presents a more complete set of results than we present here.

After evaluating all the selected scenarios for a base set of model parameters, we investigated the impact of variations in hydrogeologic parameters such as hydraulic conductivity and gradient.

Model Development

Model development for the hypothetical model consists of selecting a numerical grid and then assigning parameter values and, where appropriate, boundary conditions to the grid cells.

We selected a three-dimensional grid which was 25 meters on each side, in which each cell measured 1 x 1 x 1 meter. Figure 1 illustrates the grid.

Table 1 summarizes the selected hydrogeologic parameter values. The key hydrogeologic parameter values assigned to the model are horizontal and vertical hydraulic conductivities. We used a base horizontal and vertical hydraulic conductivity value of 8.64 meters per day (m/day) (which corresponds to 0.01 centimeters per second). For the sensitivity analysis, we lowered the horizontal conductivity to 0.864 m/day, lowered the vertical conductivity to 0.864 m/day, and both raised and lowered the transverse horizontal conductivity to 86.4 m/day and 0.864 m/day.

We used fixed head boundary conditions at two ends of the modeled grid, no flow boundary conditions at the sides and bottom and a free surface boundary condition at the top. The fixed head boundary conditions were set to produce a gradient of 0.05 for the base parameter set and varied to produce a gradient of 0.005 during the sensitivity analysis. The thick and thin plume geometries had length times width times height dimensions of 9 x 9 x 9 and 9 x 9 x 1 meters. The leachate source had lateral dimensions of 9 x 9 meters and was applied at the groundwater surface. This combination of grid dimensions and plume
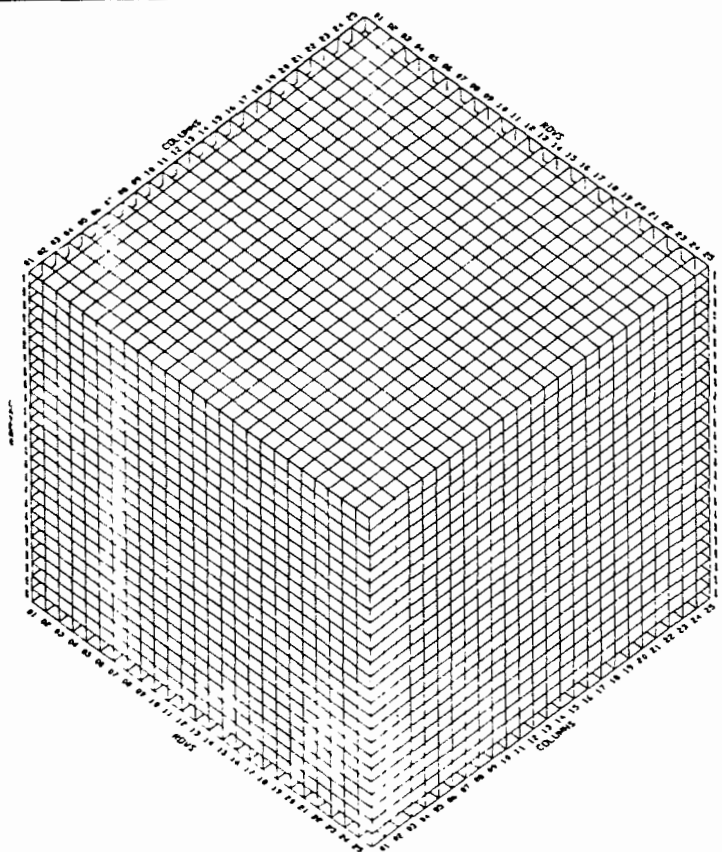
Figure 1
Model Grid 25 x 25 x 25

size provided a high degree of resolution, allowing clear distinctions between horizontal and vertical well performance and minimization of edge effects from boundary conditions. The absolute size of these plumes is smaller than the typical sizes of real plumes which require remediation. The objective in modeling plumes of these dimensions, however, was not to mimic the size of a typical plume, but rather to maximize the detailed resolution of groundwater extraction by both vertical and horizontal well orientations. The modeled plume size is largely irrelevant since the purpose here is to compare the effectiveness of various withdrawal schemes per unit volume of contaminant plume. The principles for extraction effectiveness and sensitivity to parameter changes demonstrated here apply also to larger plumes.

These two ambient plumes were represented in MODPATH by assigning particles to each block for the plume at time zero. The particles were then transported with the water and either captured by the extraction wells or carried past the wells by the ambient flow. For the active landfill or lagoon simulation scenario, we prescribed an initial loading of particles in each cell. We then applied water recharge to the landfill cells, which carried the particles down into the rest of the aquifer.

Another key parameter is the pumping rate from the wells. We recognize that horizontal well production rates are typically higher than for vertical wells. This phenomenon is due in part to the greater screen length typical of horizontal wells. In order to provide a reasonable basis of comparability, we used a pumping rate of one cubic meter per day (m³/day) per meter of screen length for all of the wells. Each well simulated in this study, unless otherwise noted, had nine meters of screen and was, therefore, pumped at 9 m³/day. Therefore, scenarios with two wells had total pumping rates of 18 m³/day and scenarios with three wells had total rates of 27 m³/day.

Pumping Well Orientation

In real remediation problems, well orientations are decided on a case-by-case basis. The exact locations are based on site access, contaminant distribution and geologic and hydrogeologic conditions. Previous studies of well removal effectiveness as a function of orientation have compared well placements at the center of the plume, downgradient of the plume and along the flanks of the plume.[7] The number of vertical wells modeled in these previous studies ranged from 1 to 4 and are generally oriented symmetrically about the plume. Our modeling of well orientations followed a similar approach and we used many of the same vertical well orientations.

Figure 2 shows the set of vertical and horizontal well arrays we selected for this study. Within each array, we refined the well locations to optimize a combination of the contaminant capture rate (mass per time) and total mass of contaminants captured. For example, the best location for the single horizontal and vertical wells was somewhat downgradient of the centroid of plume mass. In the absence of an ambient gradient, the best location would be at the plume centroid. The steeper the gradient, the further downgradient the wells should be located. Locating the wells closer to the downgradient edge of the plume enables the wells to achieve a higher total capture rate in many instance, but at the cost of reducing the rate of capture. The tradeoff between capture rates and total capture of contaminants is a consideration that is most often resolved by regulatory constraints or cleanup goals.

Contaminant Capture Performance

Figure 3, 4 and 5 illustrate contaminant capture effectiveness for a variety of pumping well orientations (Figure 2) under the base parameter set (Table 1). These results show the following:

- For the thick plume, several horizontal and vertical orientations can produce generally comparable performance orientations, though the fastest capture rate is produced by horizontal well orientation G.
- For the thin plume, horizontal well orientations G and B provided the best performance.

Table 1
Model Parameter Sets Used for the Hypothetical Model

Parameter Set	Delta X Spacing (meters)	Delta Y Spacing (meters)	Delta Z Spacing (meters)	Boundary Conditions	Simulation Type	Layer Type	Hydraulic Conductivity (meters/day)	Transverse Hydraulic Conductivity (meters/day)	Vertical Hydraulic Conductivity (meters/day)	Gradient	Total Recharge (M³/day)	Pumping Rate per Cell (M³/day)	Modification of Parameter Set 1
1	1	1	1	Constant head along rows 1 and 25; all other cells active	Steady state	Layer 1 unconfined; layers 2 through 25 fully convertible between confined and unconfined	8.64	8.64	8.64	0.005	9	1	None
2	"	"	"	"	"	"	"	"	"	"	18	1	Well location shifted slightly, two well scenario only
3	"	"	"	"	"	"	"	"	"	"	"	Well #1 at 0.9 Well #2 at 1.1	Wells pumping at different rates, two well scenario only
4	"	"	"	"	"	"	0.864	"	"	"	9	1	Change in hydraulic conductivity values
5	"	"	"	"	"	"	8.64	"	"	0.05	"	"	Change in gradient values
6	"	"	"	"	"	"	"	"	0.864	0.005	"	"	Change in conductance values
7	"	"	"	"	"	"	"	0.864	8.64	"	"	"	Reduction in transverse hydraulic conductivity anisotropy value
8	"	"	"	"	"	"	"	86.4	"	None	"	"	Increase in transverse hydraulic conductivity anisotropy value
9	"	"	"	"	"	"	"	8.64	"	"	"	"	Radial flow source inserted at grid center and recharge from wells eliminated

Horizontal Well Scenarios (Plan View)

Vertical Well Scenarios (Plan View)

Legend: Contaminant Plume / Recharge Zone / Horizontal Well / Underlying Horizontal Well / ● Vertical Well / A Scenario Designation
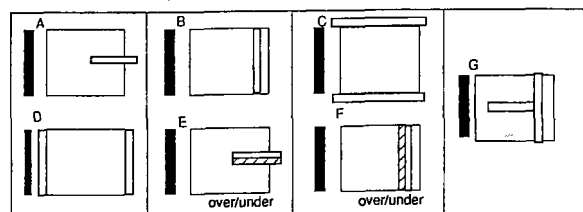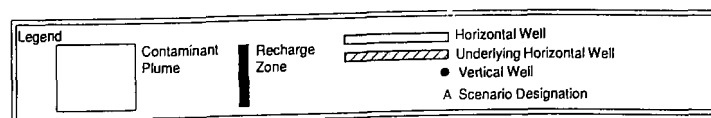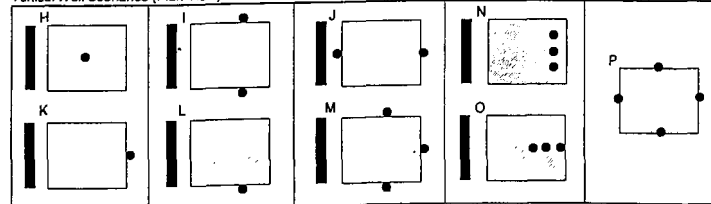
Figure 2
Horizontal Well Scenarios (Plan View)
Vertical Well Scenarios (Plan View)
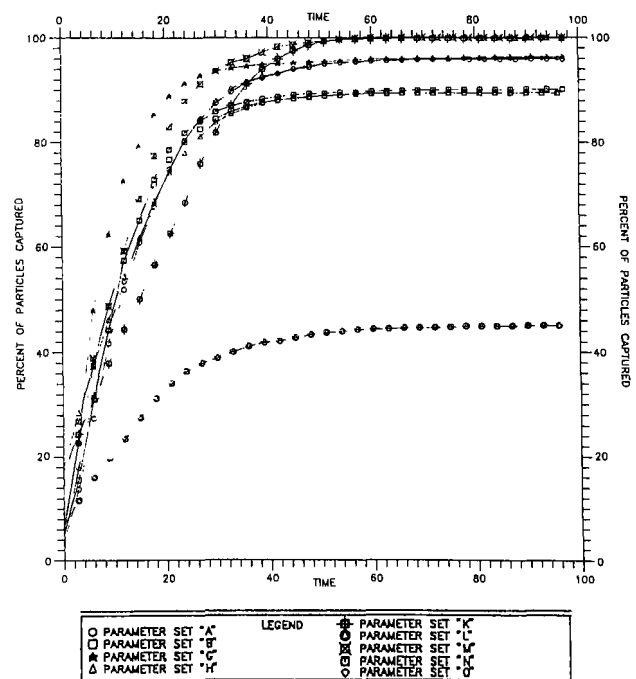
Figure 3
Contaminant Plume Ratio 9L:9W:9T
Percentage of Contaminants Captured vs. Time
Various Well Orientations;
Parameter Set 1

- For the radial recharge situation with obstructed access, horizontal well orientations A and B provided significantly better performance than vertical well orientations.

Several variations of aquifer characteristics were evaluated, including
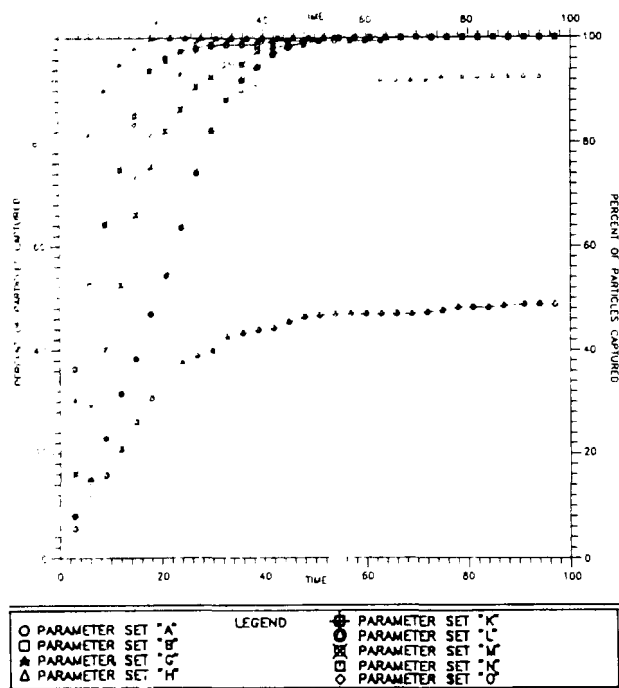
Figure 4
Contaminant Plume Ratio 9L:9W:1T
Percentage of Contaminants Captured vs. Time
Various Well Orientations;
Parameter Set 1
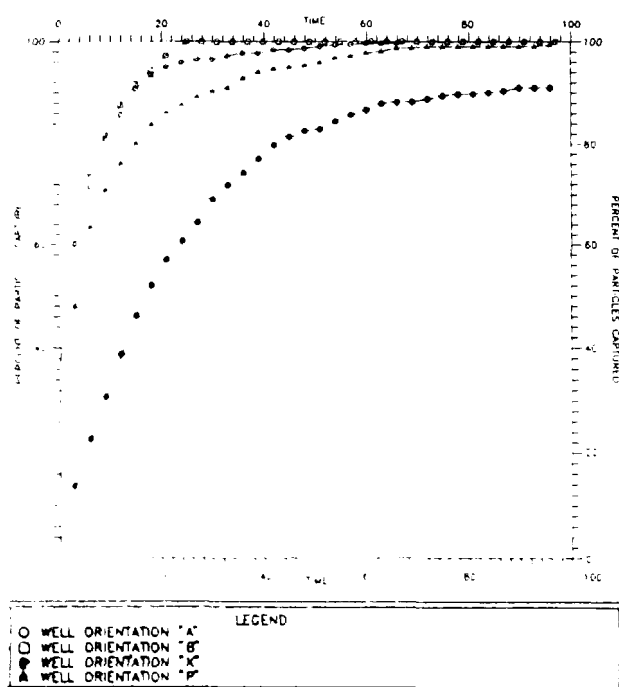
Figure 5
Plume 3
Percentage of Contaminants Captured vs. Time
with a Radial Recharge and Contaminant Source
Various Well Orientations;
Parameter Set 9

horizontal, vertical, and transverse hydraulic conductivity and groundwater gradient. Table 2 summarizes these results. ADL[1] provides more details and illustrations of these results.

CASE STUDY EXAMPLE

This portion of the study focused on numerical modeling incorporating real site hydrogeology and an approximation of real site contaminant history. The site used in this study was selected solely for the purpose of demonstrating horizontal well performance; we are not proposing an alternative remedial strategy or cleanup criteria for this site. For purposes of this study, volatile organic contaminants are assumed to be present in the groundwater.

The site is underlain by glacially derived, unconsolidated overburden of variable thickness, which rests unconformably on crystalline basement rock. These unconsolidated sediments range in thickness from approximately 30 feet in the northern part of the site to more than 100 feet thick in the central part of the site.

Glacial sediments consist of stratified sands and gravels in the upper portion, which overlie a dense glacial till at the bedrock interface. Thin, discontinuous clay rich layers are interstratified throughout the upper sand and gravel material. The basal till, consisting of clays and silt, is not continuous, and at some locations the sand and gravels and the underlying bedrock are in direct contact. Where the till is present (in thicknesses of up to 30 feet), it is characterized as a clay and pebble-rich, densely packed material of high compressive strength. Crystalline bedrock underlying the till consists of gneisses and schists. The upper 5 to 10 feet of bedrock are characterized by a high degree of fracturing and chemical weathering. The bedrock surface was sculpted by glacial activity resulting in a trough which slopes to the southwest at the northern end of the site and to the south at the southern end of the site.

The site hydrogeology is characterized by an upper stratified sand and gravel unconfined aquifer, ranging in thickness from 30 feet to more than 100 feet, a basal aquiclude consisting of densely packed till and a thin lower confined aquifer in the upper weathered bedrock surface. A groundwater divide is present on-site, crossing from east to west. Rainfall recharge entering the site either flows south toward a small river or north toward a small brook. Lateral groundwater flow across the site, toward the north and south, is interrupted by a number of surface geologic features, including glacial ponds and surface seepage areas. The depth to groundwater varies from a maximum of 40 feet to essentially 0 feet at surface seeps and ponds. Horizontal hydraulic conductivities vary across the site from a minimum of 0.02 meters per day (m/day) in dense till material to a maximum of approximately 40 m/day in highly transmissive sands and gravels. Vertical hydraulic conductivities vary from a 0.0003 m/day minimum to a maximum of approximately 1.8 m/day. Recharge flux to groundwater across the site ranges from a minimum of 0 to a maximum of 0.74 m/year. Specific yield is generally in the range of 0.2 to 0.3.

Groundwater flow within the highly weathered upper bedrock aquifer is significant under the entire site due to its fractured nature. The low permeability till and silt aquitard overlying the fractured bedrock insulates the hydraulic characteristics of the upper bedrock aquifer from the overlying aquifer within the unconsolidated glacial sediments and moderates the movement of contaminants downward.

Groundwater Flow and Contaminant Transport Modeling

The MODFLOW and MODPATH groundwater flow and contaminant transport codes used for the hypothetical modeling study also were used for modeling this site. ADL[1] provides a complete description of the model development. A few issues are summarized below.

We discretized the site into five layers, three upper layers of predominantly sand and gravel, a fourth layer of predominantly glacial till and a bottom layer of fractured weathered bedrock. The average thicknesses of these layers are approximately 15 feet each for the upper three layers, 10 feet for the till, and 6 feet for the bedrock. Horizontally, we established a 97 x 97 grid which extended to the streams on the north and south, to the drainage basin divide on the west and far enough east to minimize the influence of that boundary on the results. We used a uniform horizontal cell size of 25 meters (82 feet) in each

Table 2
Performance of Horizontal and Vertical Well Orientations as Measured by Rate Of and Total Particle Capture

	Base Case Parameter Set		Reduction in Horizontal Hydraulic Conductivity		Increase in Groundwater Gradient		Reduction in Vertical Hydraulic Conductivity		Reduction in Transverse Hydraulic Conductivity		Increase in Transverse Hydraulic Conductivity	
Rate/Total Capture Matrix	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume
Horizontal Well Orientation	FR/TC	FR	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC		FR/TC	FR/TC	FR/TC	T
Vertical Well Orientation		TC						FR/TC				T

	With Vertical Recharge		With a Horizontal Recharge Doublet		With a Vertical Recharge Doublet		With No Recharge		With Radial Recharge and Contaminant Source
Rate/Total Capture Matrix	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Thin Plume	Thick Plume	Radial Plume
Horizontal Well Orientation	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC	FR/TC
Vertical Well Orientation									

FR = Well orientation that had the fastest rate of contaminant capture.
TC = Well orientation that achieved the highest total particle capture in the shortest amount of time.
T = Tie

dimension. This relatively fine mesh was selected to assure that the hydraulics of horizontal wells could be adequately characterized at any location on-site.

Parameter values such as hydraulic conductivities and recharge values were based on the site data and the experience gained from previous modeling work reported by others. The model was calibrated against measured groundwater head values in a network of wells on-site. We achieved adequate calibration with relatively few changes to the initial parameter set.

The contamination was simulated in two steps. First we developed base line conditions by modeling each contaminant source as a constant strength source during its period of operation until it closed. In order to accomplish this task, three steady-state groundwater flow fields were developed to allow for the changing contaminant source and hydrogeologic conditions. This base line condition was used as the initial condition for containment removal operations.

Well Field Design

We evaluated two arrays of wells for this simulation. One evaluation was conducted on a set of eight vertical wells that had been previously proposed for use at the site. The other was a set of four horizontal wells we selected. The proposed design total pumping rate for the vertical wells was 709 gallons per minute (gpm), based on maximum acceptable drawdowns in each well of approximately 10 feet. Vertically, these wells were placed in the most highly contaminated layer, the glacial till. We established the pumping rates by specifying a maximum acceptable drawdown of approximately 10 feet. Using this drawdown produced a total pumping rate of 662 gpm, approximately 6% less than the vertical wells.

Well Field Performance

Figure 6 summarizes the vertical and horizontal well field performance in terms of containment removal versus time. Tables 3 and 4 list contaminated aquifer volumes, contaminant mass balances and concentration data for distinct time periods. The well field performance
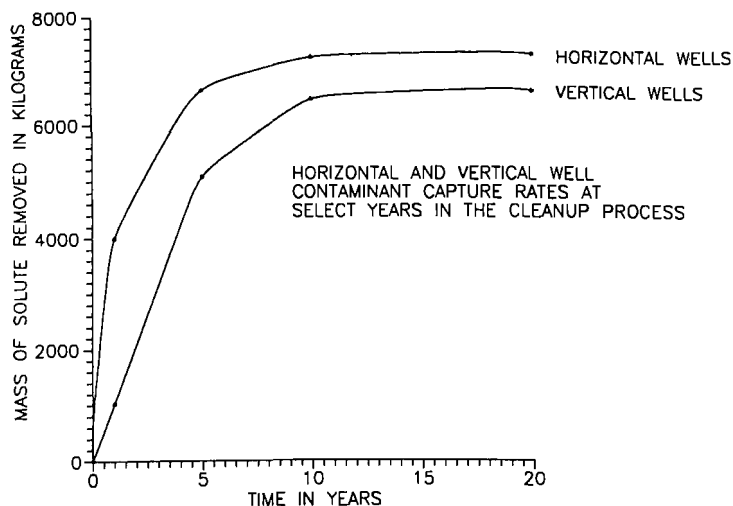
Figure 6
Horizontal and Vertical Well Contaminant Capture Rates
at Select Years in the Cleanup Process

Table 3
Contaminant Cleanup over Time

Measure of Performance	After 5 Years of Pumping Wells Horizontal Vertical		After 10 Years of Pumping Wells Horizontal Vertical		After 20 Years of Pumping Wells Horizontal Vertical	
• Total Volume of contaminated water in the aquifer (M³)	354,000	492,000	210,000	260,000	102,000	101,000
• Average concentration of the contaminated grid cells (ppb)	3,628	6,380	1,901	2,229	1,509	1,421
• Percentage of contamination removed by wells	77	59	84	75	85	76
• Percentage of contamination that traveled offsite (e.g., rivers, model boundaries, etc.)	12	16	12	20	13.4	22.3
• Percentage of contamination remaining in the aquifer on-site	11	25	4	5	1.6	1.7

Table 4
Maximum Contaminant Concentration in Model Layers at Select Years

After 5 Years	Vertical Extraction Array	Horizontal Extraction Array
Layer 1 (ppb)	3320	1971
2	6499	4930
3	10775	9966
4	135121	40943
5	628213	283286
After 10 Years		
Layer 1 (ppb)	934	0
2	3586	3586
3	6612	6954
4	17516	13742
5	57706	22296
After 20 Years		
Layer 1 (ppb)	0	0
2	2465	1793
3	2108	2046
4	9058	10159
5	2914	3935

after 5, 10 and 20 years of operation is discussed below.

After 5 years of pumping, the horizontal wells removed approximately 77% of the contaminants that were on-site in 1984. Also, the average concentration of contaminated cells was reduced by approximately 56% from base line conditions. The contaminants not captured by the wells are either still on-site or have migrated off-site into one of the rivers. By comparison, over the same 5-year time period, the vertical well array removed only 59% of the contaminants on-site in the base line condition, 18% less than removed by the horizontal well array. Additionally, the average concentration of contaminated cells was lowered only 22% from 1984, compared to the 56% reduction achieved by the horizontal wells.

After 10 years of pumping, the horizontal wells removed approximately 84% of the contaminants, decreased the average concentration of contaminated cells by 77% and essentially eliminated the two lagoon plumes. Conversely, the vertical wells over this time period removed 75% of the contamination, 9% less than the horizontal wells after 10 years, and not yet up to the 5-year horizontal well performance. Also, under vertical well pumping, the average concentrations of con-

taminated cells are approximately 4% higher than for the horizontal wells, and none of the plumes have been eliminated. The trends observed between 5 and 10 years suggest that with time the total cleanup differences between vertical and horizontal wells decrease at this site. Most of the contaminants that eventually will be captured by the wells already have been captured after 10 years and continuing to operate either pump-and-treat system becomes less and less efficient on a contaminant extraction per gallon of groundwater removal basis. This phenomenon is due to a combination of the relatively high ambient flow rates at this site, the proximity of the landfill to the river, the well field design and the reduction in contamination available to be pumped.

At 20 years of pumping, 85% of the contaminants have been removed by the horizontal wells, only 1% more than at 10 years, and the average concentration of contaminated cells has leveled off at about the 10-year level. By comparison, the vertical wells have achieved a total capture that is still approximately 9% less than the horizontal wells, and they have also removed only about one additional percent of contaminants over the 10- to 20-year time period. Also, the average concentration of contaminated cells is approximately 6% less than the horizontal wells. The last result regarding average cell concentrations is a reversal in trends from previous years. It does not, however, represent improved extraction efficiency by vertical wells, but rather subtle variations in the flow field generated by the two well arrays. The horizontal wells tend to keep contaminants on-site longer than vertical wells, rather than allowing flow to surface water discharge points. The overall results for this time period confirm that the contaminant removal effectiveness decreases with time at this site. Additionally, most of the contaminants that will be captured at this site have been captured after 10 years. Therefore, it is likely that the vertical well system will never be able to capture as much total contamination as the horizontal wells. Most of the contaminants on-site after 20 years that have not been captured by wells are located in the southern portion of the site in a plume area that is not directly addressed by either well system.

ECONOMIC EVALUATION

Approach

In some situations, the appropriateness of horizontal wells may be determined on a purely technical basis; in others, there may be economic advantages available from using horizontal wells. As part of the site modeling study, we conducted an economic analysis of groundwater extraction and treatment alternatives. We selected three treatment

technologies, air stripper, air stripper with emission controls, and carbon adsorption, for cost comparisons. These technologies are commonly used for groundwater remediation.

We developed cost estimates, including capital and O&M (operations and maintenance) costs, for the groundwater extraction and treatment options using a U.S. Environmental Protection Agency computer program entitled CORA (Cost of Remedial Action) for all cost elements except the horizontal wells. The horizontal well cost estimates were based on information supplied by the Eastman Christensen company. CORA is a model which consists of an expert system and a cost system designed to estimate site-specific remedial action costs for Superfund sites. We prepared cash flow projections under three assumptions, including no inflation, 5% annual inflation and 10% annual inflation. These cash flow estimates were then used to develop net present value estimates at three hurdle rates (10, 12 and 15%) and cumulative cash flow estimates.

Groundwater Recovery and Recharge System Costs

As described earlier, the vertical well groundwater recovery system consists of eight extraction wells pumping at a total rate of approximately 710 gallons per minute (gpm), and the horizontal well groundwater recovery system consists of four extraction wells pumping at a total rate of approximately 660 gpm. Using vertical well diameters of 6 inches and an average depth of 70 feet, we estimated installation costs to be approximately $85,000 for the eight vertical wells, or slightly more than $10,000 per well. Using horizontal well diameters of 6 inches, average vertical depths of approximately 60 feet, and horizontal lengths of 500 feet per well, we estimated installation costs to be approximately $300,000 for four horizontal wells, or $75,000 per well.

Operations and maintenance of the groundwater recovery system includes regular inspection, monitoring and sampling. The differences in O&M cost between vertical and horizontal extraction systems are negligible, and were not, therefore, considered further in this comparative economic evaluation.

Recharge or groundwater disposal facilities also need to be constructed. Since we anticipate that the same system would be used for either vertical or horizontal wells, recharge system costs were not considered in this comparative economic evaluation.

We assumed that personal safety protection levels D or C would be used for either vertical or horizontal well installations. It should be noted that in some situations, use of horizontal drilling would allow work at lower levels of protection, thereby achieving a relative cost savings.

Treatment System Costs

Data requirements for estimating costs associated with treatment system construction and operation include flow rate, contaminant concentration, nature of contaminants, length of transfer piping and required effluent concentration. Extraction rate of contaminated groundwater determines the required capacity of the treatment system. In general, higher flow rates through a treatment system result in higher capital and O&M costs to construct and maintain the operation. We used a 700 gpm flowrate to estimate both capital and O&M costs. We performed sensitivity analyses with respect to flowrate and found that the cost differences between flowrates of 660 gpm (horizontal well flow rate) and 710 gpm (vertical well flowrate) are negligible.

Influent contaminant concentration influences O&M costs of carbon adsorption systems to a greater degree than air stripper systems. Carbon loading rate is increased as contaminant concentration increases, resulting in more frequent regeneration of carbon. We used an influent concentration of 1000 μg/L for VOCs and 2000 μg/L of total organic carbon in our cost estimates. While measured VOC concentrations at the site reach 10,000 μg/L, the average concentrations from pumping wells are much lower. For example, after five years, vertical wells have removed 7.04 x 10^9 liters of water and 6.5 x 10^{12} μg of contaminant, producing an average contaminant concentration of 923 μg/L. Similarly, horizontal wells remove 6.58 x 19^9 L of water and 7.79 x 10^{12} μg of contaminant over 5 years for an average contaminant concentration of 1184 μg/L. The cost implications of the concentration difference (923 μg/L versus 1184 μg/L) is negligible for comparative cost purposes. We

therefore used an average VOC concentration of 1000 μg/L consistently for treatment cost estimations. Influent VOC concentrations are likely to decline over time for both horizontal and vertical well extraction systems. We neglected the influence of this decline in our cost estimates.

Natural groundwater contains variable quantities of TOCs, generally in the form of fulmic or acetic acid. TOC content may have a significant effect on treatment costs for carbon adsorption systems because it is adsorbed on the carbon and, therefore, reduces the useful life of the carbon. We chose a value of 2000 μg/L TOC for inclusion in treatment cost estimates.

Connecting eight vertical wells to a treatment system will require more piping than connecting four horizontal wells to a treatment system. We used 5000 feet of transfer piping for vertical well extraction systems and 2500 feet of piping for horizontal well systems.

The required effluent concentration ultimately determines residence time of contaminated groundwater within a treatment system. This impacts the flowrate and directly influences the cost of the treatment system from both a capital and O&M standpoint. We used an effluent VOC concentration of 20 μg/L when developing our cost estimates.

We estimated capital costs for an air stripper system handling approximately 700 gpm, to be approximately $180,000. The capital cost does not change significantly at the lower horizontal well flowrate of 660 gpm. We estimated annual O&M costs, including power, repair, etc., to be approximately $50,000.

We estimated capital costs for an air stripper plus a vapor phase carbon collector to be approximately $450,000. Operation and maintenance costs of the carbon system are a function of flowrate and contaminant concentration. Using an air flowrate of approximately 2000 cubic feet per minute (cfm), we estimated a carbon loading rate of approximately 9 pounds per day based on average contaminant concentrations. Under these conditions, vapor collection O&M costs are approximately $130,000 per year, for a combined O&M cost of approximately $170,000 annually.

We estimated capital costs for the carbon adsorption system to be approximately $1,100,000 for a contaminated groundwater flowrate of 700 gpm. Operations and maintenance figures are a function of the carbon loading rate, which is directly proportional to the product of influent contaminant concentration and flowrate. At a flow rate of 700 gpm, with VOC concentrations of 1000 μg/L and TOC of 2000 μg/L, carbon usage will approach 175,000 pounds annually. Using a unit rate of $1.50 per pound for carbon use and regeneration, this will cost approximately $260,000 annually. Additional O&M factors increase annual costs to approximately $330,000.

Comparative Economic Evaluation

The principal issue addressed in this economic evaluation is whether the increased contaminant capture rate achieved by the horizontal wells can shorten remediation periods enough to justify the additional capital cost generally needed to construct horizontal wells. This question can be addressed in general terms by simply evaluating the O&M costs associated with the treatment technology selected for a given site and then comparing the differences in net present value of the O&M for various treatment periods. If the cost of investments needed to shorten the treatment period is less than the reduction in O&M, then the investment is financially worthwhile. We present the evaluation here in terms of the specific site modeled above, considering the specific performance of the selected horizontal and vertical well systems.

We recognize, as discussed earlier, that where drilling access to an unfractured aquifer containing dissolved contaminants is not restricted, it generally is possible to construct several vertical wells in a manner that will approximate the hydraulic performance of a horizontal well. The cost of drilling those several vertical wells, relative to the horizontal well cost, will depend on the depth at which the screens must be placed. As the screen depth increases, the horizontal wells become relatively less expensive. At the particular site modeled earlier, additional vertical wells could be installed to increase the contaminant capture rate, though possibly at the expense of also increasing the flowrate to the treatment system. If site conditions were more restrictive, the options for vertical well placement could be more limited. For example, if there

were a building just southeast of the landfill, which is the principal source of contamination, the horizontal wells still could be placed as shown, but vertical well placement would be restricted.

The evaluation focuses on the comparative economics of the remediation systems under consideration. There is also an intangible value associated directly with reduced remediation time. While this value cannot be quantified easily, for many companies faced with remediation obligations, there is significant value in simply shortening the cleanup period and hastening the day when that liability can be written off their books.

For a real site remediation, cleanup criteria and methods of measuring when those cleanup criteria were met are established on a site-specific basis. Issues such as regulatory requirements, results of a health risk assessment and technical feasibility typically are considered when establishing the cleanup criteria. Issues such as sensitive receptor location, site hydrogeologic characteristics, contaminant distribution, treated water discharge system and the degree of public health or environmental quality risk posed by the site typically are considered when establishing the method of measuring whether the cleanup criteria have been met.

Instead of site-specific criteria, we used total contaminant mass removed as the comparison criterion between the horizontal and vertical well systems. As shown in Figure 6, the characteristic of the ambient groundwater flow, combined with the extraction system design, produce a situation in which after 10 years of operation, neither the vertical nor the horizontal wells achieve significant additional contaminant capture. The horizontal well system requires somewhat less than 5 years to achieve the cleanup level achieved in 10 years by the vertical well system. We therefore focused our cost comparisons around the first 10 years of operations for the vertical wells and 5 years for the horizontal wells. Depending on the actual cleanup criteria, the treatment period could extend considerably longer for either system.

We present three forms of financial data in this evaluation: (1) annual cash flow estimates, (2) cumulative cash flow estimates and (3) net present value estimates. First we present the basic cash flow values under two inflation assumptions, 5% and 10%. We did not tabulate the cash flow under the no inflation scenario since it is simply a continued annual expenditure of the year one costs. While our comparative evaluation focuses on the 5 and 10 year time frames, we presented cash flow estimates for a 30-year period to facilitate the reader making other comparisons for different treatment periods or other assumptions. Second, we present and compare net present values (NPV) of capital and O&M costs for three hurdle rates, 10, 12 and 15%. In most economic evaluations, NPV of all costs is the principle value used for decision-making. The cash flow values can easily be used to estimate NPVs for other hurdle rates. Third, we present and compare cumulative cash flow values. While we recognize that NPV is typically used for decision-making, cumulative cash flow requirements must be considered for budgeting purposes.

ADL[1] presents the complete tables of these cash flow, NPV and cumulative cash flow values. Summary tables and figures for selected representative scenarios are presented in the following discussions.

Table 5 presents a summary of NPV and cumulative cost values for the groundwater treatment O&M costs at treatment periods of 5, 10, 15, 20, 25 and 30 years of operation. These values, when combined with the capital costs described above and the extraction effectiveness shown in Figure 6, can be used to develop economic comparisons. As described earlier, the most appropriate comparison for the specific site and extraction system evaluated here is 10 years of operation for the vertical wells against 5 years of operation for the horizontal wells. Table 6 presents these computations for the three treatment systems evaluated here using 5% inflation and a 12% hurdle rate. These results show that for the 5-year treatment period differential considered here, and with the stated economic assumptions, the higher capital cost of horizontal wells is more than compensated for by the reduced O&M costs for the air stripper with vapor phase carbon adsorption and the carbon adsorption systems. For the simple air stripper system, a 5-year treatment differential is not enough to offset the increased capital cost associated with the horizontal wells in terms of NPV. The horizontal well system does, however, produce a lower total cash flow.

Table 5
O&M Net Present Value Summary

FLOW RATE 662 GPM TO 708 GPM

	Air Stripper		Air Stripper w/Carbon		Carbon Adsorption	
	Base Case	5% Inflation Differential	Base Case	5% Inflation Differential	Base Case	5% Inflation Differential
5 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	222,768	249,147	621,605	916,898	1,533,024	1,714,562
@ 12%	214,123	238,673	789,723	881,006	1,473,536	1,643,858
@ 15%	202,377	224,939	746,402	829,614	1,392,704	1,541,968
Cumulative O&M Calculated At:						
5% Annual Increase	272,775		960,560		1,422,363	
10% Annual Increase	306,409		1,084,823		1,595,966	
10 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	332,219	409,745	1,225,282	1,511,210	2,266,240	2,619,750
@ 12%	309,234	378,187	1,140,509	1,394,819	2,128,084	2,602,577
@ 15%	279,874	338,164	1,032,224	1,247,208	1,926,016	2,327,152
Cumulative O&M Calculated At:						
5% Annual Increase	561,565		1,967,623		2,829,290	
10% Annual Increase	730,216		2,555,739		3,650,922	
15 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	400,179	537,011	1,475,929	1,980,591	2,753,920	3,695,563
@ 12%	363,207	479,084	1,339,569	1,766,943	2,499,488	3,296,920
@ 15%	318,399	410,001	1,174,312	1,512,154	2,191,135	2,821,513
Cumulative O&M Calculated At:						
5% Annual Increase	930,142		3,252,919		4,624,923	
10% Annual Increase	1,409,539		4,924,663		6,960,449	
20 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	442,373	637,858	1,631,548	2,352,531	3,044,288	4,389,562
@ 12%	393,827	552,142	1,452,502	2,036,393	2,710,208	3,799,683
@ 15%	337,557	455,594	1,244,970	1,680,310	2,322,976	3,135,272
Cumulative O&M Calculated At:						
5% Annual Increase	1,400,551		4,893,318		6,916,658	
10% Annual Increase	2,503,597		8,739,840		12,290,475	
25 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	468,571	717,774	1,728,171	2,647,273	3,224,576	4,939,519
@ 12%	411,204	605,056	1,516,592	2,231,550	2,829,792	4,163,826
@ 15%	347,681	484,520	1,280,093	1,786,993	2,388,512	3,334,332
Cumulative O&M Calculated At:						
5% Annual Increase	2,000,925		6,986,930		9,841,556	
10% Annual Increase	4,265,589		14,884,220		20,874,535	
30 YEARS						
O&M Year 1	46,500		171,500		320,000	
O&M NPV						
@ 10%	484,837	781,098	1,788,162	2,880,824	3,336,512	5,375,798
@ 12%	421,067	643,387	1,552,967	2,372,921	2,897,664	4,457,?8
@ 15%	351,819	502,889	1,297,589	1,854,740	2,421,120	3,4??,?39
Cumulative O&M Calculated At:						
5% Annual Increase	2,767,171		9,658,967		13,574,550	
10% Annual Increase	7,103,294		24,779,806		34,699,251	

Figure 7 presents summaries of remedial costs and remedial effectiveness in terms of NPV. The evaluation shown in Figure 7 corresponds to Case 2 in Table 6. The bottom portion of this figure is taken from Figure 6, the summary of contaminant extraction effectiveness. The top portion of this figure presents graphical summaries of the NPV, including capital costs, for the three treatment alternatives.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The principal conclusions which can be drawn from this study include:

- The hypothetical model study results provide introductory comparison of vertical and horizontal well performance for recovering contaminated groundwater. These results not only demonstrate contaminant recovery performance, but also illustrate the flow patterns produced by single and multiple horizontal wells.

- In many situations, horizontal wells can provide groundwater contaminant recovery performance superior to that available from greater numbers of vertical wells. For example, in our real site case study, four horizontal wells substantially outperformed eight vertical wells, even though the horizontal wells were pumping at a lower total rate than the vertical wells. In situations where direct vertical access to the plume is restricted, better performance of horizontal wells is even more dramatically apparent than that of vertical wells. In situations where vertical access is not restricted, however, a sufficient number of vertical wells can, theoretically, approximate the performance achieved by a horizontal well. Horizontal wells generally offer better performance than vertical wells when dealing with relatively thin plumes. As plumes get thicker, however, or as the vertical

Table 6
Example Cost Sensitivity Calculations

Case 1: Air Stripping of Contaminated Groundwater

A) Capital Costs	
1) Vertical well array	$ 85,000
2) Horizontal well array	$300,000
3) Air stripping system	$175,000
B) Annual Operating and Maintenance Costs	
1) Air stripping	$ 47,000
C) Years of Operation	
1) Horizontal wells	5
2) Vertical wells	10
D) Cumulative Cash Flow of O&M[1]	
1) Horizontal wells	$273,000
2) Vertical wells	$562,000
E) Net Present Value of O&M[2]	
1) Horizontal wells	$239,000
2) Vertical wells	$378,000
F) Total Cumulative Cost (A + D)	
1) Horizontal wells	$748,000
2) Vertical wells	$822,000
G) Total NPV (A + E)	
1) Horizontal wells	$714,000
2) Vertical wells	$638,000
H) Cost Differential (Horizontal vs. Vertical)	
1) Cumulative Cost	$ 74,000
2) NPV	($ 76,000)

[1]Based on 5% inflation rate
[2]Based on 12% hurdle rate
Note: (-) Indicates a negative value

Case 2: Air Stripper with Vapor Phase Carbon Adsorption

A) Capital Costs	
1) Vertical well array	$ 85,000
2) Horizontal well array	$300,000
3) Air stripping with Carbon Adsorption	$440,000
B) Annual Operating and Maintenance Costs	
1) Air stripping with carbon adsorption	$171,500
C) Years of Operation	
1) Horizontal wells	5
2) Vertical wells	10
D) Cumulative Cash Flow of O&M[1]	
1) Horizontal wells	$ 960,000
2) Vertical wells	$1,968,000
E) Net Present Value of O&M[2]	
1) Horizontal wells	$ 881,000
2) Vertical wells	$1,395,000
F) Total Cost (A + D)	
1) Horizontal wells	$1,700,000
2) Vertical wells	$2,493,000
G) Total NPV (A + E)	
1) Horizontal wells	$1,621,000
2) Vertical wells	$1,920,000
H) Cost Differential (Horizontal vs. Vertical)	
1) Cumulative Cost	$ 793,000
2) NPV	$ 299,000

[1]Based on 5% inflation rate
[2]Based on 12% hurdle rate

Case 3: Carbon Adsorption

A) Capital Costs	
1) Vertical well array	$ 85,000
2) Horizontal well array	$ 300,000
3) Carbon adsorption system	$1,100,000
B) Annual Operating and Maintenance Costs	
1) Carbon adsorption	$320,000
C) Years to Achieve Cleanup	
1) Horizontal wells	5
2) Vertical wells	10
D) Cumulative Cash Flow of O&M[1]	
1) Horizontal wells	$1,422,000
2) Vertical wells	$2,829,000
E) Net Present Value of O&M[2]	
1) Horizontal wells	$1,644,000
2) Vertical wells	$2,603,000
F) Total Cost (A + D)	
1) Horizontal wells	$2,822,000
2) Vertical wells	$4,014,000
G) Total NPV (A + E)	
1) Horizontal wells	$3,044,000
2) Vertical wells	$3,788,000
H) Cost Differential (Horizontal vs. Vertical)	
1) Cumulative Cost	$1,192,000
2) NPV	$ 744,000

[1]Based on 5% inflation rate
[2]Based on 12% hurdle rate

hydraulic conductivity decreases, vertical well performance improves relative to horizontal wells.

• The real site modeling and comparative economic evaluation showed that for two of the three treatment technologies evaluated, the initially higher cost of a horizontal well system is more than compensated for by the reduced treatment system operation and maintenance costs associated with the shorter cleanup period. For the third treatment system, air stripping without air emission control, the initially higher costs of the horizontal wells are approximately balanced by the reduced treatment system operation and maintenance costs. It should be noted, however, that increasingly strict regulatory guidelines on air emissions limit the application of air stripping without air emission control. As operation and maintenance costs for a treatment system increase, the economic advantages of faster contaminant recovery also increase.

Recommendations

The results presented in this study provide a solid foundation for understanding how horizontal wells perform when used to recover dissolved groundwater contamination. Studies which would provide additional useful information about horizontal well performance include:

• Expanding the hypothetical model study evaluation to include contaminant removal performance normalized by the total pumping rate. This evaluation would provide an enhanced understanding of the relative performance of vertical and horizontal wells.
• Evaluating the performance of alternative vertical and horizontal well systems at the site used for the case study presented in this report or other case studies.
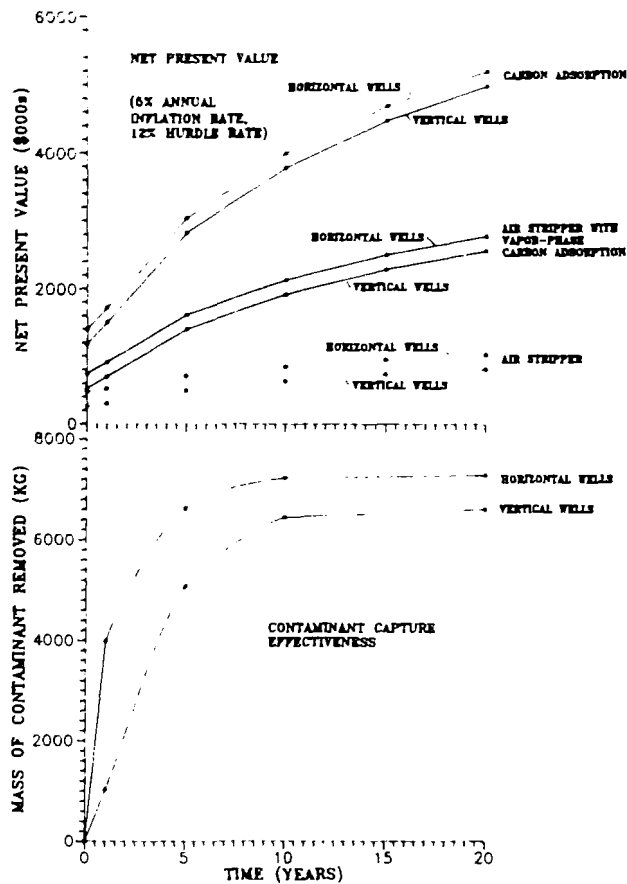
Figure 7
Extraction Effectiveness and Treatment Cost Summary:
Net Present Value

- When horizontal well pump test data become available, performing a numerical modeling study of the test. This study would provide an opportunity to calibrate a groundwater model to test data generated by horizontal wells and provide further confirmation of the modeling method.
- Evaluating the relative costs of horizontal and vertical wells as a function of the depth to the contaminated groundwater for well designs which produced comparable hydraulic performance.
- Evaluating the benefits of horizontal wells in situations where minimizing the hydraulic stress on the aquifer is important, such as areas where salt water intrusion is an issue.
- Evaluating nonaqueous phase contaminant recovery using horizontal wells.
- Evaluating horizontal well performance in the unsaturated zone, especially related to design parameters for landfill or lagoon monitoring.

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Use of Specialized Mining and Petroleum Drilling Technology for Environmental Applications

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ABSTRACT

Numerous types of drilling and coring techniques and equipment have been developed for specialized applications in the mining, construction and petroleum industries which have direct use in environmental characterization and site remediations.

The emphasis of this paper is primarily toward applications of non-fluid sonic coring to environmental applications. In addition to a cursory discussion of the sonic drilling technology, other topics discussed focus on applications of this drilling method for gaining uncontaminated samples in adverse conditions such as deep unconsolidated sediments where poor core recoveries are a problem; drilling in areas of high groundwater flows where sample collection and monitor well completions are difficult; drilling in the ecologically sensitive areas of wetlands, tundra, karst and permafrost where the movement of equipment and the act of drilling can cause serious damage; directional drilling techniques to allow for sampling and groundwater remediation under ponds pits, landfills and occupied, operating buildings; and remote controlled drilling when working in areas of high chemical and radiation contamination.

Other technologies such as large diameter drilling and pipe jacking are summarized.

INTRODUCTION

There are many types of drilling and coring technologies that have been developed in the mining, construction and petroleum industries that are essentially unknown in the environmental arena. Many of these technologies have direct application to site characterization and remediation. One of these techniques is the use of sonic drilling and coring. Uses of this technology are particularly applicable when:

- Working in areas of abundant boulders
- There are loose overburden conditions
- Working in areas of very high groundwater flows
- Working in very ecologically sensitive areas such as wetlands, tundra, karst and permafrost
- There is a history of poor core recovery
- There is a need to sample under a waste lagoon or pond or an occupied, operating building
- There is a need to initiate an interim drainage control system for leaking ponds, pits and landfills.

The emphasis of this paper is on the application of sonic drilling technology to environmental problems. Sonic drilling tools were developed for use in gold placer exploration where the economic success of an operation absolutely requires an uncontaminated sample and is most often carried out in very remote areas where the weight of the rigs must be kept to a minimum. The technology relies on establishing resonance within the drill string through means of a sonic hammer, does not use any conventional drilling media such as air, water or mud, provides very pure samples, is readily adaptable to directional drilling techniques and can be readily transported by helicopter, boats, barges or "swamp buggies."

SONIC DRILLING TECHNOLOGY

Sonic drilling differs substantially from conventional drilling techniques. The technology was perfected in Canada in about 1974 under patents held by the late Dr. A.G. Bodine.

Operationally, there is neither a conventional drill bit nor a conventional drill pipe. The drill bit consists of relatively large diameter hardened steel with tungsten carbide inserts set into the hardened steel. Drill casing, similar to auger tools without the flutes, constitutes the rest of the drill string.

Drilling is accomplished by means of a sonic head located on the drilling derrick (Fig. 1). This sonic head produces a frequency close to the natural frequency (approximately 70-150 hz) of the drill column allowing the drill string to act as a flywheel transferring the entire energy of the drill string in bursts to the bit. Drill cuttings are displaced into the annular space or into the core barrel with the core. The disposition of the cuttings is dependent on the bit configuration. In practice, the bit does not leave the cutting surface when drilling. The significance of this point is discussed later.

Actual drilling is affected three ways depending on the rock or soil material being drilled:

- Displacement where soil or rock particulates, such as unconsolidated sands, are fluidized by the vibration of the drill column. This occurs only when there is sufficient porosity in the drilled medium to accept the drill cuttings. In this instance, the sonic drilling method is similar to driving casing.
- Shearing which is affected when drilling in plastic clays and shales. In this instance, the induced amplitude must be sufficiently large to overcome the inherent elasticity of the medium. When not used with rotation, the sonic method is similar to split tube sampling. When rotation is used, the drilling is similar to conventional coring.
- Fracturing occurs when the inertial moment of the bit is sufficiently large to cause fragmentation. Typically, this will occur when drilling in brittle material. A analogy is to a hollow downhole hammer.

Penetration and bit life may be improved when groundwater is present or water is introduced through the drill string at the surface. The penetration rate is improved by more efficiently moving the cuttings from the bit face. However, water is not required since there is more than adequate room for the displacement of these cuttings either into the annular space or into the core barrel. It is important to remember that any introduced fluids are only under the pressure of the liquid fluid column — there is no mud pump or air compressor to force the cuttings away,

to spread contamination or to cause hydrofracturing.

It should be pointed out that it is possible to use sonic drilling technology with fluids through the use of a modified water swivel. We have successfully used this adaptation in the drilling of exceptionally hard conditions on a freeze pipe installation project in Milwaukee, Wisconsin. The conditions of this effort required the drilling through a buried steel slag dump. Materials encountered were lake sediments, wooden piers, slag from a rolling mill and nodules of rolled steel up to 7 inches thick.
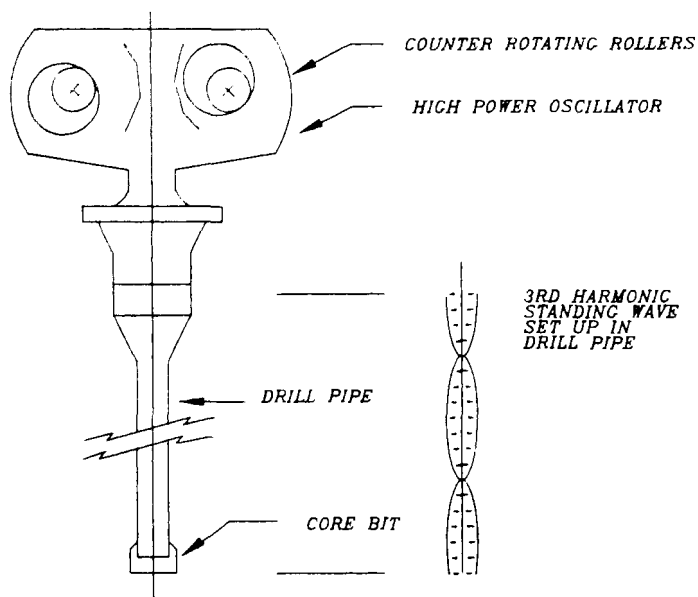
Figure 1
Basic Principles of Operation of the Sonic Drill

LIMITATIONS

Sonic drilling utilizes only limited weight on the bit surface, relying on the inertial moment of the induced vibrations and slow rotation to affect penetration. Thus, in terms of depth limitations, any significant damping effort of the drilled medium will obviously inhibit the vibration and eventually cause penetration to stop. To overcome this limitation, especially where there are surface clays, a high torque rotary head can be added and conventional auger tools used to refusal. At refusal, the rotary head is moved out of the way and with the auger tools still in place, sonic tools are deployed through the auger tools. Should the need arise, such as when drilling through deeper clay units, downsizing is easily accomplished. Simply leave the tools in place, put on a reducing coupling and continue drilling with smaller diameter tools—through the entire existing drill string! The maximum depth reported thus far is more than 700 feet.

Another limitation, especially when drilling without fluid, is the length of the core. The combined friction of drill cuttings and of the cut core in the core barrel, the lack of any significant weight from the drill string to force the core into the core barrel and the lack of lubrication from a drilling medium, sometimes cause early core refusal. This may necessitate short core runs. However, through the use of modified wireline core recovery tools, this drilling speed is not significantly affected.

A third limitation is that there is a degree of uncertainty of the porosity and permeability laboratory measurements from cores derived in this method. That is, there is the possibility that additional micro-fracturing and/or compaction from the drilling action may be present and artificially influence these measurements. Until these variances, if present, are quantified, the use of sonic drilled cores is not recommended.

APPLICATIONS

Sample Collection

The most immediate application and the one for which this technology was developed, is to produce a sample of very high purity through highly variable conditions such as clays and sands and boulders and rock. Since the drill bit never leaves the drill face and since most of the cuttings are most often directed into the core barrel, there is only a remote possibility of cross-contamination. Even so, any cross-contamination will be confined to samples of a particular core run unless groundwater is present. Further, boulders, the bane of all drillers, are easily cut and included as part of the sample. Boulders to four feet in diameter have been cored and sampled in the drilling of gold placer deposits in Alaska, California and Montana.

This application has been successfully used at the Radioactive Waste Management Complex at the Idaho National Engineering Laboratory in Idaho and at the Rocky Flats Site in Colorado.

In a drilling demonstration at the Rocky Flats Site in Colorado, actual penetration through the Rocky Flats Alluvium was in excess of 15 ft/hr. Actual on the job performance at the Rocky Flats Site is not available for inclusion in this paper. In this instance, it was necessary to downsize the drill rods and to modify the core barrel assembly. Following the sampling effort, the smaller diameter drill tools were removed and larger diameter tools were used for well installation. This will be discussed in greater detail below.

At the RWMC at INEL, the sampling was affected without rotation. The reason for this is that there was a concern while sampling through buried containers of uncertain materials related to the possibility of generating sparks and other safety concerns. Again, smaller diameter drill tools, albeit larger than those used for the Rocky Flats work, were employed. Following the sampling event, epoxy resin fiberglass casing was installed through the drill string.

A substantial time savings can be realized by using this drilling methodology versus conventional auger and rotary drilling methods. These figures were part of a technical proposal made to a large environmental contractor at his request. The first bar represents the contractor's estimate of the time required using conventional methods (Fig. 2). The second column is our time estimate and the basis for our bid. The percentage estimate of the time saving is shown in the first column on Figure 3. Depending on the task, this time saving (time in the field) is from 5% to almost 30%. Thus, a significant savings can be made from the time required to have people in the field and the coincident PPE requirements.
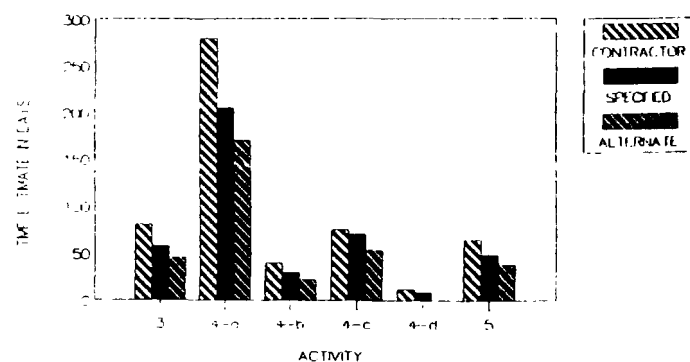
Figure 2
Estimated Drilling Days by Task

Conversion to Other Drilling Methods

A second application which was alluded to earlier is the ability to change from conventional drilling methods to sonic drilling. This can also be done in reverse. The specified plan called for auger drilling to install surface casing, then moving from the well while the cement set, moving back over the hole and sampling, coring and installing

piezometers and/or wells. Conventional drilling through hollow stem auger tools had resulted in abandoning the well because the augers were stuck in the hole. This is the justification for the surface casing phase. Since it is not necessary to change rigs or remove the tools from the hole, this operation is relatively easily affected and results in an even greater time saving.
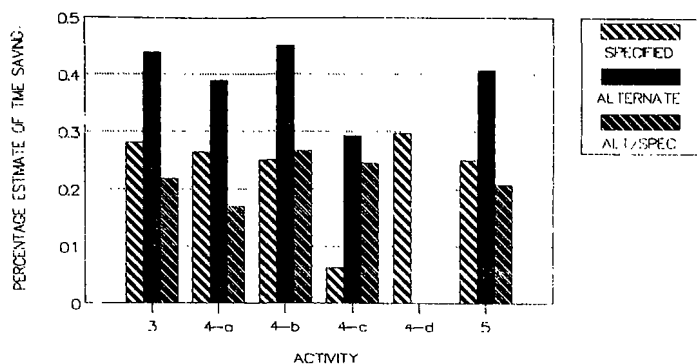
Figure 3
Estimated Time Savings by Task

Again referring to Figure 2, column 1 represents the contractors estimate of the field time and column 3 represents our estimate of the time required to complete the task without the need to change rigs. Figure 3, column 2 illustrates the percentage time estimate of these savings and ranges from 30% to 45%. Thus, the ability to convert between sonic and conventional drilling tools dramatically reduced the field time.

Minimizing Ecological Damage

A third application is where there is the need to drill in very ecologically sensitive areas, such as wetlands, tundra and permafrost. There is no need to consider the need for disposal of drilling fluids, except in areas of artesian flow, or of the drill cuttings, except when sampling is not being undertaken in conjunction with well installations.

Further, since the equipment does not require a heavy superstructure, does not need an air compressor or mud pump, uses a lightweight drill string and the rig itself is light in weight, tools are easily transported by helicopter or modified for use on swamp buggies, Unimaks or barges. This method of operation has been used successfully while drilling on the ice of the Bearing Sea in Alaska. Water depths were on the order of 90 feet. However, freezing of the samples was a problem.

Well Installations

The next application concerns well installations. As previously mentioned, monitor wells can be installed either conventionally, i.e. removing the drill string, or installed through the drill string. There is no need to discuss conventional well installation. After the well string is put into place, installation of casing, sand pack, seals and cement can take place inside the drill string. This method is particularly important in areas of high groundwater flow or where there is a consideration of loose material caving above the interval being drilled.

The time of extraction of the drill string depend on local conditions. If warranted and risks associated with this process are deemed acceptable, the drill string can be left in place until the grout or cement has set and extracted by drilling inside the initial drill string with smaller diameter tools.

When installing monitor wells in cases where there is the potential to lose the hole, such as in loose ground, by cavings or high groundwater flows, it is preferable to disconnect the sonic head from the drill string, install the casing, reconnect the sonic head, remove the appropriate length of rods, install the sand or gravel pack, measure the depth to insure that an appropriate amount of sand has been installed, reconnect the rods, remove the appropriate length of rods, install the sealing material and measure. Depending on the conditions, cement

can then be installed through the drill rods and vibrated as the rods are extracted to assure an effective seal or the drill string can be extracted and the cement conventionally installed.

It should be further pointed out that at any time during the installation procedure, the drill string can be vibrated to set the material thereby greatly minimizing void space. This process greatly facilitates the time required to install the well installation materials.

This method of well installation has also been used successfully at the RWMC at INEL for possible geophysical and in situ vitrification uses.

Directional Drilling

Another application of this technology is in the field of directional drilling. By incorporating existing petroleum and mining technology to wedge or shim at the drill face, using the lightweight drill string and maintaining a close survey of the hole, it is possible to drill up, down, left and right from the original vector of the hole.

In practice, this is relatively commonly accomplished at 5° deviation on a 100 foot radius. We do not yet know the limits to this application with sonic drilling technology but we feel that it is greater than 10° on a 100 foot radius. Thus, high purity samples can be taken underneath waste storage lagoons, ponds, landfills or occupied, operating buildings. Since there is no need to use drilling fluids, there is no possibility of hydrofracturing through a waste storage pond or lagoon, thereby spreading contaminants.

As an extension of this technique, interim remedial actions can be initiated. A possible application is shown in Figure 4. By drilling an arcuate array of drainage wells, cementing casing and employing various types of petroleum perforating technologies, a series of "French drains" can be created. These would then drain into a geotextile, concrete lined sump. Thus, the volume of hazardous fluids which previously had been entering the groundwater can be significantly minimized.
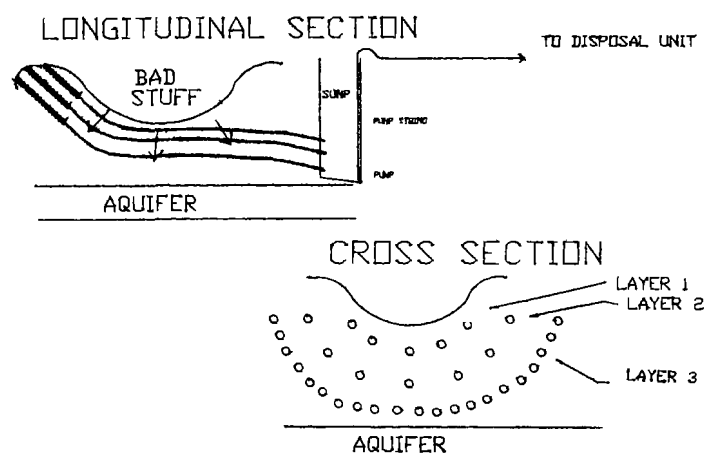
Figure 4
Application of French Drain Installation

Another extension of directional drilling applications is to identify fracture systems and anastomosing, fluvial channel systems. Combining first the identification of the geologic setting and second, interim remediation as discussed above, environmental hazards from chemical and radiation contamination can be substantially mitigated (Fig. 5).

Well Abandonment

Conventional methods of abandoning inadequate wells involve various combinations of methods of cementing, perforating, milling, pulling, etc. These methods have an inherent uncertainty to them unless it is possible to completely extract the original well casing. Figure 6 is an illustration of this technique. Through the use of the large diameter sonic drill steel, it is possible to 'overcore' the entire drill string

employing a large kerf to create a relatively large annular space. Then, after the well casing is free and with the large diameter steel still in place, go inside the casing with smaller diameter rods, attach an interior pipe clamp at the bottom of the casing string, and then pull the casing as a complete unit.

Cement which is adhered to this casing is removed to allow cutting the casing into manageable lengths and removing it to the appropriate location on the site for storage pending ultimate removal.

An alternative method, and the method proposed for the deeper wells which may be beyond the drilling capacity of sonic technology, is to not drill around the existing casing, relying on the sonic rig's vibration capability to free the casing and cement en masse. However, the alternative method probably will require removal in stages with the casing cut as appropriate with either conventional petroleum engineering technology such as explosive or chemical casing cutters. This is a less desirable alternative for the shallow wells because of the uncertainties.

Following removal of the existing casing from the well, open hole geophysical logs can be run at the discretion of the contractor and the well can be recompleted or abandoned.

These techniques were responsible for extraction of casing from drilling evaluations conducted on the Athabasca Tar Sand deposits in Alberta. Here, literally thousands of feet of otherwise serviceable steel casings were removed where all other methods had failed.

Remote Controlled Drilling

A final application of this technology deals with remote controls to the drilling apparatus. Specific use of this technology is in areas where contaminant levels are very high and apply to either chemical or radiological hazards. The drilling rig is very easy to operate and readily adaptable to electronic controls. In an area of high contamination where drilling in Level A or B personal protective equipment (PPE) is required, the driller could be situated relatively far from the rig and be exposed only for rig up and rig down; the helper(s) could be exposed only long enough to seal the core and for rig up and rig down. Similar equipment was developed for site characterization at Three-Mile Island.

It must be pointed out that while we have every confidence that this can be done, we have not yet made the necessary modifications to attempt this.

OTHER TECHNOLOGIES

There exist a great number of other technologies which can have a very direct, positive influence on Site Characterizations, RI/FS, Site Remediations, Environmental Restorations and other activities such as these for which "wheels" have already been invented. With only slight modifications, these "wheels" can be adapted to help solve the problems which are encountered. Two of these that I would like to address are pipe jacking and large diameter drilling.
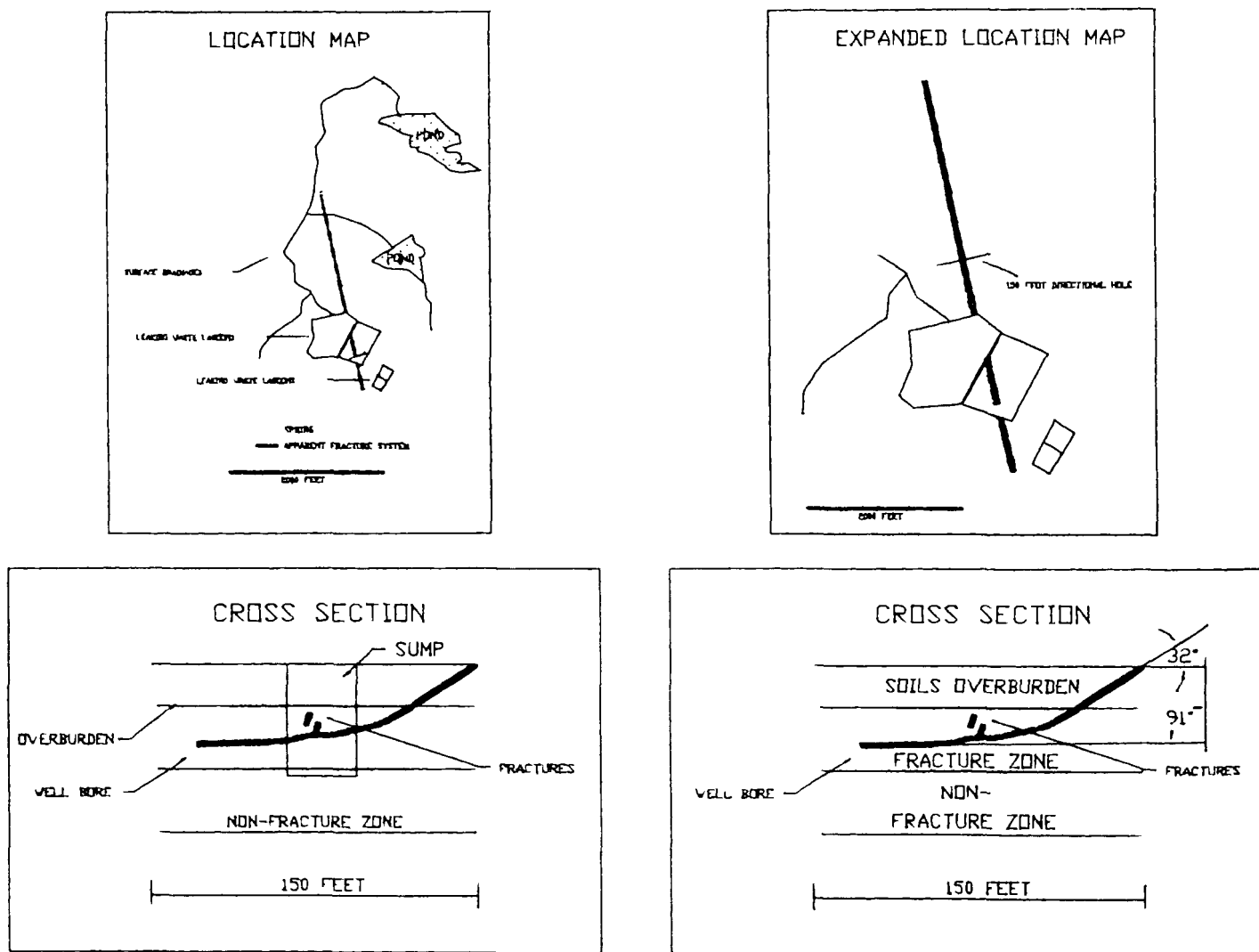
Figure 5
Fracture Identification and Remediation
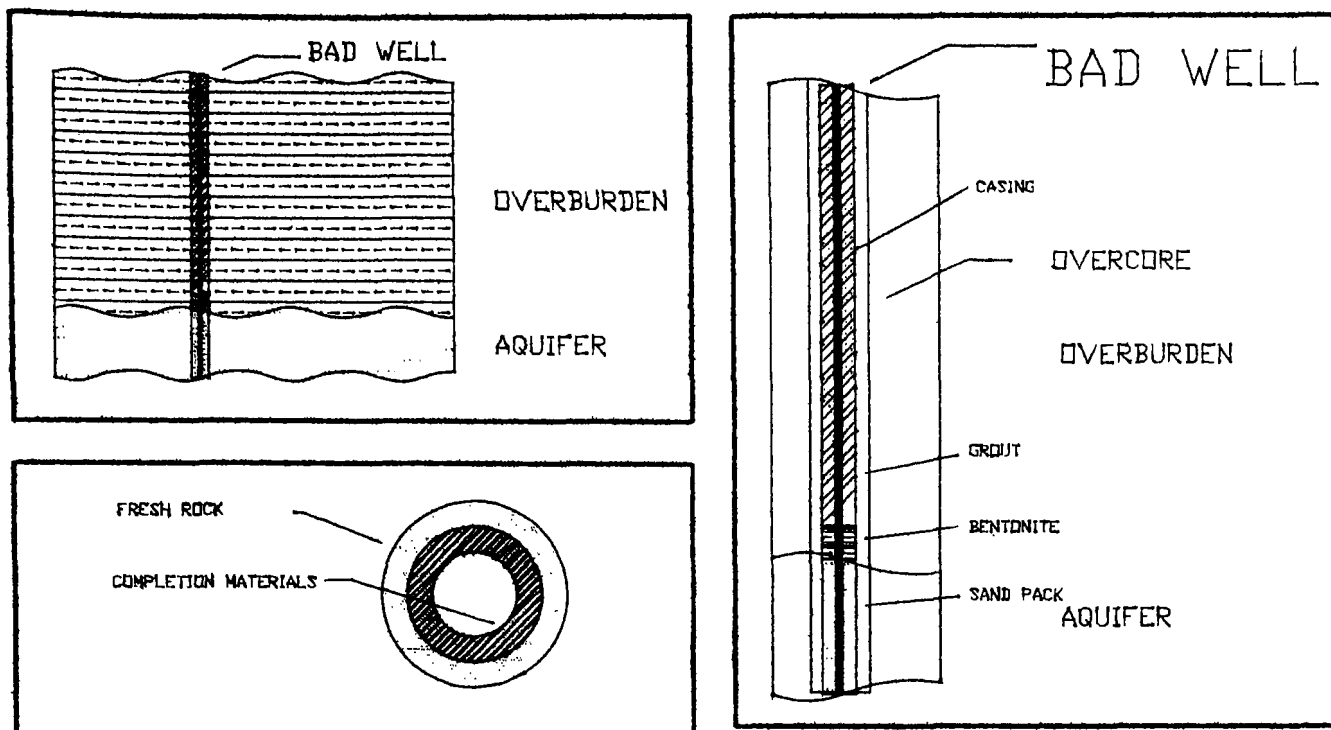
Figure 6
Demonstration of Well Extraction Procedures

SITUATION
LEAKING LANDFILL

REMEDIATION PLAN
LEAKING LANDFILL

IMPLEMENTATION OF PLAN
LARGE DIAMETER HOLES OVERLAPPED TO FORM CONFINING TRENCH

LEAKING LANDFILL
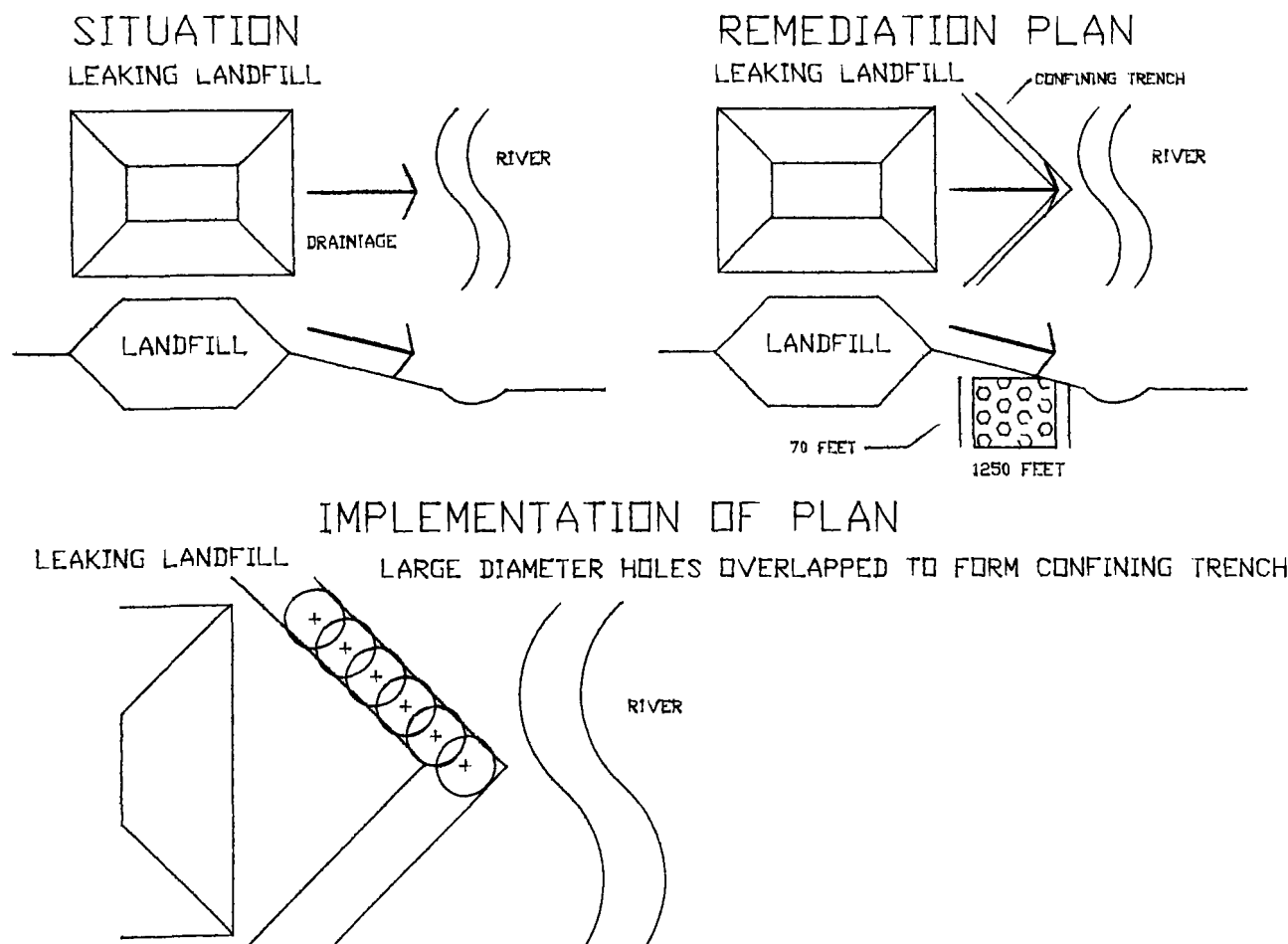
Figure 7
Demonstration of Well Extraction Procedures

Pipe Jacking

Pipe jacking is a process of using a tunnel boring machine or as they are called in the vernacular, a "mole," to excavate a tunnel. The size of these moles range from 4 inches to 9 feet and perhaps larger. The smaller diameter moles are obviously remotely controlled. As the mole is advanced, the excavated materials are evacuated, usually in a slurry, and sections of pipe are pushed or "jacked" into the tunnel with a separate slurry of mud acting as a lubricant. Typical applications for this technology are for the installation of water lines, sewerage lines, dewatering systems and fiber optic cable installations.

Applying this technology to remediation activities, there is little reason that these cannot function as "French Drains" beneath leaking landfills. A format for this application was shown earlier.

Large Diameter Surface Drilling

Drilling of large diameter (four to six feet) holes from the surface was developed in Europe where there is a great need to install caissons and pilings into saturated rock. This installation is typically beyond the capabilities of pile drivers. This technology has subsequently been adapted to the bulk sampling of mineral deposits where there is a need for treatability studies or for economic considerations.

Aside from an obvious application to the environmental arena for bulk sampling, perhaps in terms of a feasibility study, there are two other applications which come to mind: first, installation of grout walls with quite a high degree of certainty of forming an impermeable boundary and second, application as a confining trench. An example of the latter is shown in Figure 7.

CONCLUSION

Throughout this short paper, I have tried to emphasize that there are many applications for use of mining, petroleum and construction equipment which perhaps are little known outside these industries. While there has been and probably will continue to be a significant influx of people from these industries to the Environmental industry, it has been my experience that we, as humans, most often choose to emphasize our differences rather than our similarities. However, there is little difference between sampling for a PA/SI and a reconnaissance survey for metals exploration; sampling for an RI is very similar to an exploratory drilling program; a feasibility study is a feasibility study regardless of the reason for which it is undertaken; soil remediation activities are in reality mining operations; and groundwater remediations are directly analogous to petroleum exploitation.

There is a wealth of technology and expertise available at what at first blush may be considered a most unlikely source. I would urge those among you who are prime government contractors to work closely with your subcontractors to affect solutions to your characterization and remediation problems which may save the government money and may result in your getting a contract which would have gone to another contractor.

Similarly, subcontractors and potential subcontractors who wish to be involved in these efforts absolutely must gain contacts to the thought processes of the prime contractors. By working together, we all stand to increase our reputations, reap financial rewards and have a better world in which to live.

Groundwater Extraction System to Control Both Vertical and Horizontal Migration of Contaminants

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ABSTRACT

ENVIRON Corporation has performed groundwater modeling work for the conceptual design of a groundwater extraction system to remediate groundwater contamination at a Superfund site in New Jersey. The extraction system has been conceived to protect the quality of deeper, uncontaminated groundwater and halt migration of dissolved contaminants to the adjacent river and residential area. To achieve the desired vertical capture zone, the remedial system aims to maintain an upward flow component beneath the contaminated areas. ENVIRON's three-dimensional model of groundwater flow indicates that reversal of natural downward flow components calls for shallow extraction wells distributed throughout the contaminated area. Each well can reverse downward flow out to a radius of approximately 400 feet. Model sensitivity tests show that this radius and the resulting well density depend on the vertical hydraulic conductivities of the silty units separating the major sand units.

The pumping rates required to prevent horizontal migration off the site and into the river have been calculated by setting a target water level at each well. Each target water level has been estimated based on the surface water heads on streams surrounding the site. The target head method, which controls the gradient between a line of extraction wells and a stream, assures capture of contaminants and minimal capture of water from the stream's channel and its opposite bank.

INTRODUCTION

ENVIRON has used a numerical groundwater flow model for the conceptual design of an innovative groundwater pump-and-treat system. This system has been developed for the special needs of a Superfund site, shown in Figure 1, to remediate shallow groundwater contamination in a complex aquifer system. The system's objectives are: (1) to protect the quality of uncontaminated groundwater, and (2) to expedite remediation of groundwater in areas where contaminants have migrated off-site. These objectives were selected to be protective of public health and the potable groundwater resources of the region. To conform to regulatory requirements, the system must also contain all contaminated groundwater currently migrating toward the river adjacent to the site.

The conceptual design of the pump-and-treat system was based on the results of previous investigations of the site's hydrogeology and contaminant distribution by AWARE Incorporated (now ECKENFELDER INC.) and a numerical model by ENVIRON of groundwater flow in the principal aquifers underlying the site. Results of these investigations that significantly affected the conceptual design of the remedial scenarios are summarized below.

Hydrogeologic Conditions

The principal hydrostratigraphic units at the site are described in Table

1 and shown in cross section in Figure 2. More than 1000 feet of unconsolidated deposits exist under the site. Of that the upper 200 feet (approximately) have been investigated and modeled. The significantly contaminated zones are within approximately 100 feet of the surface. The unconsolidated deposits in the zone investigated include thick layers of well sorted coarse, medium and fine sands. Between these sand units are layers composed of fine sand, silt and, in some cases, intervals of clay. Some of these silty and clayey units have sufficient areal extent and sufficient vertical flow resistance to act as aquitards. Field water level observations show that heads and flow directions in the second and third sand units are close to those in the first sand unit. By contrast, heads and flow directions in the fourth sand unit are distinctly different from those of the shallower units.
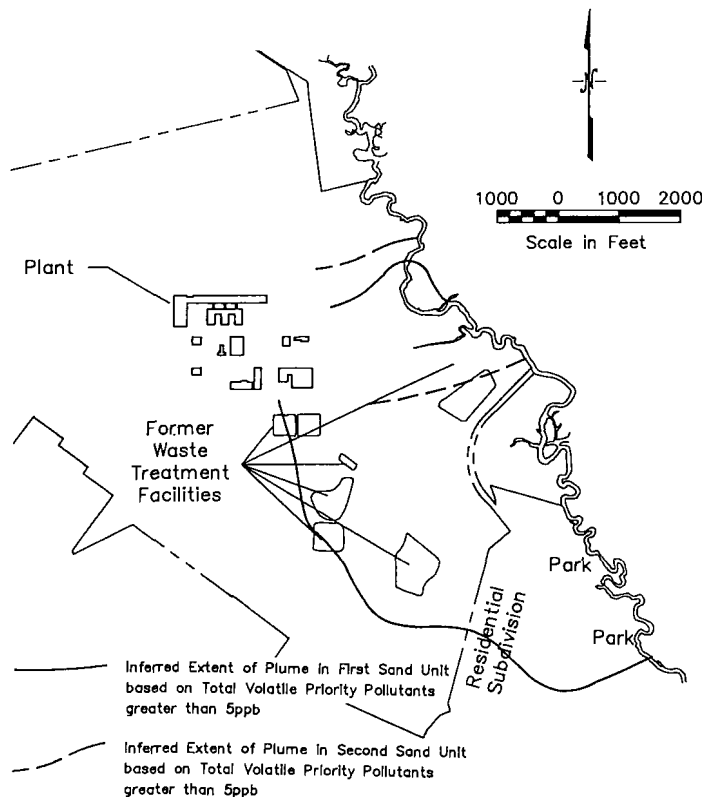
Figure 1
Site Map with Shallow and Deep Plume

Table 1
Hydrostratigraphy at the Site

Hydrostratigraphic Unit	Relative Hydraulic Conductivity	Thickness Where Penetrated (ft)	
First sand unit	High	10	50
First silty unit	Moderate	5	32
Second sand unit	High	2	36
Second silty unit	Moderate	17	39
Third sand unit	High	16	34
Third silty unit	Low	37	46
Fourth sand unit	High	4	11
Fourth silty unit	Low	16	21
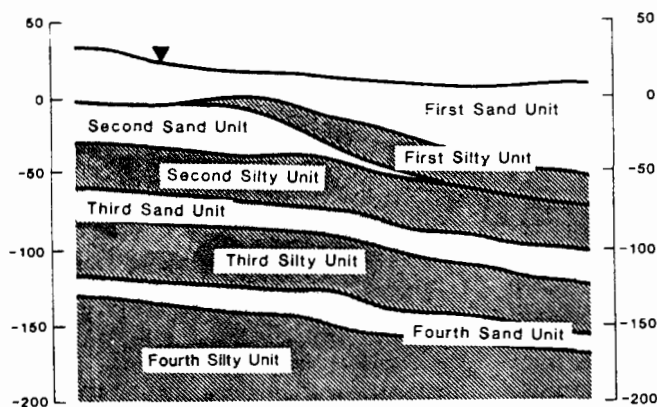
Figure 2
Typical Hydrostratigraphic Cross Section at the Plant

Groundwater flows within the first, second and third sand units are controlled by surface water features, with flow in all three being to the east and southeast toward the river. East of the river, flow in these units is predominantly southward to southwestward toward the river. The river acts as a drain to intercept the eastward movement of contaminants from the site within the first, second and third sand units. Because of the greater depth of the fourth sand unit and the semi-confining character of the unit above it, groundwater flow there is less influenced by surface water features than are flows in the overlying aquifer.

Although the sand units are separated by sediments of lower permeability, to some extent they are all interconnected. Areas exist to the west and east of the river where the vertical component of groundwater movement is downward. Near the alluvial valley of the river, the movement is upward due to the river's draining effect, which causes the heads to be lower in the near-surface zones than they are in the deeper aquifers. Wherever a downward component of seepage exists at the base of a contaminated unit, the potential exists for contaminants to be transported to a lower unit such as the third sand unit. The prevention of such possible future movement is a primary constraint in the selection of remedial alternatives.

Contaminant Distribution

Organic contaminants originating from the plant have been found primarily in the first and second sand units in the areas outlined in Figure 1. Although no organic contaminants have been detected in the third sand unit, localized inorganic contaminants detected there may represent the leading edge of the plume. The eastward movement of contaminants within the first and second sand units will be limited by the draining effect of the river, even in the absence of remedial pumpage. Note in Figure 1 that most of the plume is on the plant site and the southern edge extends into a residential subdivision southeast of the plant. Although contaminants may locally move east of the river channel (as they have at a meander near the plume's north edge on Figure 1), both field data and numerical groundwater flow simulations have shown that the contaminants discharge into the river without leaving the alluvial

valley of the river. For this reason, the contaminants do not pose a threat to regional groundwater resources in the first and second sand units.

Numerical simulations of flow have shown that water in the fourth sand unit may flow eastward under the river due to a combination of natural hydraulic gradients and public water supply pumpage a mile east of the river. If contaminants were allowed to move downward into this aquifer, they might eventually become a threat to drinking water supplies east of the river. For this reason, remedial alternatives that limit the possibility of downward contaminant migration have been emphasized.

Development of the Numerical Flow Model

A three-dimensional, steady-state, numerical flow model for the plant site and surrounding region was developed by ENVIRON. The model was first applied to demonstrate that the adjacent river effectively limits eastward migration of contaminants. The model later helped to confirm that another Superfund site is probably responsible for contaminants discovered east of the river. In addition, it has been used to test a wide range of proposed remedial scenarios.

The model developed is a detailed representation of the regional water balance, including natural surface infiltration, stream base flow, water supply demands and stratigraphy. The regional model encompasses the important surface water bodies surrounding the site and a large area to the east of the river. The flow model was developed using MODFLOW, the USGS modular groundwater flow simulation program by McDonald and Harbaugh.[1] The three-dimensional model developed has five layers, two for the first sand unit and one each for the second, third and fourth sand units. The resistance to flow between adjacent layers includes the resistance of any intervening silty unit. The model can provide high resolution using software developed by ENVIRON to create a wide range of local models based on the regional model input and output. The simulation results presented in the following sections were produced by a local submodel using a relatively fine cell size of 125 feet.

NUMERICAL EVALUATION OF THE GROUNDWATER EXTRACTION SYSTEM

The extraction system described here was selected based on three-dimensional numerical simulations of numerous remedial alternatives. Site-specific experience gained from those analyses leads to the conclusion that the objectives could not be achieved without installing a widely distributed network of recovery wells in the uppermost sand units. Only by pumping from the first and second sand units can the natural downward seepage of groundwater and contaminants into the third sand unit be reversed under contaminated areas. With a remedial system not specifically designed to protect against downward migration, contamination of the third sand unit and, conceivably, the fourth sand unit could occur even during remediation of the first and second sand units.

Assuring a Net Upward Component of Flow

Tests with the current best-fit flow model indicate that a single well can easily reverse the downward seepage due to surface infiltration out to a radius of approximately 400 feet. That radius of flow reversal is much less sensitive to the pumping rate than one might anticipate. The radius depends largely on the local intensity of recharge, the vertical permeability of the silty units, the horizontal permeability of the sand units and the spatial variations of layer thickness. Of these controlling parameters, the horizontal permeabilities and layer thickness are relatively well-established so the most important material property uncertainty is the vertical permeability. Identifying areas of greater than average recharge intensity also is critical. These numerical model results have been confirmed with the help of an analytical model by Jacob[2] of a fully penetrating well in a leaky aquifer.

The limit on the flow reversal radius imposes a constraint on the spacing between wells. The well layout needs to assure that every point in the contaminated zone is within the flow reversal radius of at least one recovery well.

A swale running from the area of the former landfill eastward toward

the river appears to be an area of higher than average surface infiltration where upward flow is more difficult to maintain. The model showed that locally increasing the density of wells can control the downward migration.

The model indicates upward flow under the critical areas of the residential subdivision southeast of the plant, but some areas of suspected or known low-level contamination are beyond the reach of the recovery wells. The model indicates that maintaining upward flow may not be possible in these areas without placement of wells in the residential area.

Stopping the Horizontal Spread of Contaminants

The recovery wells need to be located to control further horizontal migration. Wells need to be positioned at or near the river boundaries and other property lines where contaminants can potentially leave the site. Where contaminants have already moved off-site, extraction wells are required to intercept them before they reach the river. Capturing contaminant mass as close as possible to the areas of concentration recovers the greatest mass with the least tendency to spread it. Thus, wells are situated downgradient of each potential source area.

At this site, the combination of property line wells, river wells and source wells does not by itself provide a dense enough network to maintain the upward component of vertical flow required to protect underlying aquifers. The additional extraction wells required upgradient of the boundaries and sources add to the initial cost of the system, but their impact on the overall volume rate to be treated is relatively modest.

Wherever the second sand unit exists in sufficient thickness and contains significant levels of contamination, recovery wells in that unit are

currently planned to supplement the recovery wells in the overlying sand unit. Each deep recovery site will have a pair of wells to separately screen the first and second sand units. The separate well approach will require careful balancing of pumpages to maintain prescribed conditions of head difference between the two aquifers. However, this approach affords more control over flow than two less costly alternatives, capturing second sand unit contaminants with wells in the first sand unit or screening several sand units with one well.

Selected Well Layout

Figure 3 shows the layout of the 42 proposed well sites. Each site has a well screened in the first sand unit. These sites were selected by a committee of engineers from the site owner's company and hydrologists from ENVIRON and ECKENFELDER. Figure 3 also marks the nine sites where an additional well screened in the second sand unit is proposed. Of the sites shown, seven are at sites of existing recovery wells.

The recovery well configuration consists of wells on the downgradient side of each potential contaminant source, wells to intercept the plume where it can reach the river and wells on other property lines where the plume might leave the property. Wells at the perimeter of the southeast subdivision promote flushing of the first sand unit by inducing upward seepage under as much subdivision as possible without intrusive placement of wells inside the residential area. Additional recovery wells are planned for the intermediate zones between the property boundaries and the sources to assure upward flow in those areas. Supplementary recovery wells upgradient of the sources are proposed to assure upward seepage beneath the remainder of the facilities on the
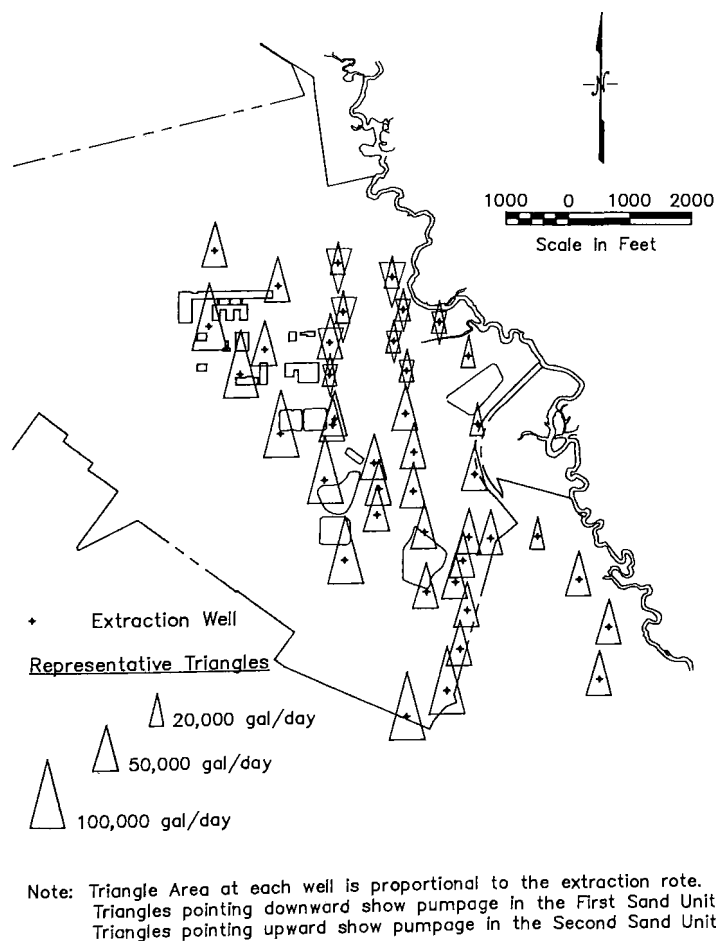
Figure 3
Extraction Well Locations and Pumping Rates.

Note: Triangle Area at each well is proportional to the extraction rate. Triangles pointing downward show pumpage in the First Sand Unit. Triangles pointing upward show pumpage in the Second Sand Unit.

Extraction Well

Representative Triangles

△ 20,000 gal/day

△ 50,000 gal/day

△ 100,000 gal/day
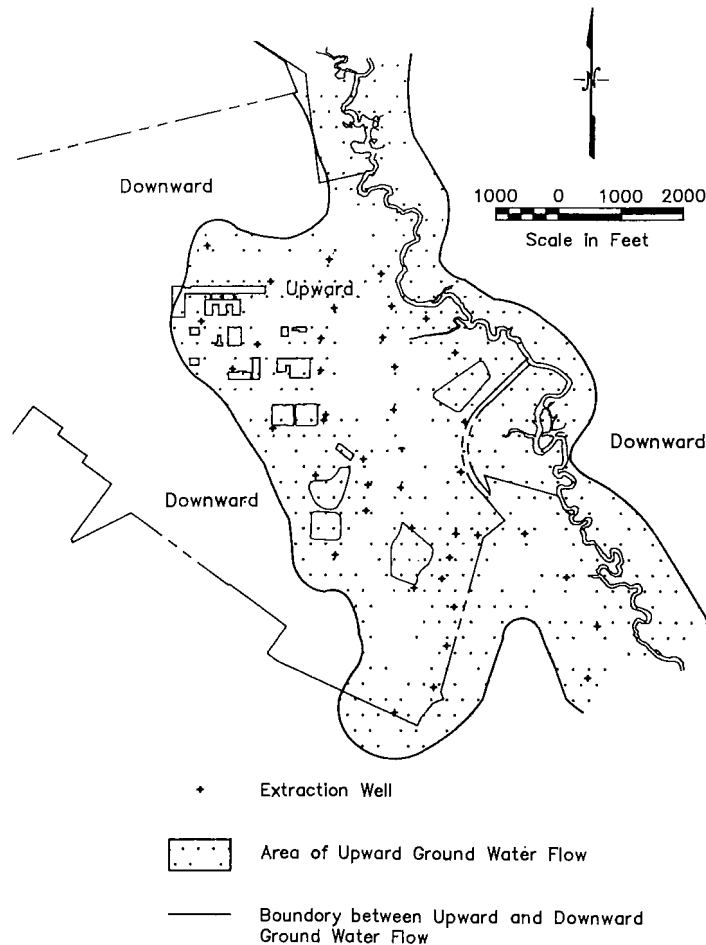
Figure 4
Vertical Flow Direction across the Second
Silty Unit Forecasted by Model

Extraction Well

Area of Upward Ground Water Flow

Boundary between Upward and Downward Ground Water Flow

site. Finally, recovery wells along the entire length of the plant's southeastern property line will prevent downward and outward migration of possible contaminants that may be present south of the identified plume.

PUMPAGE SELECTION WITH THE ASSISTANCE OF THE NUMERICAL MODEL

Excessive pumpage can cause a number of problems. Pumpage will inevitably reduce the base flow to the river. If the pumpage rate is high enough, the groundwater movement toward the river reverses, either locally (e.g., at certain loops in the meandering channel) or over a long segment of the river. When pumpage withdraws water from the channel, the simulations show that it also draws groundwater from the opposite bank (where groundwater movement is naturally directed toward the river). Drawing excess water from the river would unnecessarily increase pumping and treatment costs. The flow model has shown that groundwater contaminants from another Superfund site are present on the opposite side of the river and excessive pumping on the plant property would risk spreading them.

Excessive pumpage causes problems in vertical flow as well. Simulations have shown that excessive pumpage at one location can induce downward seepage in other areas. For example, according to the model, excessive shallow pumpage limited to the source areas would pull water from deeper aquifers, water that might be replenished in part by increased downward flow in other ares of the site. Excessive pumping could even significantly alter the upward flow zone along the river.

The Target Head Method for Pumpage Selection

Various methods are available for estimating the appropriate pumpage with the help of a groundwater flow model. The specified discharge method we have used for many early pumpage scenarios requires the analyst to select and simulate a trial set of pumping rates, create and analyze a set of vertical flow direction maps (Fig. 4) and path line maps and judge which pumping rates to adjust for the next trial. The result of many trials is an approximate distribution of pumpage. Fine comparisons between two similar scenarios are difficult because the bias of the manually selected approximation is not consistent from one scenario to the next.

An alternate method that has been used with excellent results is to specify a target head value at each well and allow the simulation program to calculate the required pumpage. Because the water level and discharge of a pumping well are interdependent variables, either the water level or the discharge can be preselected and the other variable will be controlled by the aquifer characteristics. Target heads can be modeled by representing each well as a single-point drain, as described in the Appendix. The procedure is similar to that of the specified discharge method described above except that target heads rather than discharges are selected for each trial.

Selecting target heads is particularly good for adjusting pumpage near the river to rates that capture contaminated water moving toward the river without drawing river water. Each well in the line closest to the river has a target head a few feet below the time-averaged river elevation so that the highest heads between wells in the line will be approximately even with the nearest surface water heads. Groundwater heads controlled in that fashion assure that the line of wells, rather than the river, will intercept the contaminated groundwater from the west. As a first approximation, the target head for each well in the second sand unit has been set to match its counterpart in the first sand unit. The target head method is a reliable way to control head gradients between the wells and the river. Reliable control over those gradients is needed to limit the withdrawal of water from the river channel or from the east bank. As the capture zone of Figure 5 shows, very little water comes from the channel or the opposite bank except at the northern edge of the plume. There, cross-river flow is needed to accelerate the flushing of contaminants that currently are found under the river channel's meander.

The target head method has been extended from river wells to all recovery wells on the site with very good results. Target water levels

are based on the surface water elevations of the river and smaller streams surrounding the site. The target water level calculation for each well uses the surrounding stream water elevations, the weighting being based on the well's distance from the various stream reaches. The calculated target heads are tested by the model. When most of the wells meet the desired standards of vertical and horizontal capture, target levels of individual wells can be adjusted to achieve the standards. Such adjustments have been used for wells along the plant's southeastern property line which must prevent groundwater migration into the adjacent residential area.

+   Extraction Well

———   Potential in Feet Above Mean Sea Level

———   Boundary of Extraction Well Capture Zone
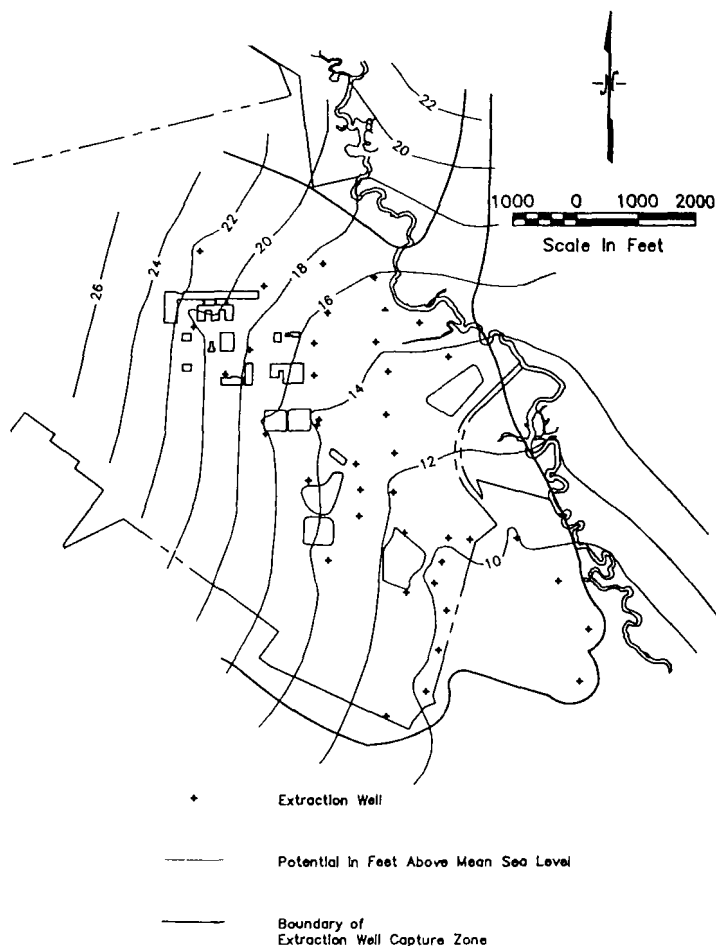
Figure 5
Capture Zone and Equipotentials in the
First Sand Unit Forecasted by Model

Figure 3 graphically shows the calculated pumpage for each well. The overall recovery pumpage is 2.5 million gal/day.

Adjusting Pumpage to Field Conditions Using Target Heads

The actual pumpage rates required to produce the target heads in the field may differ from the pumpage rates estimated by the model. Target water levels can be used to adjust pumpages to accommodate field conditions that differ from the model assumptions. Field permeabilities near individual wells (and thus individual well pumping requirements) will differ from those modeled. However, the total pumpage requirement of the entire set of wells is likely to be close to the predicted value. The engineering design of the recovery well needs to allow individual well pumping rates to be adjusted to meet the water level targets without modification to any of the facilities. Maintaining heads at target levels based on the adjacent stream water level provides strong hydraulic evidence that the system is capturing contaminated groundwater in accordance with regulatory requirements.

Model Results for the Selected Layout

Figure 4 delineates zones of upward flow across the second silty unit, based on a simulation of the well layout in Figure 3. The model results indicate an unbroken area of upward flow beneath the potential contaminant sources and the known on-site contaminant plumes.

The potentiometric surfaces and capture zones modeled in the first and second sand units are shown in Figures 5 and 6, respectively. The overall capture zone for the well network is outlined by a solid curve. At wells immediately upgradient of the eastern plant property line, pumping rates and well spacings have been adjusted to prevent off-site migration. At wells further upgradient, the requirement for adequate pumping and spacing is to maintain upward flow. Extraction wells in the first sand unit capture second sand unit water as well. This indirect capture occurs within the solid capture zone boundary line in Figure 6. Extraction wells screened in the second sand unit provide direct capture to expedite remediation of that unit, especially under the river channel meander near the plume's northern edge. A broken curve in Figure 6 delineates the direct capture zone.

+   Extraction Well

————   Potential in Feet Above Mean Sea Level

— — —   Boundary of Direct Capture by Extraction Wells in Second Sand Unit

————   Boundary of Capture including Indirect Capture by Extraction Wells in First Sand Unit
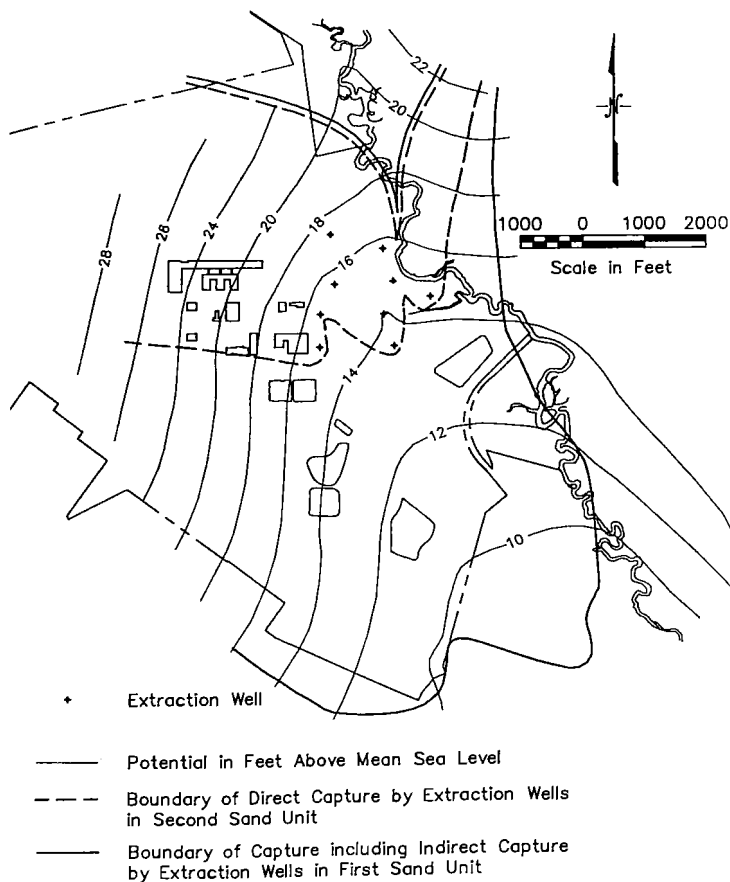
Figure 6
Capture Zone and Equipotentials in the
Second Sand Unit Forecasted by Model

CONCLUSIONS

The conceptual design simulations show that a carefully planned system of recovery wells can stop off-site contaminant migration, remediate existing off-site contamination and prevent additional groundwater contamination. Such a system of wells would be completed in both the first and second sand units with a total pumpage of approximately 2.5 million gal./day. The well layout consists of 51 extraction wells, 42 in the first sand unit and nine in the second sand unit. This system of wells induces upward movement of groundwater from the third sand unit to the first and second sand units, thus protecting the quality of water in the third and fourth sand units.

In terms of horizontal capture zones and upward flow zones, the well layout assures that the modeled upward flow zone covers the con-

taminated areas on-site. Additional wells at the periphery of the known contamination widen both the upward flow zone and the capture zone for horizontal flow.

Reasonable methods have been identified to cope with problem areas where downward groundwater migration has been difficult to reverse. In one of those potential problem areas, a swale, the proposed well layout has a locally higher density. In another area, the southeast subdivision, wells are situated close to the residential area to achieve the greatest possible extent of upward flow without intrusion of wells into the residential area.

The pumpage rate at each recovery well is calculated using a target water elevation to reliably prevent migration into uncontaminated areas without excess pumpage. Setting target water levels based on the time-averaged stages in the river and other bounding streams can assure that on-site groundwater cannot reach the streams. At the same time, the target levels can prevent unnecessary capture of water from the river's channel or its far bank.

APPENDIX

A single-point leakage in a numerical model can approximate a well that has a specified target head. The leakage equation for a finite difference cell is:

$$Q = C (h - z) \qquad (1)$$

where Q is the volume rate of leakage out of the domain, C is a conductance coefficient, h is the head the simulator will calculate at the cell and z is the target head in the well casing. The coefficient C can be derived from a technique for representing a well in a two-dimensional areal numerical model.

The drawdown a numerical model calculates at a well cell matches the analytical model drawdown at some radius r_e, the equivalent cell radius. That radius depends on the cell geometry and material properties rather than the well's actual radius, r_w. Beljin[3] reviews techniques to estimate r_e for two-dimensional models. For rectangular cells, the Trescott et al. program[4] uses:

$$r_e = .104 (\Delta x = \Delta y) \qquad (2)$$

where Δx and Δy are the cell's horizontal dimensions. For anisotropic aquifers, Peaceman[5] derived:

$$r_e = .28 [(\Delta x R)^2 + (\Delta y/R)^2]^{1}/2/(R+1/R) \qquad (3)$$

where

$$R = (K_y/K_x)^{1/4} \qquad (4)$$

Here K_x and K_y are hydraulic conductivities in principal directions normal to the cell faces. Given r_e, C can be derived from an analytical model of steady-state flow toward a well such as the one for a nonleaky aquifer, which yields:

$$C = 2\pi (K_x K_y)^{1/2} b / \ln(r_e/r_w) \qquad (5)$$

where b is the aquifer thickness.

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Groundwater Remediation At a Superfund Site

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ABSTRACT

This paper discusses the operation and performance of the groundwater treatment plant at the Old Mill Superfund site located in Rock Creek, Ohio. The paper also summarizes the history of the remedial activities at the site and the site's selected remedy.

INTRODUCTION

The Old Mill Superfund site is located in the Village of Rock Creek, Ashtabula County, Ohio. The site consists of two parcels of land known as the Henfield and Kraus properties. The Henfield property is approximately 3 ac in size, and the Kraus property is approximately 10 ac in size. Land use in the vicinity of the site consists of a mixture of residential, agricultural and commercial/industrial developments. The closest residences are approximately 75 ft from the site boundary. The closest commercial business, the Rock Creek Aluminum Company, is located south of the Henfield property.

This paper presents a review of the remedial actions conducted to date and a description of a groundwater treatment plant at the site. The plant performance data are provided to demonstrate the capability of the groundwater treatment plant.

HISTORY OF REMEDIAL ACTION

Response activity at the Old Mill site began in 1979 when the U.S. EPA and Ohio EPA found approximately 1,200 drums of toxic waste, including solvents, oils, resins and PCBs, stored on both properties. The Henfield property was considered to be an immediate hazard because a significant quantity of the drummed waste was flammable and access to the site was not controlled.

Superfund emergency removal activities and enforcement actions resulted in drum removal that began in November 1981 and was completed in October 1982. In addition, approximately 80 yd³ of soil from the drum storage areas on the Henfield property were removed in November 1982. A 6-ft cyclone fence was installed around a portion of the Henfield property in April 1984 under the authority of Section 106 of CERCLA in order to minimize the potential for direct contact with contaminated soil.

Between August 1983 and December 1984, a remedial investigation was conducted at the site. Soil on the Henfield and Kraus properties was found to be contaminated with organic chemicals, especially trichloroethene (TCE), as well as with heavy metals such as lead. Groundwater was contaminated with TCE, tetrachloroethene, trans-dichloroethene, 1,1-dichloroethene, vinyl chloride, 1,1,1-trichloroethane, ethylbenzene and xylene. TCE is the principal contaminant in the groundwater.

The remedy selected for the Old Mill site as identified in the August 1985 Record of Decision consisted of:

- Removal and off-site disposal of 95% of the contaminants in the soil and sediments in the drainageway
- Demolition of buildings and silos located on the site with disposal of resulting debris in an off-site sanitary landfill
- Groundwater extraction and treatment (using air stripping and carbon adsorption) for an estimated period of 30 yr
- Placement of aquifer use restrictions for as long as contaminant concentrations in the plume remain above 10^{-6} carcinogenic risk levels
- Hookup of one residence to the public water supply

Implementation of the remedy for soils required removal of approximately 5,000 yd³ of contaminated soil from 13 areas on the Henfield property with the depth of excavation varying from 6 in to 5 ft. Removal of approximately 1,300 yd³ of contaminated soil was required from two areas on the Kraus property with a 15-in depth of excavation. Approximately 100 yd³ of contaminated drainageway sediments (37 yd³ from the Henfield property and 66 yd³ from the Kraus property) were removed. Five buildings and four silos located on the Henfield property were demolished.

Remedial design incorporating the selected remedy was completed in September 1987. Remedial action was completed in August 1989 and consisted of the following:

- Cleanup of soil and sediments from the Henfield and Kraus properties
- Demolition of buildings and silos on the Henfield property
- Installation of three extraction wells (one on Henfield and two on Kraus properties) to a depth of 30 ft to extract contaminated groundwater from the deep aquifer
- Installation of a trench system on each property to extract contaminated groundwater from the shallow aquifer
- Construction of a groundwater treatment facility
- Installation of 16 compliance monitoring wells on the properties (four shallow and four deep wells on each property)
- Regrading and seeding of the properties

The contaminated soil and sediment removals from both the Henfield and Kraus properties are based on achieving the Allowable Residual Contaminant (ARC) levels as shown in Table 1. To verify that soil and sediment excavation and removal has achieved these limits, the following numbers of verification samples were collected:

	Soil	Sediment
Henfield Property	63	5
Kraus Property	40	14

In addition to testing soil and sediments for parameters shown in Table 1, 10 samples (five soils and one sediment from the Henfield property and three soils and one sediment from the Kraus property) were tested

Table 1
Allowable Residual Contaminant Criteria (ARC) For Soil and Sediment Removal[1]

Parameters	Criteria, ppm
1,1,2,2-Tetrachloroethane	0.89
Tetrachloroethane	0.035
1,1,2-Trichloroethane	3.1
Trichloroethene	0.47
Benzo(a)pyrene	1.0
Aldrin	0.016
Fluoranthene	420
4,4'-DDT	0.52
BHC (gamma)	0.13
PCB-1254	0.04
PCB-1260	0.04
Arsenic	28.6
Cadmium	170
Chromium	175
Lead	500
Nickel	1500
Selenium	100
Zinc	108

[1]Sediment from the Henfield area needed to meet only the ARC criteria for zinc. Sediment from the Kraus area needed to meet the ARC criteria for zinc and benzo(a)pyrene.

for Extraction Procedure (EP) Toxicity parameters.

Following completion of soil and sediment removal and demolition of buildings and silos, a groundwater extraction system and treatment facility were constructed. The groundwater extraction and treatment system has been in operation since January 1989. Remedial action was completed in August 1989. Minor modifications requested during the final inspection were completed in March 1990. These modifications included installation of an autodialer alarm system in the floor sump and a ventilation system at the treatment facility.

The site is considered clean-closed and only the treatment plant proper remains fenced.

OVERVIEW OF GROUNDWATER EXTRACTION AND TREATMENT SYSTEMS

The extraction system at the Old Mill site is designed to recover contaminated groundwater from both the shallow and deeper aquifers for treatment. Intercepting trenches are used for extraction of groundwater from the shallow aquifer and extraction wells are used for the deeper aquifer. The extracted groundwater from the shallow and deeper aquifers is pumped through a 2-inch diameter stainless steel underground pipe to a treatment plant located near the southern edge of the Henfield property. Groundwater treatment consists of air stripping followed by two-stage activated carbon adsorption.

The construction of extraction and treatment systems was overseen by the U.S. Army Corps of Engineers under a contract with Aptus Environmental Services. Following completion of treatment plant construction, the plant was operated in two phases consisting of system start-up using clean water (Phase 1), followed by operation using extracted groundwater (Phase 2). Phase 1 operation was initiated in January 1989, and Phase 2 operation was initiated in February 1989.

The operation of the treatment plant was transferred to WESTON under the U.S. EPA Region V Alternative Remedial Contracts Strategy (ARCS). WESTON assumed operation of the plant in August 1989 and will continue to operate the plant until May 1998. The responsibility for operating the system will be transferred to the Ohio EPA in 1999.

TREATMENT FACILITY DESCRIPTION

The treatment plant is capable of treating 10 gpm of contaminated groundwater; however, the normal operating rate is 5 gpm. The treat-
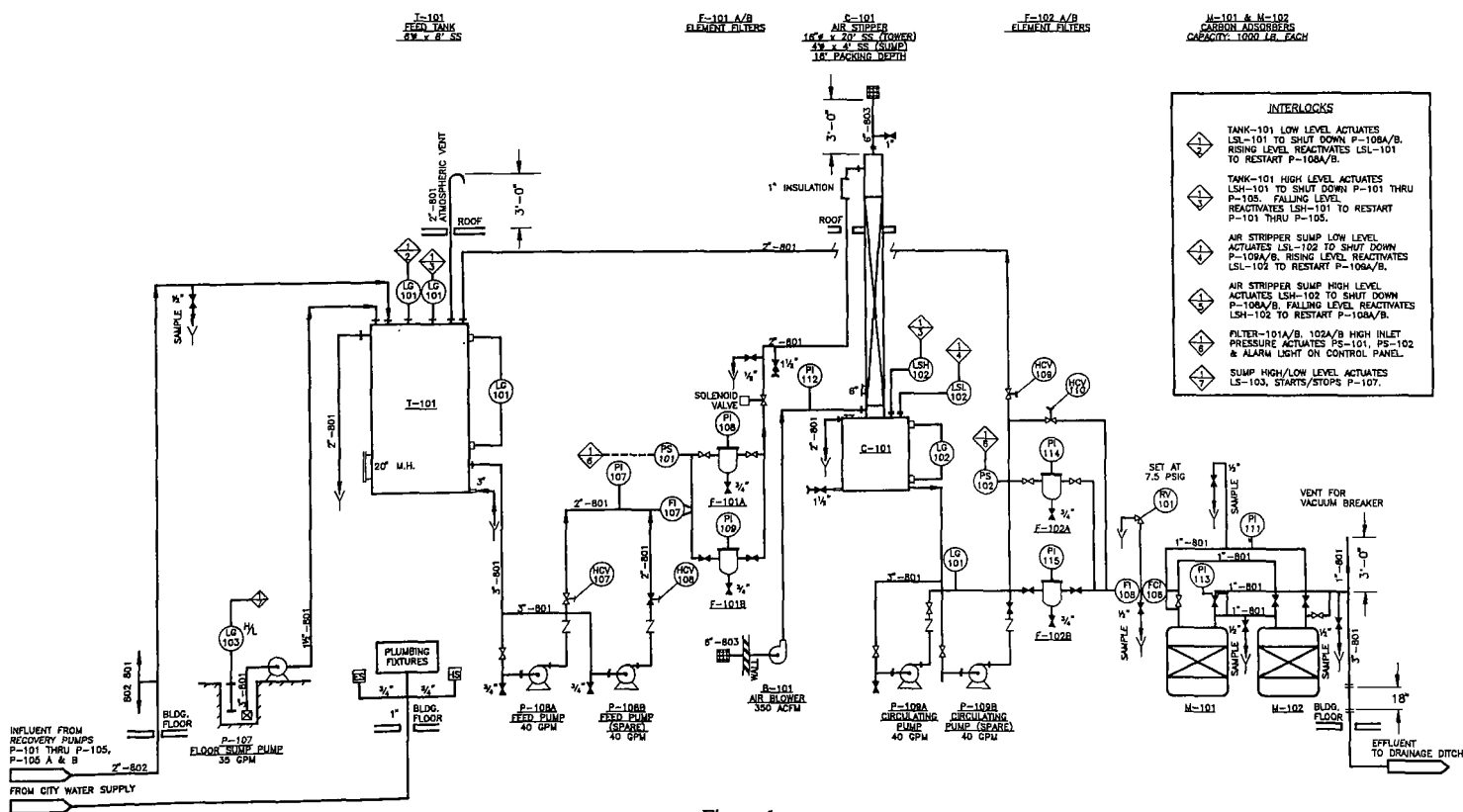
Figure 1
Process Flow Diagram
Groundwater Treatment Plant

ment plant includes a holding tank which collects groundwater pumped from the extraction system. The water from the holding tank is pumped at a rate of 15 gpm through cartridge filters to an air stripper for removal of volatile organic compounds. A portion of the effluent from the air stripper (10 gpm) is recycled back to the holding tank and the remainder (5 gpm) is pumped through cartridge filters to two-stage activated carbon columns. The final effluent is discharged by gravity to an underground stormwater drain and ultimately flows to Rock Creek.

A process flow diagram of the treatment plant is shown in Figure 1. The details of major treatment units are presented in Table 2. The extraction and treatment systems are built with sufficient instrumentation to assist in efficient operation. Pumps located in sumps and extraction wells operate independently based on level controls. The operation of these pumps can also be controlled from the main control panel at the treatment plant. The treatment plant instrumentation consists of several interlocks for pump operation, pressure switches on cartridge filter systems (set at 40 psi) to activate a light alarm at the main control panel and an autodialer alarm system activated by level switches in the floor sump. The autodialer is programmed to dial the home telephone number of the WESTON operator and the office number of the Ohio EPA office in Twinsburg, Ohio, in the event of an overflow of the sump.

TREATMENT PLANT OPERATION

The results of treatment plant operation for the period between Sept. 1, 1989 and July 31, 1990 are discussed in this paper. Prior to WESTON's assumption of operation, 727,000 gal of groundwater were extracted and processed in the treatment plant. From September 1989 to July 1990, approximately 2,015,000 gal of groundwater were treated. The monthly flow handled by the treatment plant shown in Table 3 indicates that

Table 2
Summary of Major Components of Treatment Plant

Feed Tank:	6 ft. diameter x 8 ft. high, 1,500 gallons capacity.
Cartridge Filtration:	Two units, each consisting of two filter housings to hold six 10" filter cartridges in each.
Air Stripper:	One 18-inch diameter x 20 feet high with an integral 4 feet diameter x 4 feet deep sump 16 feet packing depth consisting of 1" Koch Flexisaddle. Blower 350 ACFM capacity
Carbon Columns:	Two 4 feet diameter x 6.5 feet high with 1,000 pounds of carbon in each column.

Table 3
Summary of Monthly Volume of Groundwater Treated

Month/Year	Gallons/Month
September 1989	86,800
October 1989	147,238
November 1989	152,895
December 1989	181,156
January 1990	241,116
February 1990	234,073
March 1990	210,139
April 1990	248,545
May 1990	244,401
June 1990	103,630
July 1990	164,520
Average	183,137

Table 4
Relative Contribution of Individual Extraction System to Overall Flow

Source	Aquifer Location	Percent of Overall Flow Range	Average
Martin Sump[1]	Shallow	4.57-25.37	18.30
Henfield Sump	Shallow	15.92-24.23	19.42
Henfield Well	Deep	12.52-41.13	23.11
Kraus Sump	Shallow	0-18.27	10.50
Krauf Modified Sump	Shallow	7.21-27.80	22.77
Kraus Well	Deep	2.40-7.86	4.15
Kraus Modified Well	Deep	0.53-6.52	1.75

[1]Martin Sump is located in a property contiguous to the Henfield property.

the average monthly flow is approximately 183,000 gal/mo (6,030 gal/day). The relative flow contributed by the trench system and extraction wells to the overall flow to the treatment plant is shown in Table 4. The shallow aquifer contributes approximately 71% of the flow to the treatment plant. The relative contributions to the total flow from the Henfield and Kraus properties are 61 and 39%, respectively.

TREATMENT PLANT PERFORMANCE

The treatment plant is designed to remove volatile and semivolatile organic compounds from groundwater. The effluent discharged from the treatment plant is required to meet the criteria shown in Table 5. The treatment plant effluent is sampled on a monthly basis from sampling locations shown in Figure 2. The samples are analyzed for 12 volatile organics, eight semivolatile organics and 15 other parameters (BOD$_5$, TOC, pH, specific conductance, alkalinity, chloride, sulfate, ammonia and nitrate nitrogen, calcium, iron, manganese, magnesium, sodium and suspended solids).

The compliance monitoring wells are not sampled as part of the treatment plant operation. To date, these wells have not been sampled.

The influent concentration used as the basis for the design of the treatment plant and the range of concentrations encountered at the treatment plant are shown in Table 6. The result indicates that most of the constituents are well below the design value with the exception of trichloroethene, tetrachloroethene and 1,1,1-trichloroethane.

The performance of the air stripper in removing volatile organics from groundwater, shown in Table 7, indicates that the air stripper very efficiently removes volatile organics. This efficiency results from the concentration of influent being lower than the design value and maintenance of a high air/water ratio of 175. The air stripper was originally designed to handle a flow of up to 40 gpm, compared to the present normal flow of 15 gpm. As would be expected, the semivolatile organics are only marginally removed by the air stripper.

The characteristics of effluent from the second stage carbon column are shown in Table 8. Comparison of the discharge criteria to be achieved (Table 5) with the effluent from the second stage carbon column indicates that the treatment plant achieved compliance except for one incidence when trichloroethene exceeded the limit in June 1990. It should be emphasized that due to very large removals of volatile organics by the air stripper and very low levels of semivolatile organics in groundwater, the activated carbon columns are not organically loaded to the extent anticipated in the design. The levels of other constituents present in the second stage carbon column effluent are shown in Table 9. There are no specific discharge criteria for constituents listed in Table 9.

PROBLEMS ENCOUNTERED IN
TREATMENT PLANT OPERATION

Minor problems have been encountered in the operation of the groundwater treatment plant during the first year of operation. The level switches installed in the holding tank are of the floatless type, consisting of a counterweight that moves on a rod to activate the level switches. High iron concentrations in groundwater have caused the counterweight
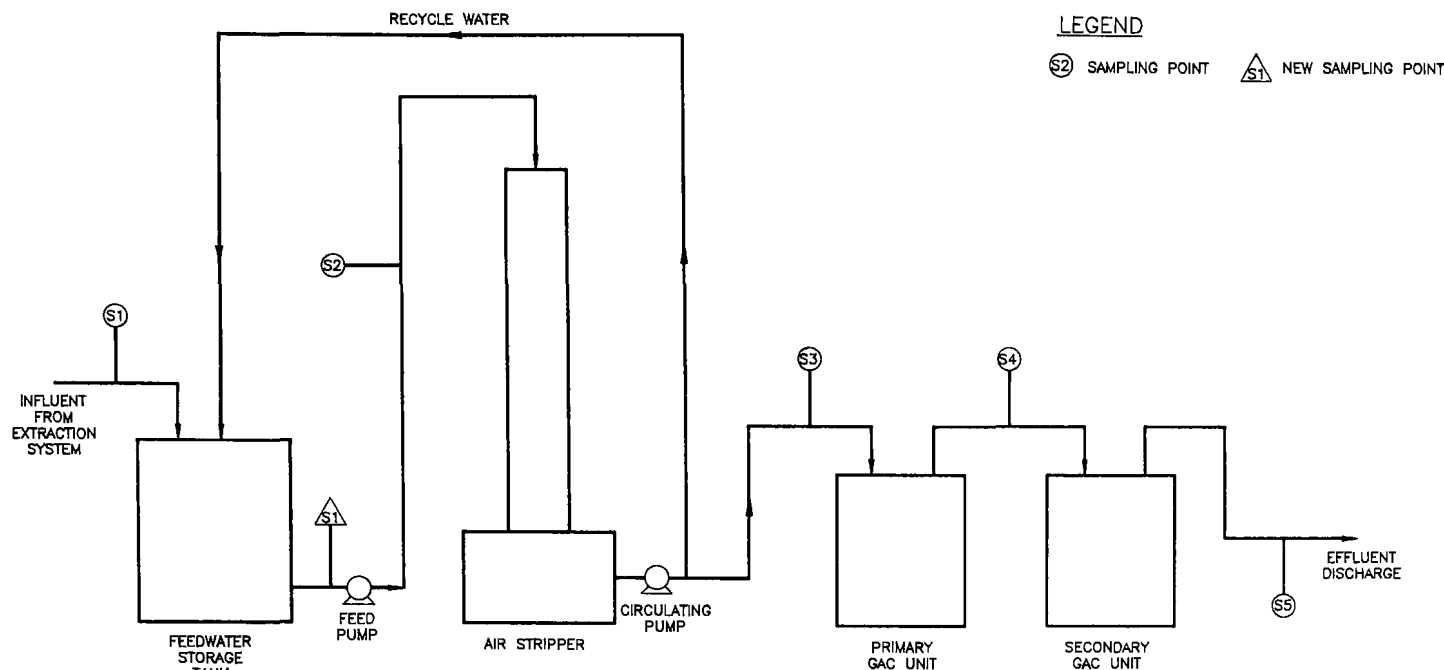
Figure 2
Groundwater Treatment System
Sampling Locations

Table 5
Groundwater Treatment Plant Effluent Criteria

Parameter	Discharge Criteria, ppb
Trichloroethene	1.9
Tetrachloroethene	4.1
1,1,1-Trichloroethane	3.8
Acetone	100
Ethylbenzene	7.2
Phthalates	2.5
Phenols	1.5
Vinyl Chloride	1.0
1,1-Dichloroethene	2.8
1,1-Dichloroethane	4.7
Trans-1,2-Dichloroethene	1.6
Chloroform	1.6
Total Xylenes	1.0
Benzoic Acid	2.0
Methylene Chloride	2.8

Table 6
Comparison of Design Influent
Calculated Influent Characteristics

Constituent	Design Influent, ppb	Calculated Influent, ppb
Trichloroethene	6,100	185-6600
Tetrachloroethene	300	6-150
1,1,1-Trichloroethane	150	2.4-105
Acetone	1,100	ND-3
Ethylbenzene	1,200	ND
Phthalates	60	6-30[1]
Phenol	580	ND
Vinyl Chloride	10	ND-6
1,1-Dichloroethene	10	ND-6
1,1-Dichloroethane	10	ND-30
Chloroform	10	ND
Xylenes	2,700	ND
Benzoic Acid	130	ND
Methylene Chloride	10	ND-3

[1] Includes dimethyl, diethyl, di-n-butyl, bis-(2-ethyl hexyl), di-n-octyl, and butylbenzyl. Concentration based on one half of detection limit for semivolatiles identified as nondetect.

ND - Nondetect

Table 7
Concentrations of Volatile Organic Compounds in Air Stripper Effluent

Constituent	Range of Concentration ppb	Percent Removal
1,1-Dichloroethene	ND	100
1,1-Dichloroethane	ND	100
1,2-Dichloroethene (Total)	ND-0.3	99.8-100
1,1,1-Trichloroethane	ND-1	85-100
Trichloroethene	ND-9	99-100
Tetrachloroethene	ND-0.3	99.4-100

Table 8
Second Stage Carbon Column Effluent Characteristics

Constituent	Range of Concentration, ppb
Trichloroethene	ND-4
Tetrachloroethene	ND-1
1,1,1-Trichloroethane	ND-1
Acetone	ND-3
Ethylbenzene	ND-0.3
Phthalates	ND
Phenols	ND
Vinyl Chloride	ND
1,1-Dichloroethene	ND
1,1-Dichloroethane	ND
Trans-1,2-Dichloroethene	ND
Chloroform	ND
Total Xylenes	ND
Benzoic Acid	ND
Methylene Chloride	ND-1

ND - Nondetect.

on the rod to stay in an intermediate position. This fouling has resulted in overflow of the tank and activation of the autodialer alarm system a number of times. This problem is being corrected by installing float-operated level switches.

The spent cartridge filters currently are being stored within the treatment plant awaiting disposal. Analysis of the spent filters has been completed and a landfill disposal facility in Ohio has been contacted regarding landfilling of the spent filters.

Table 9
Miscellaneous Contaminant Levels in Second Stage Carbon Column Effluent

Constituent	Range of Concentration, ppm
BOD,	2
TOC	1
Ammonia-N	0.1-0.49
Nitrate-N	0.58-5.8
Total Suspended Solids	5-13
Total Iron	0.03-0.089
Total Manganese	0.001-0.072
pH[1]	7.4-8.0

[1]pH value reported as unit of pH.

CONCLUSION

The treatment plant provides treatment for an average monthly flow of approximately 183,000 gal. The shallow aquifer contributes approximately 71% of the groundwater treated at the plant. The air stripper achieves a very high level of removal of volatile organic compounds. This high removal performance has resulted in lower than anticipated organic loading to the activated carbon columns.

DISCLAIMER

Although the remedial action taken at the Old Mill site was funded wholly or in part by the U.S. EPA, this paper was not. This paper has, however, been reviewed by the U.S. EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. EPA, and no official endorsement should be inferred.

Field Evaluation of a Microfiltration Technology to Treat Groundwater Contaminated with Metals

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ABSTRACT

This paper presents the field evaluation results of a microfiltration technology jointly developed by E.I. DuPont de Nemours & Company, Inc. (DuPont) and Oberlin Filter Company (Oberlin). The field evaluation was performed in April and May 1990 at the Palmerton Zinc Superfund (PZS) site in Palmerton, Pennsylvania, under the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation program.

The DuPont/Oberlin microfiltration system uses Oberlin's automatic pressure filter and DuPont's Tyvek T-980 membrane filter media to remove solids larger than 0.1 micron in diameter from liquid wastes. At the PZS site, the microfiltration technology was evaluated for treating groundwater contaminated with metals (primarily zinc). At the optimum operating conditions for the microfiltration system, the zinc and total suspended solids (TSS) removal efficiencies were approximately 99.95%; and the filter cake was approximately 41% solids by weight. At the 95% confidence level, the filtrate met the applicable metals and TSS limits for discharge into a local waterway. However, the filtrate did not meet the pH discharge standard. The filter cake passed: (1) the paint filter liquids test, (2) the extraction procedure toxicity test and (3) the toxicity characteristic leaching procedure test.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is finding new solutions to hazardous waste remediation through its Superfund Innovative Technology Evaluation (SITE) program. The SITE program was created by the U.S. EPA to evaluate new technologies that may destroy or permanently change the composition of hazardous waste by significantly reducing the waste's toxicity, mobility or volume. The SITE program generates reliable performance and cost data for these treatment technologies to be used in evaluating cleanup alternatives under the Superfund remediation process.

In January 1989, E.I. DuPont de Nemours, Inc. (DuPont) and Oberlin Filter Company (Oberlin) submitted a joint proposal for their microfiltration technology to the U.S. EPA's Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER) under the SITE program. The U.S. EPA selected the DuPont/Oberlin microfiltration technology and identified the Palmerton Zinc Superfund (PZS) site, located in Palmerton, Pennsylvania, as an appropriate site for the technology demonstration. The technology was demonstrated at the PZS site in April and May 1990 through a cooperative effort between ORD, OSWER, U.S. EPA Region III, DuPont and Oberlin. PRC Environmental Management, Inc. was contracted by U.S. EPA ORD to assist in the technology evaluation.

MICROFILTRATION TECHNOLOGY: PROCESS AND EQUIPMENT DESCRIPTION

DuPont/Oberlin's microfiltration technology is designed to remove solids from liquid wastes. Since the microfiltration system can remove particles that are 0.1 micron or larger in diameter, dissolved contaminants must first be converted to a particulate form. For example, groundwater with dissolved metals must first be treated with a precipitating agent, such as lime, to convert the dissolved metals into particulate form, such as metal hydroxides. After the dissolved metals are converted to a particulate form, the liquid can be filtered through the microfiltration unit. The microfiltration unit produces two products: filter cake and filtrate. To produce a filter cake that has a low moisture content and a filtrate that has a low solids content, DuPont/Oberlin normally uses a filter aid or filter aid/cake stabilizing agent. For this project, DuPont selected a silicate-based filter aid/cake stabilizing agent known
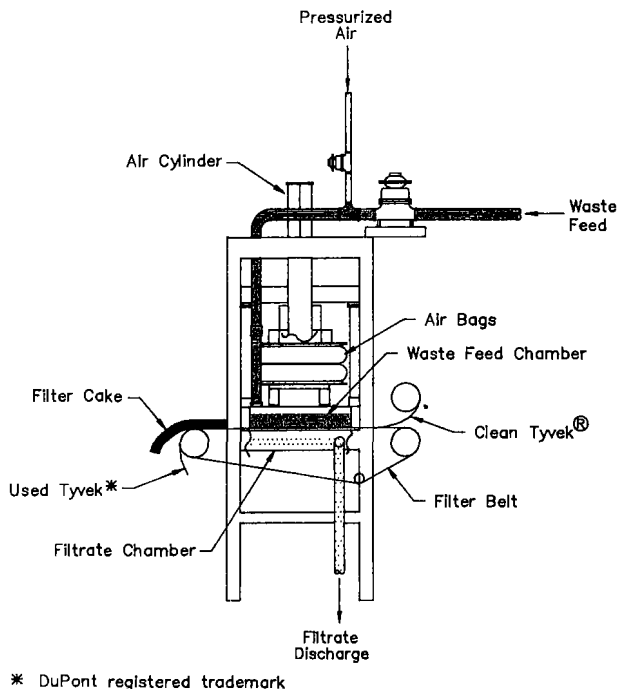
Figure 1
Schematic of Dupont/Oberlin Microfiltration Unit

* DuPont registered trademark

as ProFix, which is manufactured by EnviroGuard, Inc. of Houston, Texas.

A schematic of the DuPont/Oberlin microfiltration unit is shown in Figure 1. This microfiltration unit is an automatic pressure filter (APF) that operates on pressure signals and uses a low-cost, membrane filter—Tyvek T-980—a thin, durable spunbonded olefin fabric developed by DuPont. The APF, developed by Oberlin, has two chambers—an upper chamber for feeding waste through the filter media and a lower chamber for collecting the filtrate. The upper chamber moves vertically, while the lower chamber is fixed. The Tyvek filter lies between these two chambers. The APF unit utilized at the PZS site was 64 inches long, 33 inches wide, 83 inches high and weighed approximately 1,300 pounds. The unit had a filtering area of 2.4 square feet.

At the start of a typical filter cycle, the upper chamber is lowered to form a liquid-tight seal against the Tyvek. The liquid feed waste containing particulate matter is then pumped, at an initial air pressure of 10 psig, into the upper chamber and filtered through the Tyvek. Filtrate is collected in the lower chamber, where it drains by gravity to a filtrate collection tank. During this process, solids are deposited on the Tyvek filter. This solids buildup increases resistance to liquid flow through the Tyvek. To keep the filtration rate constant, air pressure to the pump is automatically increased throughout the filter cycle. During the initial 30 seconds to 60 seconds of the cycle, the filtrate is recirculated to the precipitation tank to keep the quality of filtrate high. At the end of 60 seconds, recirculation stops and the filtrate is drained to an effluent collection tank.

Liquid waste is pumped to the microfiltration unit until the air pressure to the pump reaches 55 psig (a pressure drop of approximately 45 psig across the filter). Liquid feed waste to the microfiltration unit is then shut off, and pressurized air (30 to 45 psig) is fed into the upper chamber to dry the filter cake. The air forces any liquid remaining in the upper chamber and in the filter cake pores to pass through the Tyvek into the lower chamber. The air pressure applied to drain the liquid remaining in the upper chamber, and dry the filter cake, is called the blowdown pressure. Once the liquid is drained from the upper chamber and the filter cake, air breaks through the filter cake. After breakthrough occurs, air continues to be fed through the upper chamber for a preset time interval to further dry the cake. The preset time interval is called the blowdown time. During the cake drying period, the filtrate is sent back to the precipitation tank to keep the quality of filtrate high. At the end of the blowdown time, the air supply to the upper chamber is automatically shut off, the upper chamber is raised and the filter cake is automatically discharged. Clean Tyvek is then drawn from a roll into the APF for the next cycle.

To avoid diluting the feed stream to the APF unit for the SITE demonstration, the filtrate was collected in a separate tank (recirculation tank) instead of being pumped back to the precipitation tank during the initial filtration and cake drying steps.

PZS SITE HISTORY

The PZS site is located in the Lehigh Valley along the Aquashicola Creek in Palmerton, Pennsylvania. During the last 70 years, zinc smelter operations resulted in 33 million tons of zinc residue accumulating and forming an extensive cinder bank at the site. The cinder bank has contaminated the surrounding areas, including the groundwater and surface water. Because of the contamination, the cinder bank was placed on the National Priorities List in 1982.[1] The shallow groundwater at the PZS site was selected as the waste stream for evaluating the microfiltration technology. Groundwater samples collected in June 1989 indicated that the shallow groundwater is contaminated with high levels of zinc (300 to 500 mg/L) and trace levels of cadmium (1 mg/L), copper (0.02 mg/L), lead (0.015 mg/L) and selenium (0.05 mg/L).

TECHNOLOGY DEMONSTRATION

The objectives of the technology demonstration were to: (1) assess the technology's ability to remove zinc from the groundwater at the PZS site under different operating conditions; (2) evaluate the system's ability to dewater the metals precipitate from treated groundwater at the PZS site; (3) determine the system's ability to produce a filtrate

and a filter cake that meet applicable disposal requirements; and (4) develop the information required to estimate the operating costs for the treatment system, such as electrical power consumption and chemical doses.

Testing Approach

The technology evaluation was performed in four phases. Phases 1 and 2 involved nine runs each, and Phases 3 and 4 involved two runs each. In Phase 1, chemical operating parameters (precipitation pH and ProFix dose) were varied, and the filter operating parameters (blowdown pressure and blowdown time) were kept constant. In Phase 2, the filter operating parameters were varied, and the chemical operating parameters were kept constant. Phase 3 runs were performed to evaluate the reproducibility of the microfiltration system's performance. Phase 4 runs were performed to evaluate the reusability of the Tyvek filter.

Table 1 summarizes the operating conditions for the demonstration runs. For Phase 1 runs, the initial operating conditions (Run 1) were based on a pilot-scale treatability study performed by DuPont/Oberlin on the PZS site groundwater. During the demonstration, the chemical operating conditions and the filter operating conditions were optimized in Phases 1 and 2, respectively. Since Run 5 conditions were selected as the optimum operating conditions for Phase 1, these were set as the initial conditions for Phase 2. Phases 3 and 4 were performed at Run 13 conditions because these conditions were selected as the overall optimum operating conditions. This experimental design assumes that there is no interaction effect between the chemical and filter operating parameters. Although this assumption is not critical to evaluating the microfiltration system based on the technology demonstration objectives, the technology developers agreed with this assumption based on their experience.

Table 1
Operating Conditions for the Demonstration Runs

Phase	Run No.	Precipitation pH	ProFix Dose (g/L)	Blowdown Time (min)	Blowdown Pressure (psig)
1	1	8	6	2	45
	2	9	6	2	45
	3	10	6	2	45
	4	8	12	2	45
	5	9	12	2	45
	6	10	12	2	45
	7	8	14	2	45
	8	9	14	2	45
	9	10	14	2	45
2	10	9	12	0.5	30
	11	9	12	2	30
	12	9	12	3	30
	13	9	12	0.5	38
	14	9	12	2	38
	15	9	12	3	38
	16	9	12	0.5	45
	17	9	12	2	45
	18	9	12	3	45
3	19	9	12	0.5	38
	20	9	12	0.5	38
4	21	9	12	0.5	38
	22	9	12	0.5	38

Sampling and Analytical Procedures

Solids and water samples were collected from the microfiltration system at the locations shown in Figure 2. The following measurements were considered critical to evaluating the microfiltration system: (1) zinc in the untreated groundwater and filtrate; (2) total suspended solids (TSS) before and after the microfiltration unit; (3) free liquids (paint filter liquids test) and moisture content in the filter cake; and (4) pH of the untreated groundwater and filtrate. Several noncritical measurements were performed, including the extraction procedure (EP) toxicity test
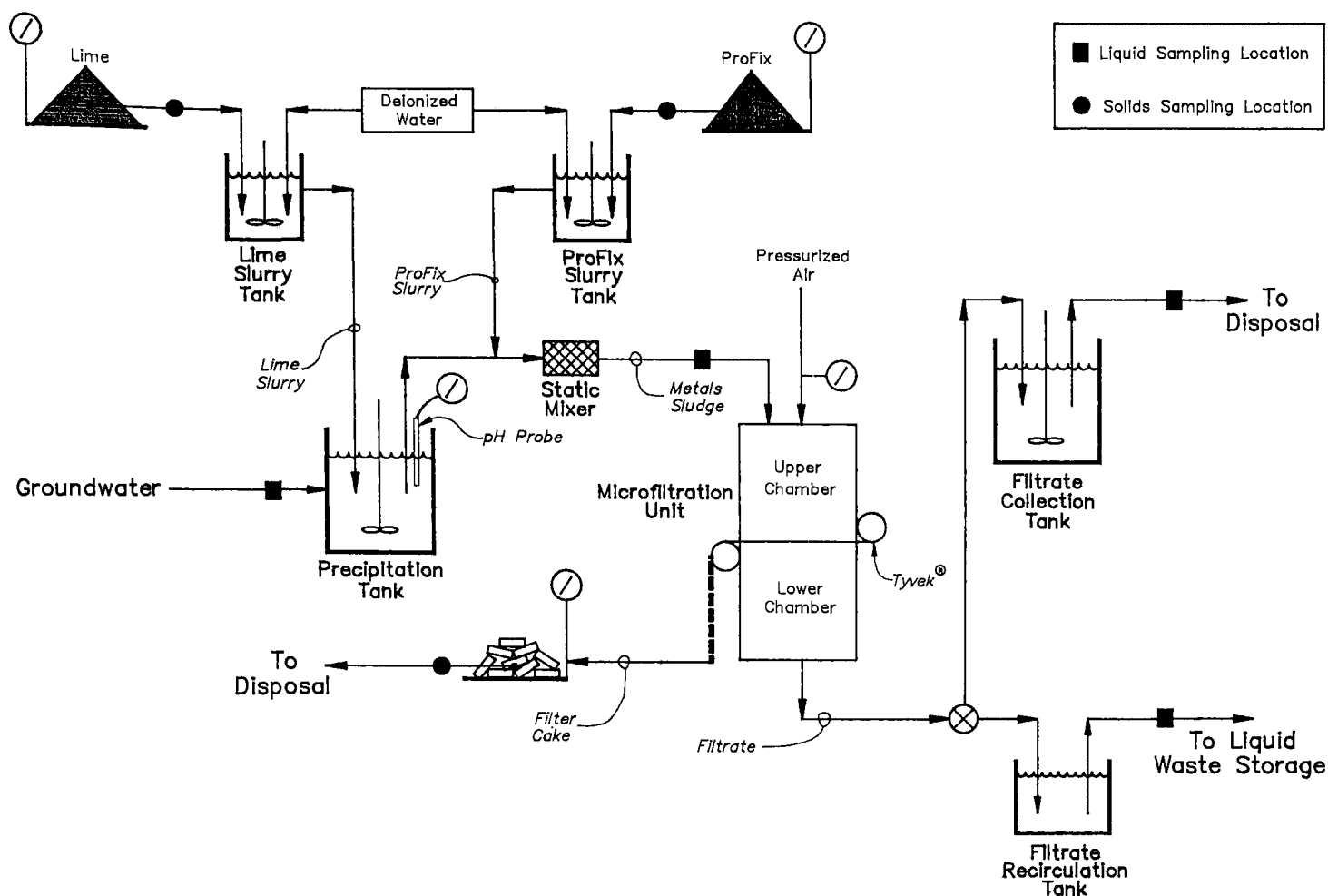
Figure 2
Microfiltration System Sampling Locations

and toxicity characteristic leaching procedure (TCLP) test for the filter cake and particle size distribution for solids remaining in the filtrate. For the critical measurements, three to six replicate samples were collected depending on the data variability. Duplicate samples were collected for noncritical measurements.

U.S. EPA-approved sampling, analytical, quality assurance and quality control (QA/QC) procedures were followed to obtain reliable data.[2,3,4,5] Details on QA/QC procedures are presented in the demonstration plan.[6]

RESULTS AND DISCUSSION

This section of our paper summarizes the results of both critical and noncritical parameters for the DuPont/Oberlin microfiltration system demonstration and evaluates the microfiltration technology's effectiveness in treating groundwater contaminated with zinc.

Summary of Results for Critical Parameters

Results for the critical parameters were evaluated for each of the four phases.

Phase 1 Results

The total zinc concentrations in the untreated groundwater and filtrate are presented in Figure 3 for varying precipitation pH and ProFix dose. The zinc concentrations in the untreated groundwater, ranging from 417 to 493 mg/L, were reduced to approximately 0.1 mg/L (except in Run 6), yielding a typical removal efficiency greater than 99.9%. In Run 6, the filtrate zinc concentration was an order of magnitude higher than the typical filtrate zinc level; this increased concentration cannot be explained. No definite trend was identified for effluent zinc levels

or zinc removal efficiencies with varying pH or ProFix dose.

During the demonstration, a sample of the influent to the microfiltration unit was filtered through a standard 0.45-micron membrane filter (commonly used to measure dissolved metals) to compare the resulting filtrate with T-980 filtrate. In all cases, the zinc concentration was less in the T-980 filtrate, indicating the possible superior performance of Tyvek T-980 filter media over standard membrane filters.

Figure 4 presents the TSS concentration profiles for influent and filtrate. These data show that the influent TSS concentrations ranged from 6,560 to 18,900 mg/L and the filtrate TSS concentrations ranged from 8.4 to 31.5 mg/L. The TSS removal efficiencies ranged from 99.69 to 99.95%. Neither filtrate TSS levels nor TSS removal efficiencies seemed to follow a definite trend with varying pH or ProFix dose.

The filter cake solids concentrations are shown in Figure 5. Cake solids ranged from 30.5 to 47.1%. This figure also shows that the cake percent solids increased as the pH or ProFix dose increased. The filter cake passed the paint filter liquids test in all runs, making it suitable for landfilling.

The filtrate pH was typically 11.5, irrespective of the precipitation pH due to the high pH (about 12.6) of the ProFix slurry added at the influent to the microfiltration unit.

At the end of Phase 1, Run 5 conditions were selected as the optimum chemical operating conditions based on (1) zinc and TSS removals; (2) zinc and TSS levels in the filtrate; (3) percent solids in the filter cake; and (4) the cost of treatment chemicals (lime and ProFix).

Phase 2 Results

Figures 6, 7 and 8 present the concentrations profiles for zinc, TSS and filter cake solids, respectively. These results are similar to Phase 1

Zinc Concentration, mg/L
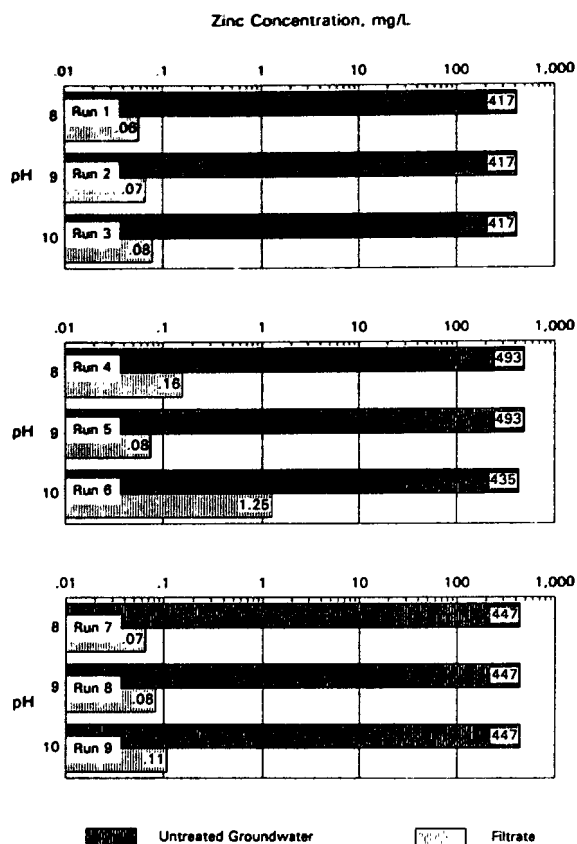
Figure 3
Zinc Concentration Profiles for Phase 1 Runs

TSS Concentration, mg/L

Figure 4
Tss Concentration Profiles for Phase 1 Runs

Cake Solids, %

Figure 5
Filter Cake Solids for Phase 1 Runs

Zinc Concentration, mg/L
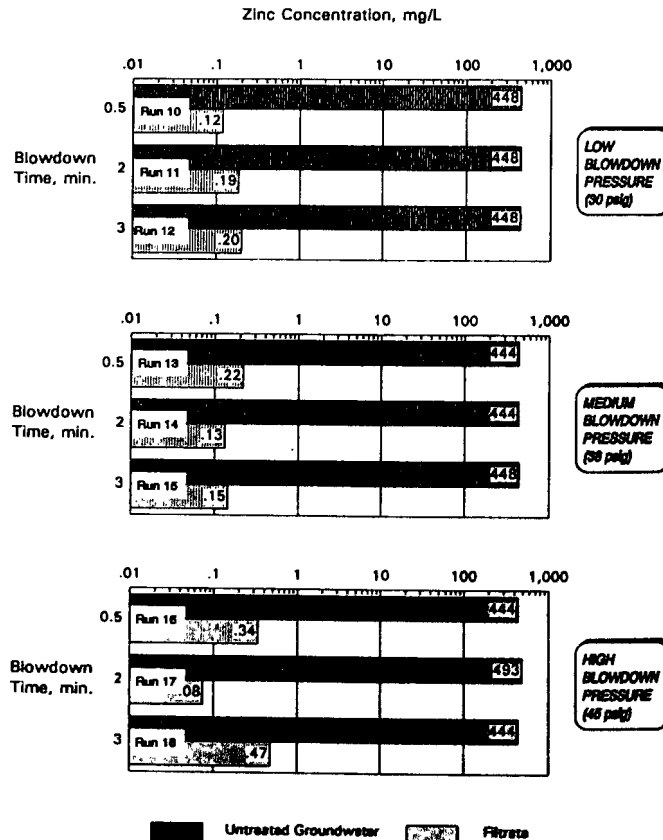
Figure 6
Zinc Concentration Profiles for Phase 2 Runs

results. The filter cake passed the paint filter liquids test in all Phase 2 runs and the filtrate pH was typically 11.5 (the same as in Phase 1 runs).

A dissimilarity noted between the Phase 1 and Phase 2 results is that in the Phase 2 runs, the zinc concentrations in the Tyvek T-980 filtrate were not always less than the 0.45-micron membrane filtrate. This dissimilarity cannot be explained.

At the end of the Phase 2 runs, Run 13 conditions were selected as the optimum operating conditions based on the criteria discussed for Phase 1, plus waste processing time (which includes blowdown time).
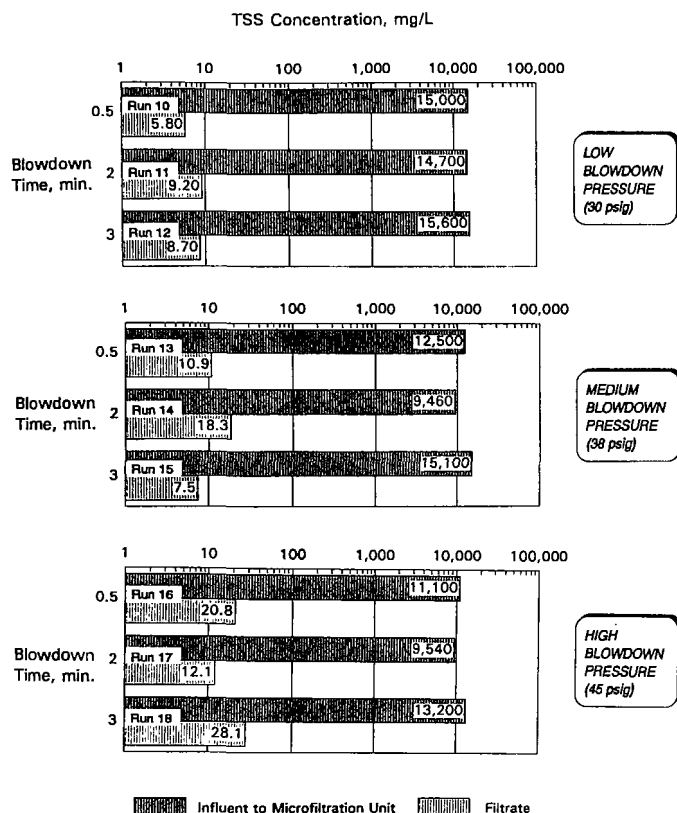
Figure 7
TSS Concentration Profiles for Phase 2 Runs

Phase 3 Results

The total zinc concentration in the untreated groundwater in Runs 19 and 20 (reproducibility runs performed at Run 13 operating conditions) was 465 mg/L. The zinc concentration was reduced by 99.95 and 99.94%, resulting in 0.24 and 0.28 mg/L of zinc in the effluent of Runs 19 and 20, respectively. These removal efficiencies agree with the removal efficiency achieved in Run 13 (99.95%), indicating that the microfiltration system's performance in removing zinc was reproducible.

The TSS concentrations in the influent to the microfiltration unit were 14,300 and 14,000 mg/L in Runs 19 and 20, respectively. The TSS were reduced by 99.95%, resulting in 7.7 and 6.8 mg/L of TSS in the effluents of Runs 19 and 20, respectively. This removal efficiency also agrees with the TSS removal efficiency observed in Run 13 (99.91%), indicating that the system's performance in removing TSS was reproducible.

Figure 9 compares regulatory thresholds with: (1) the 95% upper confidence limits (UCL) for filtrate metals (cadmium, lead and zinc) and TSS and (2) the average filtrate pH value. The regulatory thresholds are those that would be required for discharge into a local waterway (Aquashicola Creek) if a National Pollutant Discharge Elimination System (NPDES) permit were required. The UCLs were calculated using the one-tailed Student's t-test. To calculate UCLs for cadmium and lead, which were present below detection limits, their mean concentrations were estimated using standard statistical procedures. Figure 9 shows that the filtrate met the NPDES limits for metals and TSS. However, the NPDES limit for pH was not met.
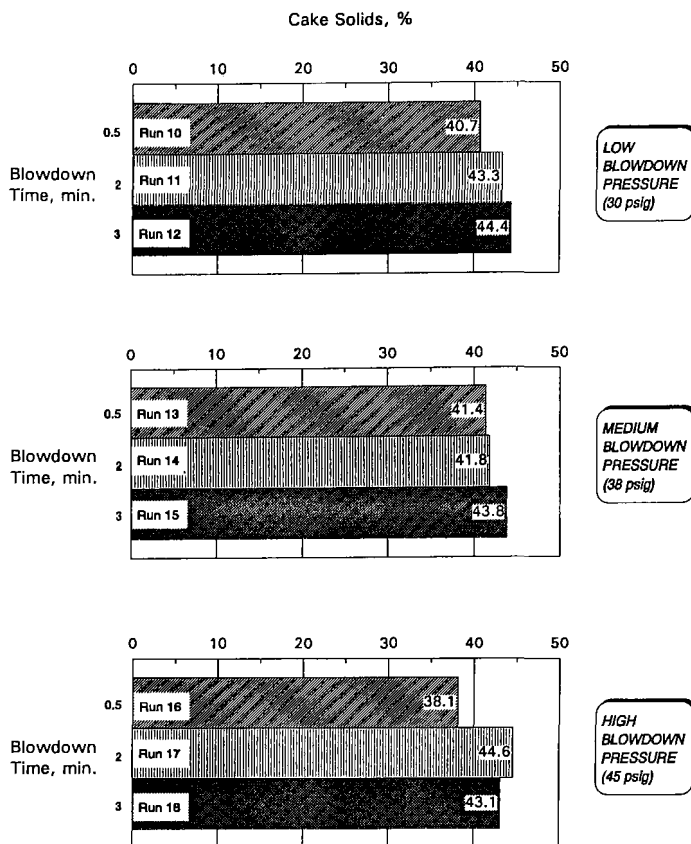
Figure 8
Filter Cake Solids Levels for Phase 2 Runs
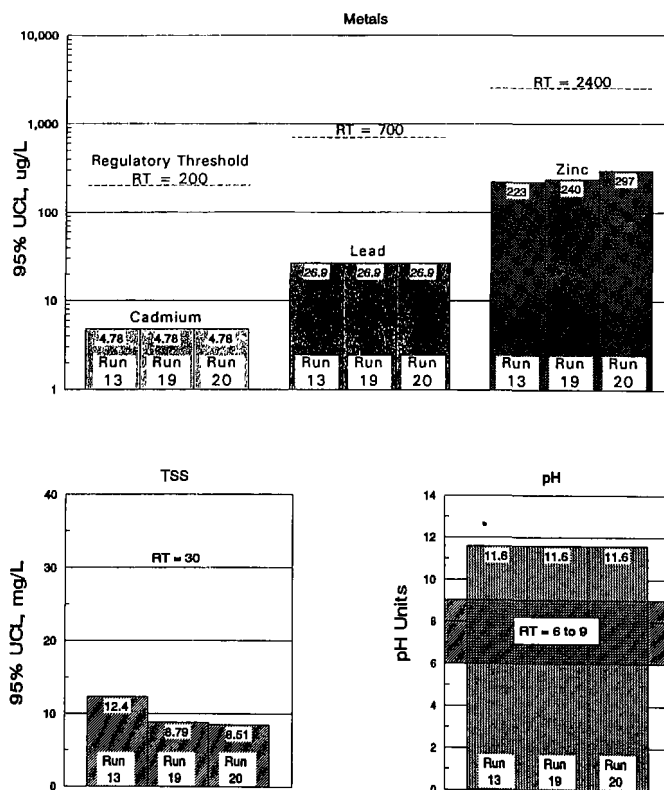
Figure 9
Comparison of Filtrate Quality for Reproducibility
Runs with Regulatory Thresholds
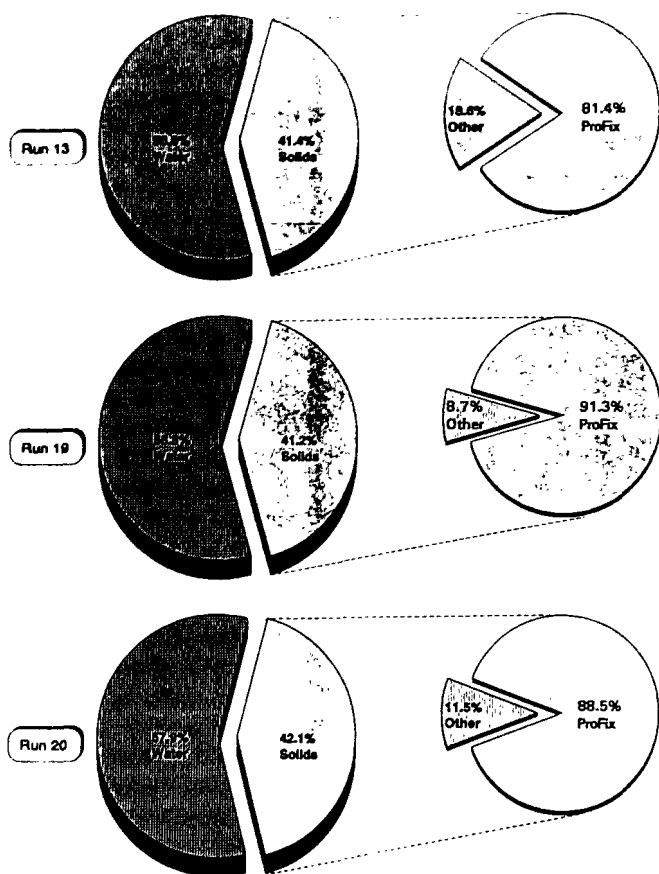
Figure 10
Filter Cake Composition for Reproducibility Runs

Figure 10 presents the composition of the filter cake in the reproducibility runs. The filter cake has approximately 41% solids. Of these solids, approximately 80 to 90% were from ProFix and the remaining were from: (1) TSS present in the untreated groundwater, (2) metals precipitated during the treatment and (3) unreacted lime from pH adjustment.

As a quality control check, a mass balance was performed for zinc and TSS in Runs 19 and 20. Figures 11 and 12 present the mass balance results for zinc and TSS, respectively. Figure 11 shows that the difference between zinc in and zinc out is approximately 15%, which is within the analytical precision for zinc measurement ($\pm$ 25%). Similarly, Figure 12 shows that TSS measurements are within the analytical precision ($\pm$ 30%).

Phase 4 Results

The results for the Tyvek reusability runs (Runs 21 and 22) are presented in Figure 13. In these runs, the same portion of Tyvek was used repeatedly for six cycles. Samples were composited after the first three cycles (Run 21) and the last three cycles (Run 22). Figure 13 shows that the microfiltration unit's performance was unaffected even after multiple uses of Tyvek.

Summary of Results for Noncritical Parameters

The demonstration also evaluated the results for noncritical parameters such as filter cake toxicity characteristics and the filtrate particle size distribution. Toxicity characteristics were considered a noncritical parameter because EP and TCLP metals were present at very low levels in the untreated groundwater. The particle size distribution measurement was included primarily to evaluate the developers' claim that the Tyvek filter can remove particles up to 0.1 micron. The filter cake toxicity characteristics were determined using EP and TCLP tests. A composite filter cake sample collected from the demonstration runs passed both these tests, indicating that the filter cake could be disposed of as a nonhazardous waste.

Zinc In = 100 g

Zinc Out = 85.0 g

Zinc In = 103 g

Zinc Out = 85.2 g

Not to Scale
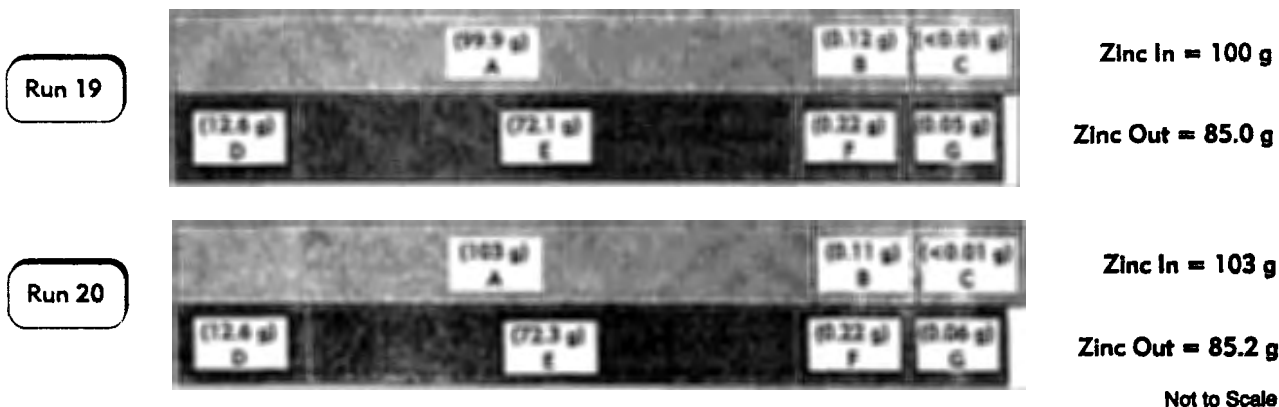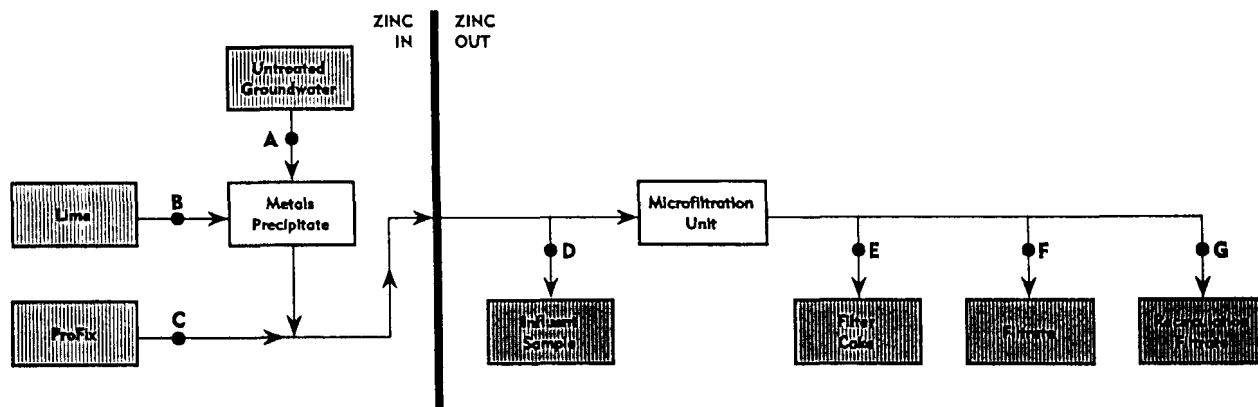
Figure 11
Zinc Mass Balance for Reproducibility Runs
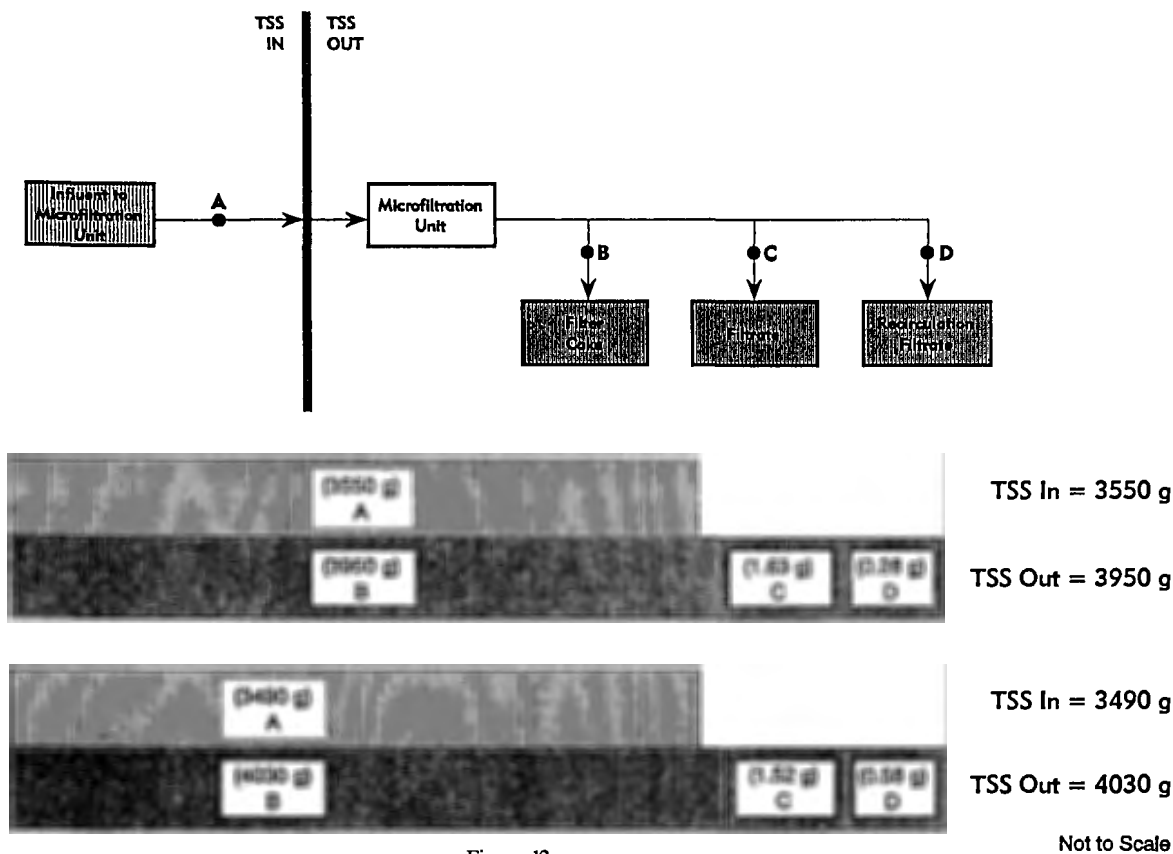
Figure 12
TSS Mass Balance for Reproducibility Runs
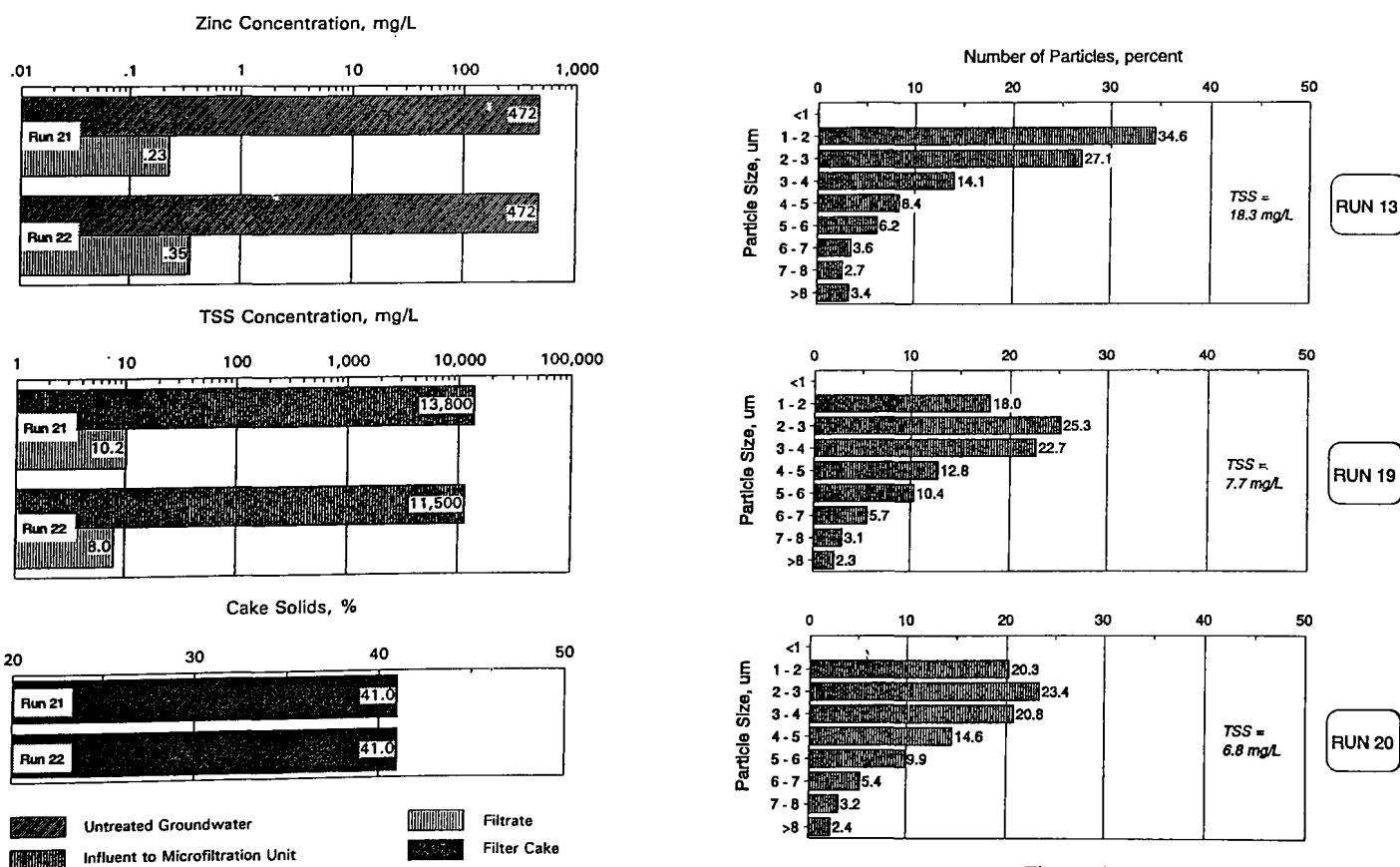
Figure 13
Tyvek Performance for Reusability Runs

Figure 14
Filtrate Particle Size Distribution
for Reproducibility Runs

Figure 14 presents the filtrate particle size distribution and TSS results for the reproducibility runs. The particle size was measured using a Coulter counter with a 0.5- to 500-micron measurement range. The data presented in this figure indicate that the majority of particles present in the filtrate were 1 to 4 microns in size. The TSS data for these runs were used together with the particle size distribution to estimate the particle concentration in each size range. In Run 13 for example, filtrate particles ranging from 1 to 2 microns and greater than 8 microns were present at 6.3 mg/L and 0.63 mg/L, respectively. These results do not support the developers' claim that the Tyvek filter can remove particles down to 0.1 micron. Similar observations were made for Runs 19 and 20.

CONCLUSIONS

The DuPont/Oberlin microfiltration system achieved the following results: (1) zinc and TSS removal efficiencies of 99.69 to 99.99% and (2) solids in the filter cake of 30.5 to 47.1%. At the optimum conditions (Run 13), the zinc and TSS removal efficiencies were 99.95%, and the filter cake solids were 41%.

ProFix contributed a significant portion (80 to 90%) of solids to the filter cake. The remaining solids were due to precipitated metals, TSS from the untreated groundwater and any unreacted lime.

The zinc and TSS removal efficiencies and the filter cake percent solids were unaffected by the repeated use (six cycles) of the Tyvek filter medium. This indicates that the Tyvek medium could be reused without adversely affecting the microfiltration system's performance.

The filtrate met the applicable NPDES standards, established for disposal into a local waterway, for metals and TSS at the 95% confidence level. However, the filtrate did not meet the NPDES standard for pH. The filtrate pH was typically 11.5, while the NPDES discharge standard is 6 to 9.

The filter cake passed the paint filter liquids test for all runs. Also, a composite filter cake sample from the demonstration runs passed the EP toxicity and TCLP tests.

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Response of Shallow Sandy Aquifers to Groundwater Remediation

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ABSTRACT

The recovery of contaminated groundwater, usually through wells, with subsequent treatment by one of several techniques (often referred to as "pump-and-treat"), is one of the more common remedial measures used to hydraulically control the under-ground movement of contamination and/or achieve some degree of aquifer restoration. Assessment of the aquifer response to remediation is a key aspect in system design and operation, as the expected degree and duration of the cleanup effort will affect operational costs and the ability to meet regulatory schedules.

A complex range of variables affects the response of an aquifer to the withdrawal of contaminated groundwater. As a result, it is difficult in most cases to accurately estimate at the beginning of recovery and treatment the length of time that will be required to reduce contaminant concentrations to a specified level. However, a common analytical approach to predicting aquifer response to contaminated groundwater withdrawal is based on the concept that contaminant concentrations in the groundwater will decline exponentially over time.

Four case study sites where groundwater contamination was addressed by the pump-and-treat method were selected from CH2M HILL projects in Florida. At all four sites, gasoline leaking from underground storage tanks had contaminated groundwater with dissolved volatile organic aromatic compounds. The use of exponential decay to describe the aquifer remediation process and the complexities created by influencing factors are illustrated by application of operational data from these sites.

INTRODUCTION

Contaminated groundwater is often recovered through wells and subsequently treated by one of several techniques in efforts to hydraulically control the underground movement of contamination and/or to achieve some degree of aquifer restoration. Designing and operating these "pump-and-treat" systems requires consideration of several important issues; of which prediction of aquifer response is one of the most critical and most difficult issues. Operational costs and the ability to meet regulatory schedules are highly dependent on the degree and duration of cleanup, but many factors influence those variables for a particular aquifer. The effect of these factors on the usefulness of the concept of exponential decay for estimating the time required to reduce aquifer contamination to a specified level is illustrated by application of data from four sites in Florida where groundwater contamination was addressed by the pump-and-treat method.

STUDY SITES

The four sites selected as case studies are located within the eastern coastal terrace areas of Florida, as shown in Figure 1. CH2M HILL has provided site assessment and remedial design for numerous pump-

and-treat projects throughout Florida; the case study sites were selected on the basis of the length of time that the remedial system had been in operation, the completeness and accessibility of the operational data base and client permission to use the available data.
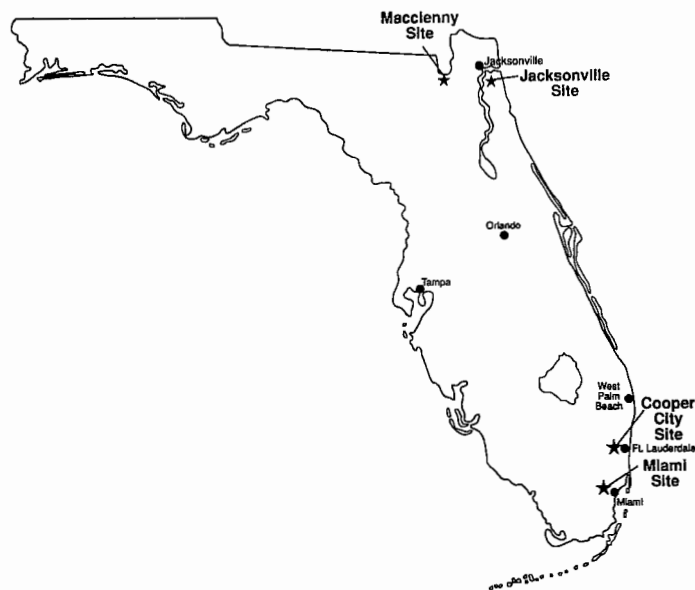
Figure 1
Case Study Site Locations

At all four sites, gasoline leakage from underground storage tanks had contaminated the groundwater with dissolved volatile organic aromatic (VOA) compounds, which include benzene, toluene, ethylbenzene and total xylene components as measured in the laboratory by U.S. EPA Method 602. Free hydrocarbon contamination also was found in the shallow groundwater beneath the Jacksonville and Miami sites. Generalized maps showing the lateral extent of groundwater contamination and the locations of monitor wells and remedial systems are provided for the Jacksonville, Macclenny, Cooper City and Miami sites in Figures 2, 3, 4 and 5, respectively.

Geologic profiles and estimates of the average horizontal hydraulic conductivity for the effective saturated depth of the surficial aquifer zone for the case study sites are summarized in Figure 6. The Macclenny site displays some characteristics atypical of the Florida coastal region in that layers of silty and clayey sands are interspersed with thin

seams of fine sands in the upper profile. The two sites in southeast Florida are underlain by the Biscayne aquifer, a highly productive limestone unit that occurs at relatively shallow depths and is overlain by sands and sands with limestone. As seen in Figure 6, the average unconfined water table surface occurs between 0.6 to 1.5 m (2 to 5 ft) below land surface at the sites.
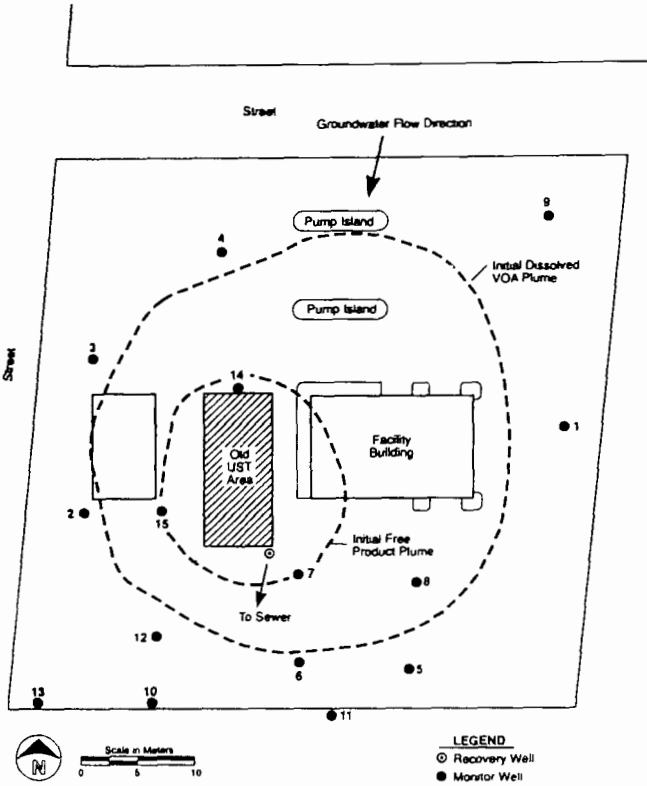
Figure 2
Jacksonville Site Plan
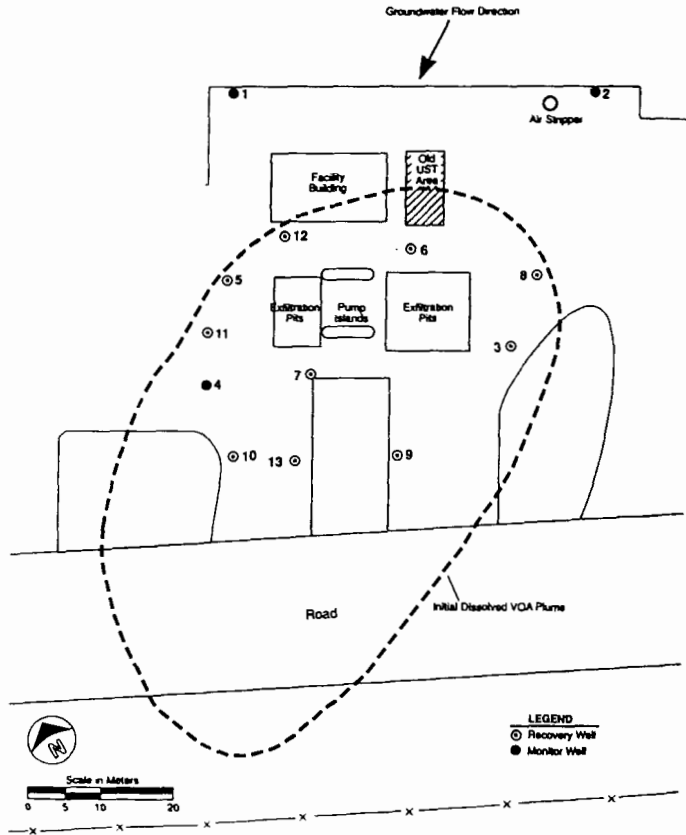
Figure 3
Macclenny Site Plan
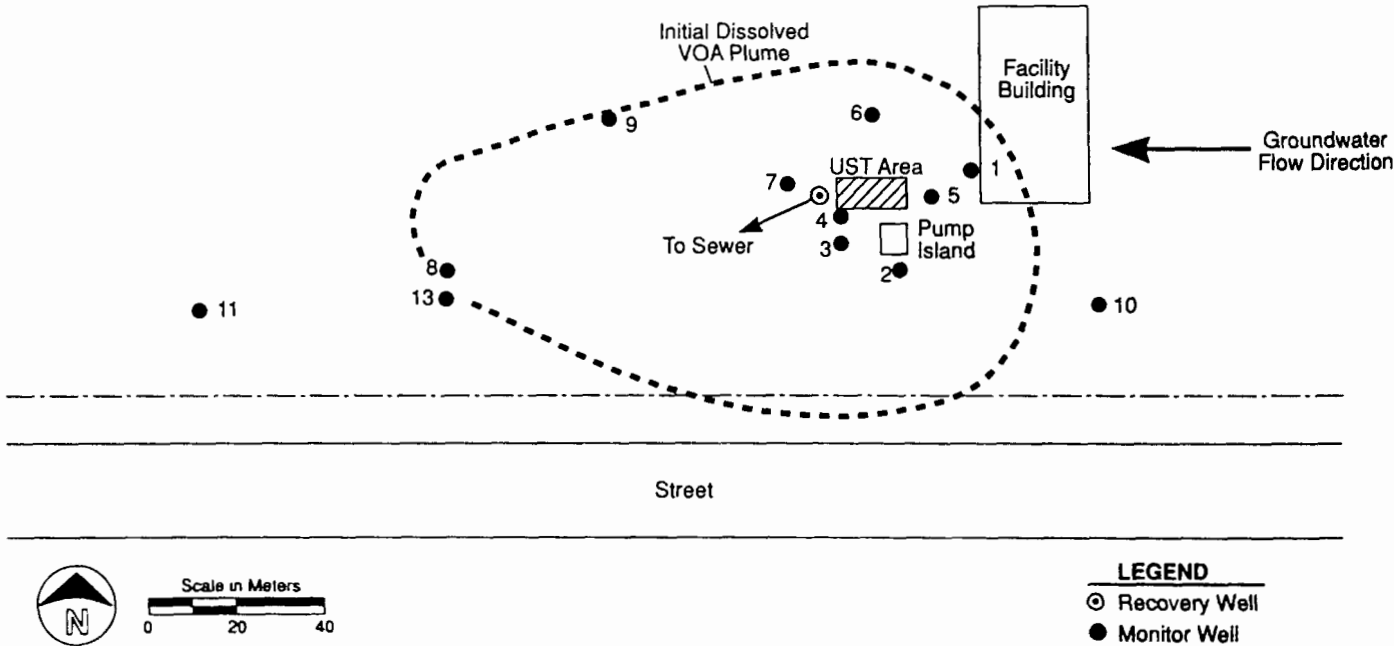
Figure 4
Cooper City Site Plan
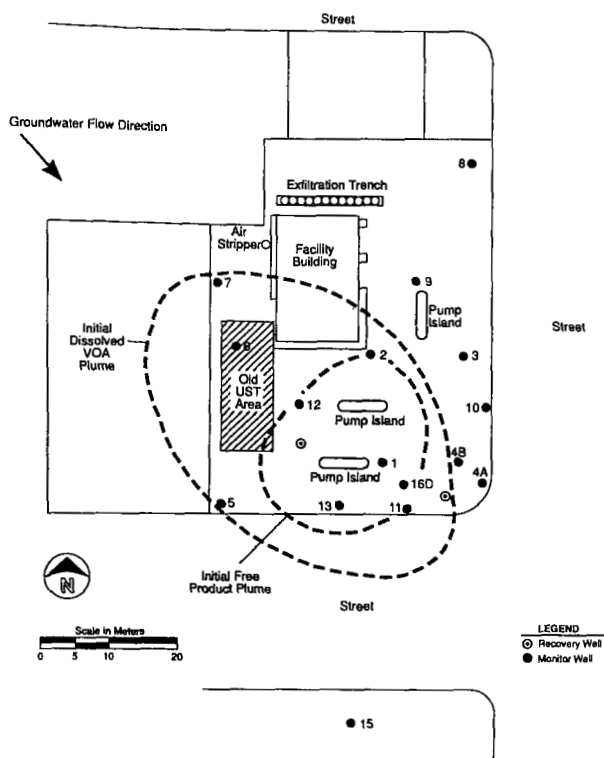
Figure 5
Miami Site Plan

EXPONENTIAL DECAY METHOD

Contaminant concentrations in groundwater will theoretically decline exponentially over time. The exponential decay method, which has been incorporated into current Florida regulations, extends this theory to recognize contaminant partitioning between solid and liquid phases; thus, it is assumed that at any point in time, a certain portion of the contamination is dissolved in the groundwater and the remainder is retained on the aquifer medium. As groundwater is withdrawn through the contaminated aquifer zone at a particular volume, the contaminants adhering to the medium are dissolved in the cleaner groundwater that flows into the area and is subsequently recovered from the aquifer system.

Mathematically, the concept of exponential decay starts from the statement that contaminant concentrations at any time are proportional to the amount present in the contaminated aquifer zone. The corresponding mathematical expression is a well-known, first-order, linear differential equation that is solved by separating variables and integrating. Table 1 shows the derivation and presents useful forms of the analytical solution. The decay constant in this application reflects the removal of contamination from the groundwater system by various remediation processes instead of by some specific form of biological decay activity alone.

INFLUENCING FACTORS

In assessing the usefulness of the exponential decay equation in this application, the major factors that influence aquifer response must be considered. Recovery of contaminated groundwater by wells with the objective of aquifer remediation generally assumes that the well system can create the capture zone required to recover the water and that
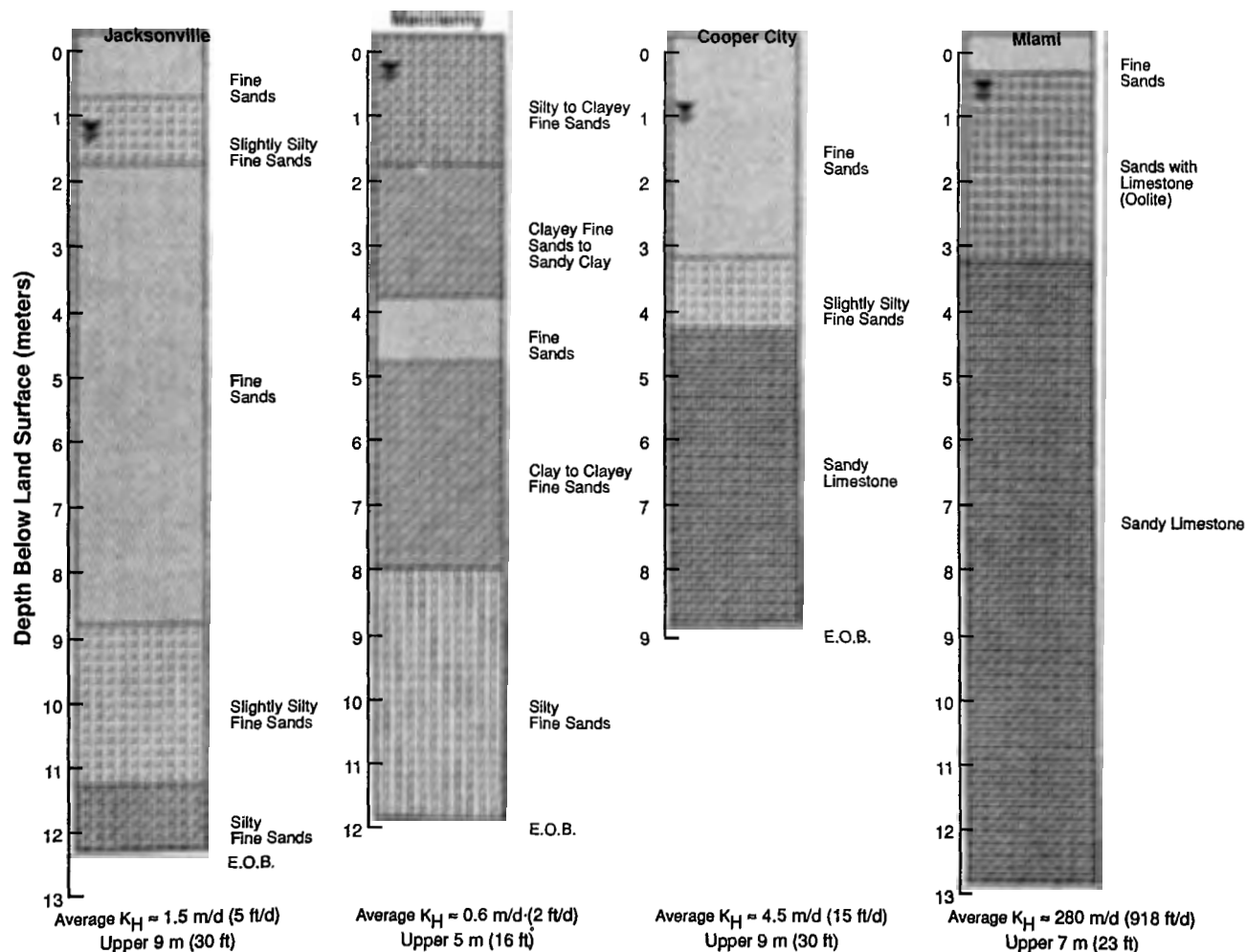
Figure 6
Hydrogeologic Profiles at Case Study Sites

Table 1
Derivation of First-Order
Exponential Decay Equation

Base Equation: $\dfrac{dC}{dt} = -KC$

Separating Variables: $\dfrac{dC}{C} = -Kdt$

Integrating: $\ln C = -Kt + C$

Solving: $C = e^{-Kt\,+C} \to C = e^{-Kt}e^{C}$
at $t = o,\ c = e^{C} = C_o$

Solution: $C = C_o e^{-Kt}$

Rearranging: $t_c = (\ln \dfrac{C}{C_o}) + -K$

Note: C in last equation is concentration at any time.

Table 2
Major Factors Influencing Aquifer Remediation
for Organic Contamination

Aquifer Characteristics

- Transmissivity
- Heterogeneity
- Thickness of Vadose Zone

Contaminant Partitioning

- Constituent Solubility
- Percent Fines and Organic Content of Aquifer Media

Well Placement and Pumping

- Constituent Travel Time
- Minimization of Stagnant Points (Multiple Wells)
- Vertical Extent of Contamination
- Minimization of Dilution Water and Cross-Contamination

Nature and Source of Contaminants

- Presence of Nonaqueous Phase Liquids
- Residual Contamination in Vadose Zone
- Definition of Lateral and Vertical Extent
- Source Identification

Remediation Criteria

- Realistic Performance Expectations
- Attainable Degree of Restoration

the contamination can be withdrawn from the aquifer system. These assumptions apply best where geologic conditions are simple, the aquifer is relatively homogeneous and only a dissolved form of contamination exists. More frequently, one or more of these conditions are not met.

Also, the need to achieve a prescribed degree of cleanup within a certain period appears to make it desirable to move large quantities of groundwater at the highest flow velocities practicable through the contaminated aquifer zone. Where aquifer conditions reasonably accommodate this objective, however, a corresponding reduction in contaminant concentrations may not be readily observed or extended periods of operation may result.

Some of the major factors that influence aquifer response to the remediation process are summarized in Table 2 and further discussed below.

Aquifer Characteristics

Aquifers comprising more permeable media yield higher pumping rates than aquifers with low permeability characteristics. Accordingly, higher groundwater withdrawal volumes and flow velocities are possible in more permeable aquifer systems, which increases the potential to achieve more timely aquifer remediation.

Heterogeneity within the aquifer system also affects remediation. Where silty or clayey layers are interspersed with sands, preferential flow paths are created during recovery in the more permeable zones. If contamination is present in the lower permeability layers, it can remain as a residual source and lengthen the remediation process, especially where groundwater fluctuations occur within these zones. If contamination is not present in the higher producing zones being pumped, dilution effects are incurred that not only impact remediation but can affect treatment system costs.

Low permeability aquifers and/or aquifers with high water table conditions may limit the volume and duration of on-site treated water discharge that may be part of a remedial system. As a result, the rate and duration of groundwater withdrawal are also restricted, which affects the remediation period.

Contaminant Partitioning

Many contaminants can be retained by the aquifer medium. This chemical partitioning to solid particulates tends to retard contaminant movement and lengthens remediation. The degree to which contaminants are sorbed and retained depends largely on the nature of the contaminants and the aquifer medium.

Generally, contaminants that are more soluble will adsorb less to solid particles and be more mobile in the groundwater system. Aquifers in which the medium has higher percentages of total organic carbon and/or clayey particles tend to adsorb and retard contaminants more than

aquifers composed primarily of clean sands.

Well Placement and Pumping

To minimize remedial system operating time, the goal in well placement is to reduce the travel time of contaminants to a point of recovery. Generally, in more permeable aquifers, a recovery well often can be located near the center of contamination to create the required capture zone. The use of a single well minimizes the hydraulic interferences and occurrence of groundwater stagnation points common with multiple-well systems. In less permeable aquifers, however, more recovery wells may be required throughout the lateral extent of the contamination plume. Special consideration may be necessary in recovery operations (e.g., alternate well pumping schemes) to mitigate well hydraulic interferences and groundwater no-flow zones and to improve contaminant travel time. The vertical distribution of contamination is an important consideration in well placement. In certain circumstances, some forms of dissolved contamination sink to lower portions of an aquifer, while other forms tend to remain at more shallow depths. The design of the recovery system must consider this vertical distribution in attempting to restore the aquifer, minimize treatment of uncontaminated groundwater and prevent contaminants from entering clean zones.

The rate of groundwater recovery may also affect the remediation process. Where contaminant partitioning or non-aqueous forms of contamination occur in the aquifer, the optimum recovery rate may be governed by the contact time required for the contamination in the solid and liquid phases to approach equilibrium conditions. If recovery rates are too high, large amounts of less contaminated groundwater may be generated, which affects the number of pore volume extractions and treatment costs.

Nature and Source of Constituents

Aquifer remediation at sites where contamination is present in the form of non-aqueous phase liquids (NAPLs) will generally take significantly longer than at sites where only dissolved contamination exists. Constituent concentrations in NAPLs are usually much greater than the concentrations that can be dissolved and transported in the groundwater flow system. As a result, a significant period of time may be required for the leaching process to culminate.

NAPLs can be more or less dense than groundwater. Where NAPL contamination is present as a floating layer on the groundwater surface, it usually is included in the recovery scheme. Residual saturation, however, may leave a percentage of the floating NAPL within the aquifer medium as a relatively immobile source of contamination. De-

pending on the degree of cleanup required, additional measures may be necessary to address residual contamination in both the saturated and unsaturated portions of the aquifer. Where NAPL contamination is more dense than water, residual saturation can be spread throughout the aquifer depth and remediation becomes even more difficult.

To achieve successful restoration, all potential sources of contamination that may affect performance of the remedial system must be identified and abated to the extent practicable, including off-site sources. The off-site migration of the contaminant plume most also be fully defined to provide a recovery system with the potential to achieve remediation. Thus, adequate field investigations are essential to remedial system design and operation.

Aquifer Remediation Criteria

Depending on the nature of contamination present, federal, state or local regulatory criteria may govern the design and evaluation of remediation. In some cases, site cleanup criteria are developed by the consultant based on a contamination and risk assessment and approved by the regulatory agencies. Florida regulations governing groundwater remediation involving hydrocarbon contamination include requirements that total VOA concentrations be reduced to 50 ug/L or less, with benzene reduced to less than 1 ug/L, in contaminated aquifers that are used or can be potentially used for drinking water. A risk assessment establishing alternative cleanup criteria may also be approved.

The performance goals of the remedial system should be realistic, based on in-depth consideration of the influencing factors, and reflected in the required degree of remediation. Once performance goals and schedules are established, they should be documented in written agreements or other legal instruments to provide a clear basis of understanding for all parties. It may not be possible to do so at the outset of projects where initial remedial actions are instigated to recover NAPLs discovered during excavations or in monitor wells, contaminated soils are excavated during removal of underground storage tanks or identified contamination poses immediate public health or environmental threats.

CASE STUDY COMPARISON

At the four case study sites, concentrations of VOAs in recovered groundwater have been routinely measured as influent to treatment systems since remedial system operations began. The data for each site were plotted for the available period of operational records as points on a graph.

The volume of groundwater within the contaminated aquifer zone at each site was then estimated based on the defined horizontal and vertical extent of dissolved contamination and effective porosity values considered representative of the saturated aquifer media at the sites. This volume was compared to the cumulative volume of contaminated groundwater recovered over time at a site to assess the number of pore volumes that had been withdrawn.

The exponential decay equation was solved using the measured data, and the resulting theoretical time distribution of dissolved VOA contamination was compared with the plotted operational data, as shown in Figures 7 through 10. For the last operational data point in the record, the figures also provide the duration of recovery, average decay coefficient, the estimated number of pore volumes that had been extracted through the contaminated aquifer zone and the ending VOA concentration.

Jacksonville Site

The theoretical exponential decay curve for the Jacksonville site shown in Figure 7 describes the general trend in decreasing VOA levels fairly well. However, after more than 2.5 years of recovery and extraction of 25 to 30 pore volumes of groundwater, influent VOA levels remained at approximately 800 ug/L, significantly above the 50 ug/L regulatory cleanup criteria. The results and the observed variations in the influent concentrations probably reflect the presence of NAPL floating on the water table, chemical partitioning of the contamination to the solid phase and the fluctuations of the water table into the vadose zone containing residual contamination.

Based on the theoretical equation and continuation of the decay coeffi-

cient, reduction of the influent VOA concentrations to the 50 ug/L level would take approximately another 2.5 years of groundwater withdrawal at the average pumping rate for the system of 10 gpm. If that were the case, an estimated total of 55 to 60 pore volumes would be extracted through the contaminated aquifer zone from startup through shutdown. With the presence of NAPLs, however, the required time and recovered volume could be even greater.

ESTIMATES AT LAST DATA POINT
Elapsed Time: 978 Days
Decay Coefficient: 0.0031 Days-1
Pore Volumes Extracted: 25-30
Concentration: 780 ppb
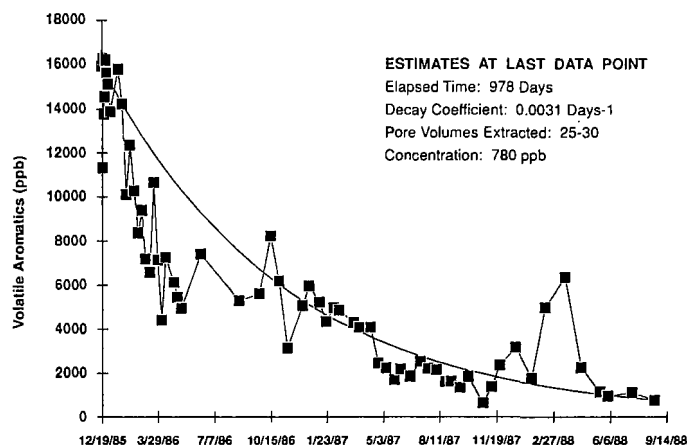
Figure 7
Measured and Theoretical Time Distribution of Dissolved
Volatile Aromatic Compounds at the Jacksonville Site

ESTIMATES AT LAST DATA POINT
Elapsed Time: 991 Days
Decay Coefficient: 0.0012 Days-1
Pore Volumes Extracted: 5-10
Concentration: 900 ppb
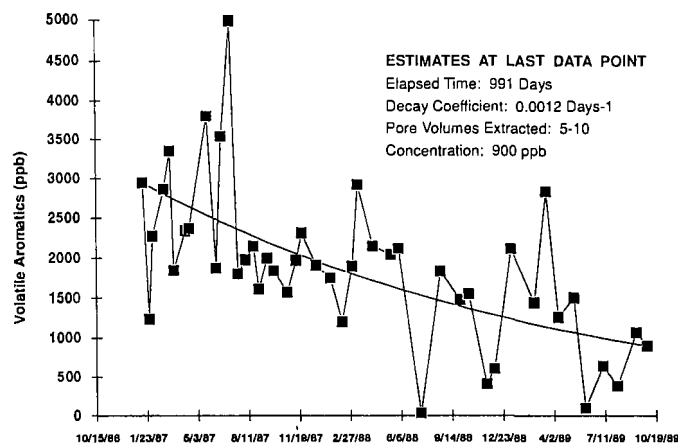
Figure 8
Measured and Theoretical Time Distribution of Dissolved
Volatile Aromatic Compounds at the Macclenny Site

ESTIMATES AT LAST DATA POINT
Elapsed Time: 530 Days
Decay Coefficient: 0.0112 Days-1
Pore Volumes Extracted: 20-25
Concentration: 18 ppb
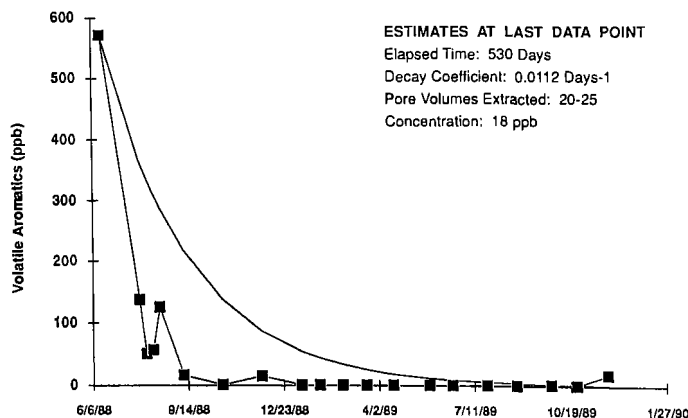
Figure 9
Measured and Theoretical Time Distribution of Dissolved
Volatile Aromatic Compounds at the Cooper City Site

ESTIMATES AT LAST DATA POINT
Elapsed Time 858 Days
Decay Coefficient 0.0046 Days-1
Pore Volumes Extracted 35-40
Concentration 152 ppb
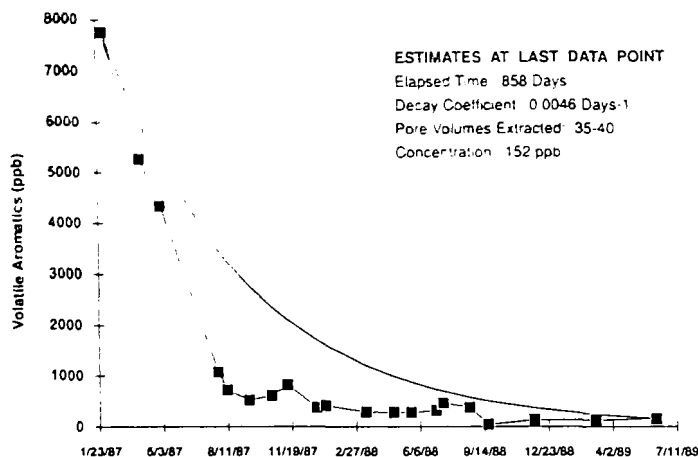
Figure 10
Measured and Theoretical Time Distribution of Dissolved
Volatile Aromatic Compounds at the Miami Site

After an extended shutdown, remedial operations have been continued at the Jacksonville site. It is anticipated that a soil vapor extraction system will be installed to address NAPL contamination in the vadose zone and to supplement the existing free product and groundwater recovery system.

Macclenny Site

Influent VOA concentrations at the Macclenny site have been erratic, but a general exponentially decreasing trend can be observed in the data shown in Figure 8. After more than 2.5 years of pumping, the influent VOA concentration of 900 ug/L remains significantly above the 50 ug/L cleanup criterion. These results and the observed variations in the influent concentrations probably reflect the heterogeneity of the subsurface profile with the presence of low permeability silty and clayey layers, chemical partitioning of the contamination to the solid phase and the fluctuations of the water table into contaminated portions of the vadose zone.

Based on the theoretical equation and continuation of the decay coefficient, reduction of the influent concentrations to the 50 ug/L level would require an additional 6.5 years of groundwater withdrawal at the average pumping rate for the system of 4 gpm. This additional recovery added to the amount of groundwater already withdrawn would roughly correspond to an estimated total of 35 to 40 pore volumes extracted through the contaminated aquifer zone since operations began.

Remedial operations continue at the site. Modifications to the remedial action plan are being developed to address contamination in the vadose zone. It is anticipated that soil excavation and thermal treatment will be recommended to supplement the groundwater recovery system.

Cooper City Site

Initial VOA concentrations were relatively low at the Cooper City site and decreased fairly rapidly upon startup of the recovery system. The theoretical exponential decay curve in Figure 9 tends to underpredict the decreasing trend in influent concentrations. The observed decline in the relatively short period of remediation probably reflects the low levels of dissolved groundwater contamination initially present, the relatively simple geologic profile, the lack of significant levels of contamination in the vadose zone, the permeable nature of the aquifer medium, and the ability to withdraw large volumes of groundwater through the contaminated aquifer zone over a relatively short period.

Remedial operations continue at the site. Groundwater influent concentrations remain below the regulatory cleanup criteria. Most site monitor wells generally yield groundwater samples that are also below the cleanup criteria, although a few exceed the allowable VOA and benzene levels. According to state regulations, remediation can generally be considered complete when samples from all monitor wells meet the criteria after recovery operations have ceased for 1 year.

Miami Site

The theoretical exponential decay curve in Figure 10 tends to underpredict the decreasing trend in influent VOA concentrations at the Miami site. Although a relatively quick decline in concentrations was experienced, the decline was followed by extended periods where little change in VOA levels occurred. Influent concentrations remained above the cleanup criteria after extraction of 35 to 40 pore volumes of groundwater over almost 2.5 years of recovery. The results may reflect the presence of NAPL floating on the water table, some chemical partitioning of the contamination to the solid phase and the fluctuations of the water table into the contaminated vadose zone. Negative effects of high withdrawal rates also may be indicated; large volumes of less contaminated groundwater may have been generated if the withdrawal rate exceeded the contact time required for the solid and liquid phases of contamination to approach equilibrium conditions.

Based on the theoretical equation and continuation of the decay coefficient, reduction of the influent VOA concentrations to the 50 ug/L level would take an additional 0.75 year of groundwater withdrawal at the average pumping rate for the system of 12 gpm. This additional recovery added to the amount of groundwater already withdrawn would roughly correspond to an estimated total of 90 to 95 pore volumes extracted through the contaminated aquifer zone since operations began. Because of the presence of NAPLs (and possibly the high withdrawal rates), however, this theoretical duration could be extended even further. Remedial operations continue at the site. Additional measures are being considered to address NAPL contamination in the vadose zone to supplement the existing free product and groundwater recovery system. Modification of the groundwater recovery system also is being considered.

CONCLUSIONS

For assessing aquifer response to continuing recovery operations, the first-order exponential decay equation appears to generally describe the decline in dissolved VOA concentrations over time. This function may, however, underpredict the actual reduction in VOA concentrations when the aquifer medium is highly permeable and large volumes of groundwater can be withdrawn through the contaminated aquifer zone over a fairly short period. The results indicate that groundwater recovery is most likely to achieve timely aquifer restoration where geologic conditions are relatively simple, the aquifer medium is permeable, residual contamination in the vadose zone is low and contamination exists only in the dissolved form. An excessive rate of groundwater recovery may extend the remediation period at some sites, and the presence of NAPL and/or residual vadose zone contamination may require a combination of soil and groundwater remedial technologies to achieve timely and cost-effective cleanup.

Aquifer remediation is an extremely complex process. Design and performance requirements for remedial systems should be developed based on in-depth consideration of major influencing factors. Site characterization, delineation of the horizontal and vertical extent of contamination, and the identification of source constituents are especially important. While the expected duration of remedial operations is often of interest to facility owners and regulatory agencies, accurate predictions are virtually impossible to make in most cases and are potentially litigious. When such predictions are required, they should be provided only with the clear understanding of their qualitative nature and with sufficient disclaimers to reflect the difficulties in making such forecasts.

The Effects of Creosote-Contaminated Groundwater On Slurry Cutoff Wall Soil Backfill

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ABSTRACT

Slurry cutoff walls have been used frequently in recent years to contain creosote-contaminated groundwater during the cleanup of wood preserving plants. However, the effectiveness of slurry cutoff walls could be limited by long-term degradation of the soil backfill from chemical reactions with creosote-contaminated groundwater. Because most of the slurry walls installed to contain creosite-contaminated groundwater have been for private-sector industries, little information is available to evaluate the effectiveness of this technology.

This paper discusses the results of compatibility tests performed on several laboratory-prepared soil backfill mixtures of on-site and off-site and creosote-contaminated groundwater from the Bayou Bonfouca Superfund site in Slidell, Louisiana. These results were used to evaluate the expected performance of a slurry cutoff wall installed at this site.

Each backfill mix tested was judged compatible with the creosote-contaminated groundwater and suitable for use as the slurry cutoff wall backfill material. Atterberg limits and flocculation tests also were conducted with both tap water and creosote-contaminated groundwater. Although inconclusive, these tests revealed no significant adverse changes in the characteristics of the bentonite.

INTRODUCTION

Slurry walls effectively reduce groundwater flow beneath dams and controlling inflow into deep excavation. Within the last decade, slurry wall technology has been used extensively to contain hazardous waste and to prevent clean groundwater from entering a contaminated site. However, the effectiveness of slurry wall technology is limited by the potential for degradation resulting from contamination with site-specific leachates.

The long-term effectiveness of slurry walls used to contain contaminated groundwater has not been determined with certainty. Most of the slurry walls installed for pollution control have been in place for relatively short periods of time. Little information is available to evaluate the effectiveness of this technology. Therefore, the long-term performance of the walls in the presence of chemical contaminants has not been well documented.

The information regarding the long-term (10 to 20 years) interaction between contaminated groundwater and soil-bentonite backfill can be obtained only from field performance. In the laboratory, the long-term effect is generally predicted by permeating at least two pore volumes of contaminated groundwater through the soil-bentonite samples and determining whether any measurable changes occur in the permeability of the soil-bentonite backfill.

Mitchell and Madsen[12] reported that the previous available results of compatibility tests in which organic chemicals were used as permeants have been both conflicting and confusing for the following reasons:

- Two million organic chemicals are known to exist
- Different test types and test parameters are used
- Permeant concentrations have varied
- Synergistic chemical effects are unknown
- Clay mineralogical properties vary widely

Although soil-bentonite slurry cutoff walls have been used to contain creosote-contaminated groundwater, these slurry walls were constructed primarily for privately owned firms. Quantitative information about the long-term performance of such walls was obtained by permeating soil-bentonite backfill with creosote-contaminated groundwater. These tests have revealed no significant increase in the permeability of soil-bentonite backfill.

CLASSIFICATION AND INDEX PROPERTIES OF AS-RECEIVED SOIL SAMPLES

Two 5-gallon buckets of off-site non-contaminated soils and 11 5-gallon buckets of on-site contaminated soils were used for testing. The index properties and classifications of the soils are described in the following paragraphs.

Off-site Non-Contaminated Silty Sand

The off-site non-contaminated soils were visually classified as light brown slightly silty sand containing approximately 8 percent of fines passing the No. 200 sieve with a coefficient of uniformity of 2.3. The soils were classified as SP-SM in accordance with the Classification of Soils for Engineering Purposes (ASTM D-2487).

On-site Contaminated Sandy Lean Clay

The on-site contaminated sandy lean clay had a natural moisture content of 30.4 percent, a liquid limit of 35 percent and a plastic limit of 15 percent. This soil contained approximately 59 percent of fines passing the No. 200 sieve. The soil was classified as CL in accordance with ASTM D-2487.

On-site Contaminated Clay

The on-site contaminated clay was generally yellowish-brown and brownish-gray. The natural moisture content of the clay was 31.1 percent; the liquid limit was 62 percent; and the plastic limit was 17 percent. This soil contained 94.3 percent fines passing the No. 200 sieve. The clay was classified as CH-type soil in accordance with ASTM D-2487. The particle size distribution is presented in Figure 1 and the Atterberg limits are shown in Figure 2.

The Atterberg limits of the composite fat clay sample also were determined after hydration in creosote-contaminated groundwater for 24 hours at a moisture content near the liquid limit. After hydration in the creosote-contaminated groundwater, the plastic limit equalled 17

percent; the plasticity index was 40 percent and the liquid limit was 57 percent. Although the liquid limit and plasticity index decreased slightly, the creosote-contaminated groundwater does not appear to affect the plasticity of the fat clay significantly.

Grain Size in Millimeters
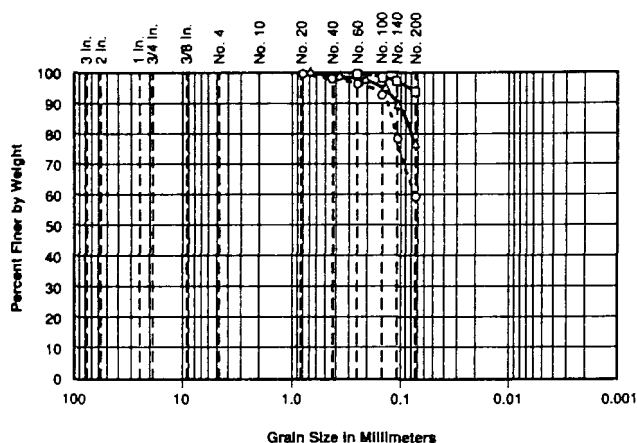
GRAVEL		SAND			SILT	CLAY
Coarse	Fine	Coarse	Medium	Fine		

SYMBOL	SAMPLE	DESCRIPTION	-200 (%)	PI (%)
□	Onsite Fat Clay	Yellowish-Brown and Gray Fat Clay (CH)	94.3	45
○	Onsite Sandy Lean Clay	Brown and Gray Sandy Lean Clay (CL)	58.7	20
△	Onsite Fat Clay-Sandy Lean Clay at 3:2 By Volume	Brown and Gray Lean Clay with Sand (CL)	75.3	32

Figure 1
Particle Size Distribution of On-site Fat Clay,
Sandy Lean Clay and Fat Clay-Sandy Lean Clay Mixes

CHARACTERISTICS OF CREOSOTE OIL AND CREOSOTE-CONTAMINATED GROUNDWATER

Fifteen 2-liter amber bottles of creosote oil and creosote-contaminated groundwater were used in the testing program. A summary of the results of chemical analyses conducted on the creosote oil and creosote-contaminated groundwater is shown in Table 1.

Before being used in the laboratory compatibility tests, the 11 creosote-contaminated groundwater samples were mixed together to create one composite sample. The composite sample was then filtered with Watman 541 filter paper (98 percent retention efficient of 20- to 25-μ size particles) to remove suspended particles.

CHARACTERISTICS OF BENTONITE PRODUCT

Federal Gel 90 bentonite was selected for use in preparing the soil-bentonite slurry wall backfill mixes. The Federal Gel 90 bentonite had an as-received moisture content of 7.7 ±0.1 percent as determined on three samples and a fines content of 96.9 percent.

Plasticity Characteristics and Effect of Creosote-Contaminated Groundwater on Clay Mineral Plasticity

The bentonite was hydrated in de-ionized water and creosite-contaminated groundwater to determine the effects of creosote-contaminated groundwater on the plasticity of the bentonite. As shown in Figure 3, after hydration in de-ionized water for 24-hours at a moisture content near the liquid limit, the Atterberg limits of the Federal Gel 90 bentonite were characteristic of a highly plastic clay with a liquid limit of 57.6 percent and plasticity index of 54.3 percent. Hydration

Liquid Limit, LL (%)
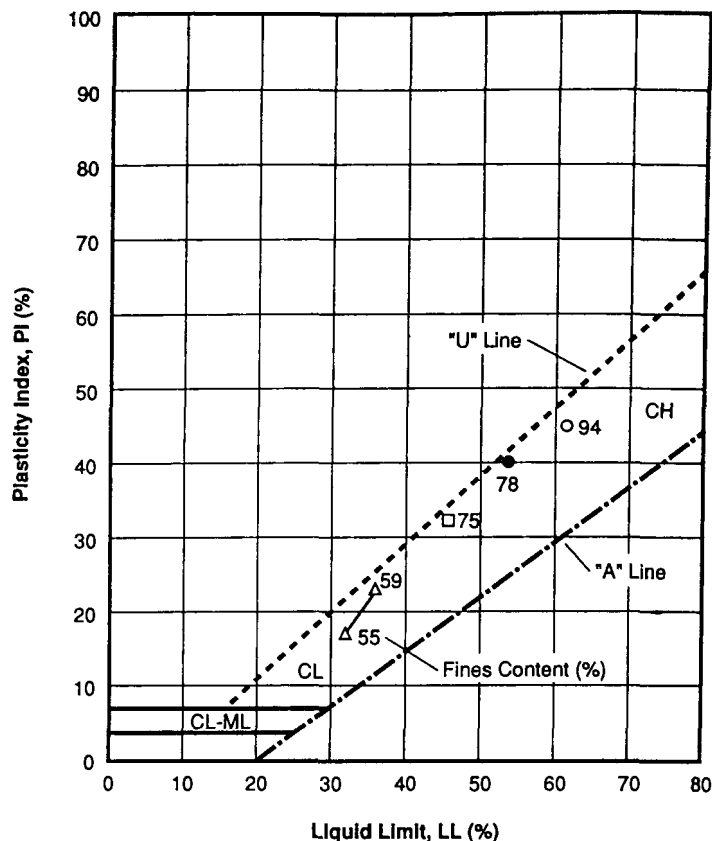
SYMBOL	SAMPLE
○	Onsite Fat Clay (CH)
△	Onsite Sandy Lean Clay (CL)
□	Onsite Fat Clay-Sandy Lean Clay Mix at 3:2 by Volume
●	Onsite Fat Clay-Sandy Lean Clay Mix at 3:2 by Volume with 4% Federal Gel 90 Bentonite

Figure 2
Plasticity Characteristics of On-site Fat Clay,
Sandy Lean Clay and Fat Clay-Sandy Lean Clay Mixes

in creosote-contaminated groundwater for 24 hours before testing at a moisture content near the liquid limit resulted in no effect on the plastic limit, a slight reduction in the liquid limit and a corresponding slight reduction in the plasticity index. Therefore, the creosote-contaminated groundwater does not appear to have a significant effect on the swelling ability and plasticity of the Federal Gel 90 bentonite clay minerals. The addition of creosote oil to the creosote-contaminated groundwater-bentonite "paste" after hydration for 24 hours at about the liquid limit resulted in a more significant reduction in the liquid limit and plasticity index was although the Atterberg limits were still characteristic of a highly plastic clay.

Settling/Flocculation Tests with Creosote-Contaminated Groundwater

The settling/flocculation characteristics of Federal Gel 90 bentonite in creosote-contaminated groundwater were compared with the behavior in de-ionized water to determine if the creosote-contaminated groundwater adversely affected the ability of the bentonite clay minerals to remain in suspension (i.e., not to floc and rapidly settle). Samples of Federal Gel 90 bentonite were hydrated in de-ionized water and creosote-

Table 1
Chemical Analysis Results of Creosote-Contaminated Groundwater and Creosote Oil

Parameter	Creosote-Contaminated Groundwater	Creosote Oil
Inorganic Constituents (mg/l)		
Calcium, Ca	101	168
Magnesium, Mg	24.0	3.20
Sodium, Na	61.7	92.8
Potassium, K	3.4	28.5
Iron, Fe	2.10	6.62
Manganese, Mn	1.13	0.20
Aluminum, Al	0.64	1.99
Antimony, Sb	<0.005	0.007
Arsenic, As	0.008	0.086
Barium, Ba	0.40	1.80
Beryllium, Be	<0.005	<0.05
Cadmium, Cd	<0.02	<0.20
Chromium, Cr	<0.01	<0.10
Cobalt, Co	<0.05	<0.50
Copper, Cu	<0.025	<0.25
Lead, Pb	<0.20	<2.0
Mercury, Hg	<0.0002	<0.0002
Nickel, Ni	<0.04	<0.40
Selenium, Se	<0.005	<0.05
Silver, Ag	<0.03	<0.30
Thallium, Tl	<0.005	<0.05
Vanadium, Vn	<0.05	0.70
Zinc, Zn	0.10	0.49
Semi-Volatile Compounds (mg/l)		
Naphthalene	30	130,000
2-Methylnaphthalene	4.1	26,000
Acenaphthene	3.4	26,000
Dibenzofuran	3.1	20,000
Fluorene	2.7	25,000
Phenanthrene	7.3	55,000
Anthracene	1.2	9,200
Fluoranthene	3.0	20,000
Pyrene	1.9	12,000
Benzo(a)anthracene	0.49	2,700
Chrysene	0.55	3,400

SYMBOL	SAMPLE
o	Hydrated in Tap Water
□	Hydrated in Creosote-Contaminated Groundwater
△	Hydrated in Creosote-Contaminated Groundwater and Creosote Oil

Figure 3
Plasticity Characteristics of
Federal Gel 90 Bentonite

contaminated groundwater at a bentonite content corresponding to approximately 40 Marsh-seconds as determined with a Marsh funnel viscometer in accordance with API RP 138 Standard Procedure for Field Testing Drilling Fluids.

The test results indicate that bentonite contents of approximately 5.2 percent in de-ionized water and 6.5 percent in creosote-contaminated groundwater are needed to achieve a viscosity of 40 Marsh-seconds. Accordingly, the creosote-contaminated groundwater had some effect on the swelling behavior of the bentonite clay minerals, as indicated by a higher bentonite content to achieve the same viscosity.

Settling tests were then performed with a slurry of Federal Gel 90 bentonite in de-ionized water at a viscosity of 37 Marsh-seconds and Federal Gel 90 bentonite in creosote-contaminated groundwater at a viscosity of 38 Marsh-seconds. The settling tests were performed in 10.2-cm diameter plexiglas cylinders with an initial height of slurry of 24.3 cm. After 68 days, the bentonite was still in suspension in both slurries, with no visible clear water interface above the clay slurry. Accordingly, the creosote-contaminated groundwater did not cause the Federal Gel 90 bentonite to floc or affect its ability to remain in suspension.

PREPARATION OF SOIL AND SOIL-BENTONITE BACKFILL MIXES

The following seven soil and soil-bentonite backfill mixes were

prepared with the off-site non-contaminated slightly silty fine sand, on-site contaminated fat clay and sandy lean clay and Federal Gel 90 bentonite:

- On-site contaminated fat clay soil backfill
- On-site contaminated fat clay and on-site contaminated sandy lean clay (at a ratio of 3:2 by volume) soil backfill mix
- On-site contaminated fat clay and on-site contaminated sandy lean clay (at a ratio of 3:2 by volume) with 4 percent Federal Gel 90 bentonite (by dry weight) soil-bentonite backfill mix
- Off-site non-contaminated slightly silty fine sand with 4, 6, 8 and 10 percent Federal Gel 90 bentonite (by dry weight) soil-bentonite backfill mixes

On-site Contaminated Fat Clay Soil Backfill

The composite sample of the on-site contaminated fat clay was mixed with tap water to moisture contents of 62 to 75 percent, and the slump was determined in accordance with ASTM C 143 Standard Test Method for Slump of Portland Cement Concrete. As shown in Figure 4, the test results indicate that moisture contents in the range of 60 to 70 percent are required for a slump of 4 to 6 inches, which is typically used for slurry wall backfill.
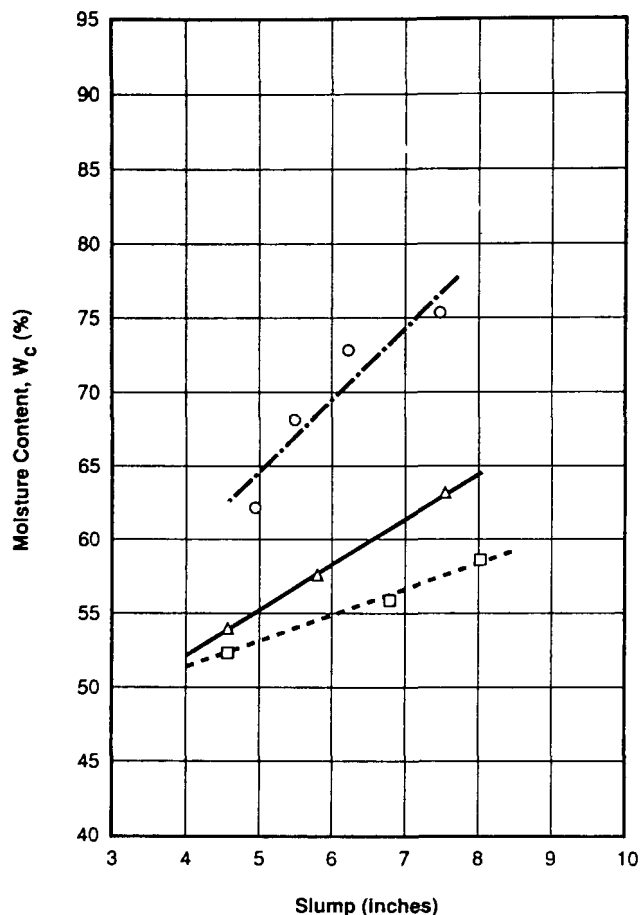
SYMBOL	SAMPLE
O	Onsite Fat Clay
□	Onsite Fat Clay-Sandy Lean Clay Mix at 3:2 by Volume
Δ	Onsite Fat Clay-Sandy Lean Clay at 3:2 by Volume with 4% Federal Gel 90 Bentonite

Figure 4
Slump vs Moisture for On-site Fat Clay, Sandy
Lean Clay and Fat Clay-Sandy Lean Clay Backfill Mixes

On-site Contaminated Fat Clay/Sandy Lean Clay Soil Backfill Mix

A composite sample of the fat clay/sandy lean clay mix was prepared by combining these soils at a ratio of 3:2 by volume at the as-received moisture contents and then thoroughly homogenizing the soils in a rotary-type mixer. The particle size distribution is presented in Figure 1, the Atterberg limits are shown in Figure 2 and the index properties of the mix are as follows:

- Moisture Content, $w_c(\%)$ 29.8
- Fines Content, -200(%)   75.3
- Liquid Limit, LL(%)   46
- Plastic Limit, PL(%)   14
- Plasticity Index, PI(%)   32
- Classification (ASTM D 2487)   CL

The mixture consisted of a brown and gray mottled lean clay with sand, classified as a CL-type soil in accordance with ASTM D-2487.

The slump test results shown in Figure 4 indicate that moisture contents in the range of 52 to 55 percent are required for a slump of 4

to 6 inches, as typically used for slurry wall backfill.

On-site Contaminated Fat Clay/Sandy Lean Clay with 4 Percent Federal Gel 90 Bentonite Soil-Bentonite Backfill Mix

A composite sample of the fat clay/sandy lean clay mix was prepared by combining these soils at a ratio of 3:2 by volume at the as-received moisture contents, adding 4 percent Federal Gel 90 bentonite by dry weight at its as-received moisture content and then thoroughly homogenizing the soils in a rotary-type mixer. The Atterberg limits of the mix are presented in Figure 2. The index properties of the mix are as follows:

- Moisture Content, $w_c(\%)$ 29.0
- Fines Content, -200(%)   78.2
- Liquid Limit, LL(%)   54
- Plastic Limit, PL(%)   14
- Plasticity Index, PI(%)   40
- Classification (ASTM D 2487)   CL

For a slump of 4 to 6 inches, which is typically used for slurry wall backfill, moisture contents in the range of 52 to 58 percent are required (Fig. 4).

Off-site Sand/Federal Gel 90 Bentonite Soil-Bentonite Backfill Mix

The off-site slightly silty fine sand was mixed with Federal Gel 90 bentonite at the as-received moisture contents at proportions of 4, 6, 8 and 10 percent bentonite by dry weight. The measured fines contents of the four sil-bentonite backfill mixes are 10.6, 12.2, 14.0 and 15.7 percent, respectively.

A summary of the slump versus moisture content determined on each off-site sand-bentonite backfill mix after hydrating for 24 hours with tap water at the test moisture contents is shown in Figure 5.

The four backfill mixes exhibit the expected trend of increasing moisture content for a given slump with increasing bentonite content. Achieving a 5-inch slump requires moisture contents of approximately 37, 41, 53 and 56 percent for bentonite contents of 4, 6, 8 and 10 percent, respectively, corresponding to an increase in moisture content of approximately 3.4 percent per 1 percent increase in bentonite content.
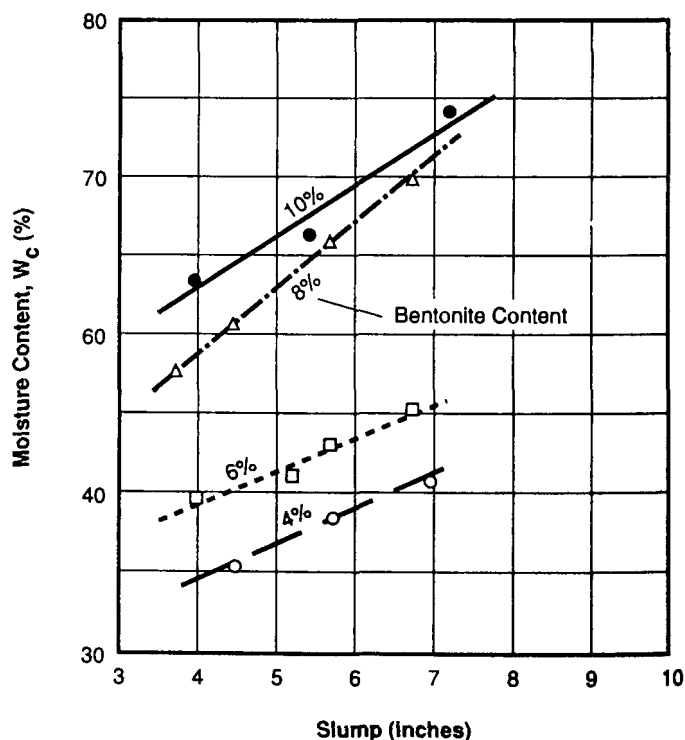
Figure 5
Slump vs Moisture Content for Off-site
Sand-Bentonite Mixes

PERMEABILITY TESTS AND COEFFICIENT OF PERMEABILITY OF SOIL AND SOIL-BENTONITE BACKFILL MIXES

The coefficient of permeability of each of the seven prepared soil and soil-bentonite backfill mixes was determined at one moisture content corresponding to a slump of between 4 and 6 inches. The test specimens were "spooned" into 3.57-cm diameter by 8.0-cm long stainless steel rigid-wall permeameters at the 4- to 6-inch slump consistency, simulating the placement of the slurry wall backfill in the field. A thin film of bentonite paste (approximately 0.5 to 0.7 grams net weight) also was applied to the inside face of the steel mold to minimize potential side wall leakage.

The specimens were then permeated with de-ionized water with net hydraulic head of 58 to 127 cm of water under a backpressure of 90 lb/in^2 to maintain saturation during flow. The hydraulic head was applied in increments, and the sample allowed to consolidate under the applied hydraulic gradient. The inflow to and outflow from each sample were monitored with time in calibrated burettes and the applied hydraulic head was measured with a pore pressure transducer. The coefficient of permeability was calculated for each recorded flow increment from the average of the inflow and outflow quantities and the average applied hydraulic head. The tests were continued until steady-state flow was achieved, as evidenced by values of inflow and outflow within approximately ±10 percent of the mean of the inflow and outflow for each increment and stable values of coefficient of permeability were measured.

A summary of the initial specimen conditions and coefficients of permeability measured on the various soil and soil-bentonite backfill mixes is shown in Table 2. The coefficient of permeability of the various soil and soil-bentonite backfill mixes varied from 2.8 x 10^{-8} to 9.2 x 10^{-8} cm/sec. The following criteria were established for an acceptable backfill:

- Slump of 4 to 6 inches
- Total Unit Weight >95 pcf
- Laboratory Coefficient of Permeability <5 x 10^{-8} cm/sec

Accordingly, the on-site fat clay soil backfill, on-site fat clay/sandy lean clay with 4 percent Federal Gel 90 bentonite backfill mix and off-site sand/Federal Gel 90 bentonite backfill mix with 6, 8 and 10 percent bentonite tested satisfy the specified criteria. Of the seven prepared backfill mixes, only the on-site fat clay/sandy lean clay and off-site sand/4 percent Federal Gel 90 bentonite backfill mixes did not satisfy the specified coefficient of permeability criterion.

Table 2
Coefficients of Permeability of Various Soil Bentonite Backfill Mixes

Sample	Moisture Content, w_c(%)	Total Unit Weight, γ_t(pcf)	Slump (inches)	Permeability Coefficient k_{rw}(cm/sec)
	Initial Conditions			
Onsite Fat Clay Soil Backfill	63.0	98.0	4.6	2.8 x 10^{-8}
Onsite Fat Clay/Sandy Lean Clay Soil Backfill Mix	52.3	96.1	4.5	9.2 x 10^{-8}
Onsite Fat Clay/Sandy Lean Clay with 4% Federal Gel 90 Bentonite Backfill Mix	51.8 / 55.8	102.0 / 99.5	4.0 / 5.2	2.9 x 10^{-8} / 4.0 x 10^{-8}
Offsite Sand/Federal Gel 90 Bentonite Backfill Mix				
4% Bentonite	35.2	109.1	4.3	7.2 x 10^{-8}
6% Bentonite	40.6	107.1	4.6	4.6 x 10^{-8}
8% Bentonite	51.5	100.7	4.7	3.7 x 10^{-8}
10% Bentonite	55.3	95.5	4.8	3.5 x 10^{-8}
10% Bentonite	55.8	98.1	5.0	2.9 x 10^{-8}

COMPATIBILITY TESTS AND EFFECT OF CREOSOTE-CONTAMINATED GROUNDWATER ON COEFFICIENT OF PERMEABILITY OF BACKFILL MIXES

The results of the above permeability tests led to the selection of four backfill mixes for compatibility testing to determine the effect of permeation with creosote-contaminated groundwater on the coefficient of permeability. The following four backfill mixes were selected for compatibility testing:

- On-site fat clay soil backfill
- On-site fat clay/sandy lean clay soil backfill mix
- On-site fat clay/sandy lean clay with 4 percent Federal Gel 90 bentonite backfill mix
- Off-site sand/8 percent Federal Gel 90 bentonite backfill mix

The samples selected for compatibility testing were extruded vertically from the stainless steel rigid-wall permeameter mold onto the bottom pedestal of a flexible-wall permeameter and encased within two 0.008-inch-thick latex membranes. The samples were consolidated in increments under an isotropic effective consolidation stress of 4 lb/in^2 with a backpressure of 94 lb/in^2. The specimens were then permeated with de-ionized water with hydraulic heads of 250 to 300 cm.

The inflow to and outflow from each sample were monitored with time in calibrated burettes and the applied hydraulic head was measured with a pore pressure transducer. The coefficient of permeability was calculated for each recorded flow increment with the average of the inflow and outflow quantities and the average applied hydraulic head. Permeation with de-ionized water was continued until steady-state flow was achieved, as evidenced by values of inflow and outflow within ±10 percent of the mean of the inflow and outflow for each increment and stable values of the coefficient of permeability were measured.

A summary of the coefficients of permeability measured on the selected soil and soil-bentonite backfill mixes with the flexible-wall permeameters and compared with the coefficients of permeability measured with the rigid-wall permeameters is shown in Table 3.

Table 3
Summary of Permeabilities Measured with Flexible-Wall and Rigid-Wall Permeameters

Sample	Rigid-Wall k_{rw}(cm/sec)	Flexible-Wall k_{fw}(cm/sec)	Ratio k_{rw}/k_{fw}
	Coefficient of Permeability		
Onsite Fat Clay Soil Backfill	2.8 x 10^{-8}	1.0 x 10^{-8}	2.8
Onsite Fat Clay/Sandy Lean Clay Soil Backfill Mix	9.2 x 10^{-8}	2.0 x 10^{-8}	4.6
Onsite Fat Clay/Sandy Lean Clay with 4% Federal Gel 90 Bentonite Backfill Mix	4.0 x 10^{-8}	1.2 x 10^{-8}	3.3
Offsite Sand/8% Federal Gel 90 Bentonite Backfill Mix	3.7 x 10^{-8}	1.1 x 10^{-8}	3.4

As a result of consolidation under the isotropic effective consolidation stress of 4 lb/in^2 and greater imposed hydraulic head, the coefficients of permeability measured with the flexible-wall permeameters were 2.8 to 4.6 times less, with an average of 3.5 times less, than those measured with the rigid-wall permeameters.

Because the measured coefficient of permeability was lower than expected, the test specimens were then dismantled, reduced from the initial length of 7.5 to 7.9 cm to approximately 4.0 cm and reset within the flexible-wall permeameters to meet the requirement of permeating the specimens with a minimum of two void volumes of flow within approximately 6 weeks. The specimens were then again consolidated under an isotropic effective consolidation stress of 4 lb/in^2 with a backpressure of 94 lb/in^2 and permeated with de-ionized water at hydraulic heads of 250 to 300 cm. The coefficients of permeability to de-ionized water were measured on the shortened specimens and, as expected, found to be essentially identical to the coefficients of permeability shown above ($k_f w$) as measured before the specimens were shorted.

The specimens were then permeated with creosote-contaminated

Table 4
Summary of Compatibility Test Results on Soil and Soil Bentonite Slurry Wall Backfill Mixes

Sample	Initial Conditions[a]		Consolidated Conditions[b]			Final Conditions				Compatibility Test Duration		Coefficient of Permeability, k_{fw}(cm/sec)	
	Moisture Content, w_c(%)	Total Unit Weight, γ_t(pcf)	Moisture Content, w_c(%)	Total Unit Weight, γ_t(pcf)	Void Volume (cm³)	Moisture Content, w_c(%)	Total Unit Weight γ_t(pcf)	Void Volume (cm³)	Saturation S(%)	Time (days)	Void Volumes of Flow	Initial	Final
Onsite Fat Clay Soil Backfill	60.2	98.4	50.7	106.5	21.9	45.8	109.6	19.6	100	90	2.29	1.1×10^{-8}	9.2×10^{-9}
Onsite Fat Clay/ Sandy Lean Clay Soil Backfill Mix	51.7	101.5	39.2	115.5	19.2	35.2	116.2	18.4	98	63	2.55	1.8×10^{-8}	1.6×10^{-8}
Onsite Fat Clay/ Sandy Lean Clay with 4% Federal Gel 90 Bentonite Backfill Mix	55.6	103.5	42.6	113.2	18.5	38.3	113.4	17.4	98	74	2.33	1.3×10^{-8}	9.7×10^{-9}
Offsite Sand/ 8% Federal Gel 90 Bentonite Mix	55.5	105.7	34.5	116.2	16.0	32.6	116.2	15.5	97	63	2.43	1.2×10^{-8}	1.5×10^{-8}

[a] Initial conditions for compatibility test specimens correspond to conditions existing at end of testing in rigid-wall permeameter prior to transferring of specimens to the flexible-wall permeameters.

[b] Consolidated conditions correspond to conditions existing after application of isotropic consolidation stress of 4 lb/cm² and hydraulic head of 250 to 300 cm of water, and subsequent trimming of specimens from initial lengths of 7.5 to 7.9 cm to 3.99 to 4.46 cm.

SYMBOL	SAMPLE
Δ	Onsite Fat Clay
●	Onsite Fat Clay-Sandy Lean Clay
□	Onsite Fat Clay-Sandy Lean Clay with 4% Bentonite
○	Offsite Sand with 8% Bentonite

Figure 6
Coefficient of Permeability vs Void Volumes
of Flow from Compatibility Test
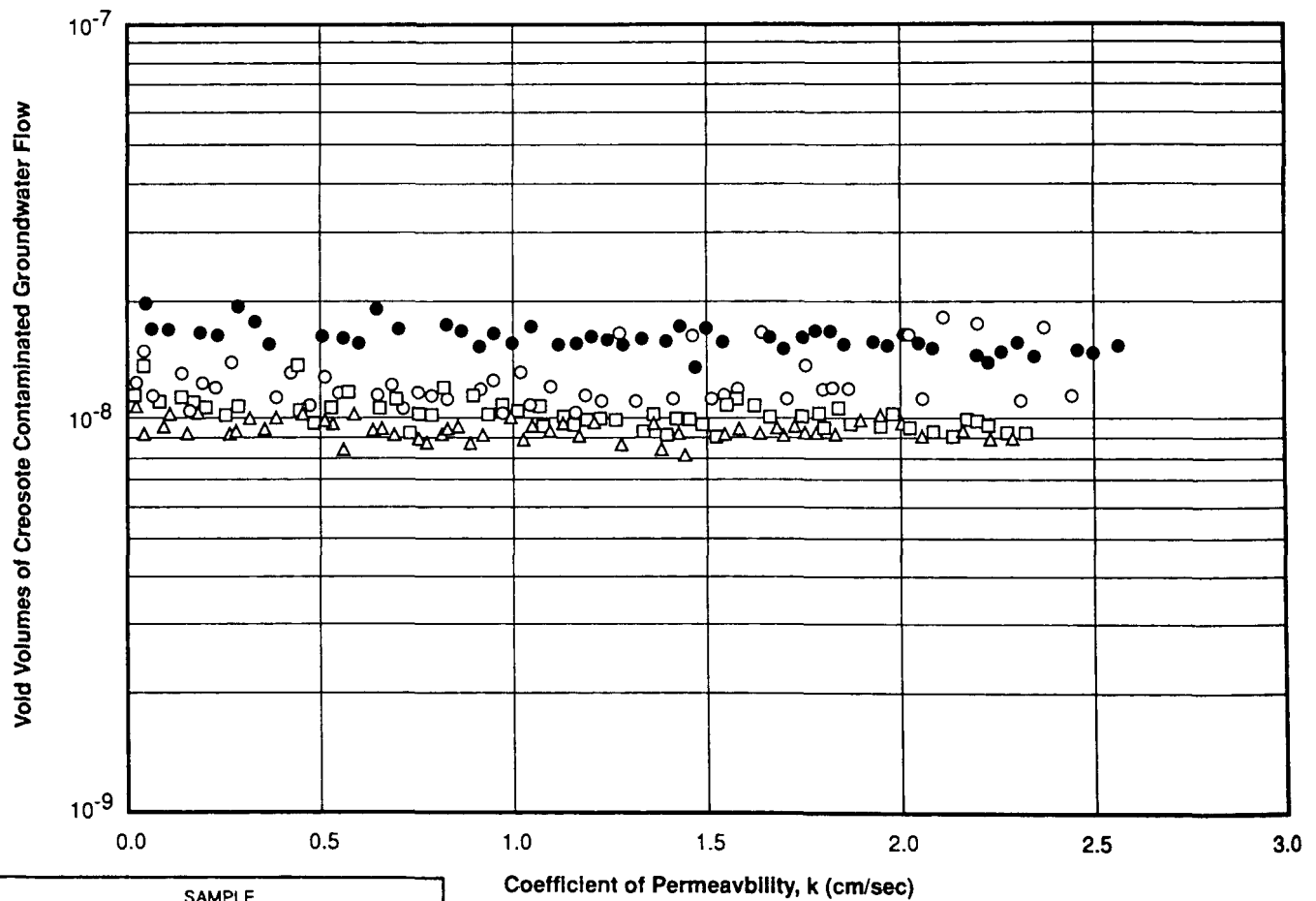
groundwater for 63 to 90 days, during which time 2.29 to 2.55 void volumes of creosote-contaminated groundwater were permeated into the test specimens. The test durations, void volumes of flow, initial and final coefficients of permeability and final physical properties of the test specimens are presented in Table 4. The measured coefficient of permeability versus void volume of flow for each backfill mix is shown in Figure 6. As shown in Figure 6, for the permeated quantities of creosote-contaminated groundwater, the coefficients of permeability remained essentially unchanged.

CONCLUSIONS

From the experimental results described above, the following conclusions can be drawn:

- After hydration in creosote-contaminated groundwater for 24 hours, the Atterberg limits of Federal Gel 90 showed no significant change from those hydrated in de-ionized water.
- Creosote-contaminated groundwater did not cause the Federal Gel 90 bentonite to flocculate or affect its ability to remain in suspension.
- After permeating soil-bentonite backfill with 2.3 to 2.5 pore volumes of creosote-contaminated groundwater, the permeabilities of the backfill remained essentially unchanged.

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Waste Without a Place—The Pentachlorophenol Problem

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ABSTRACT

The tangled web of RCRA hazardous waste classification presents a situation where hazardous waste generated through implementation of a remedial action may have no viable treatment or disposal options available under present regulations. This situation could apply to actions at RCRA Subtitle C permitted facilities, state-led or voluntary remedial actions which have to meet RCRA or equivalent state regulations and CERCLA actions by application of ARARs. The situation is particularly complicated for waste generated by remedial action which consists of soil, surface water and groundwater. The problem exists because of the RCRA Subtitle C classification and treatment standards for hazardous waste containing dioxin compounds, but also pertains to waste containing pentachlorophenol and related compounds when no specific dioxin compounds are present in the waste.

A state led remedial action, currently confidential, is used to illustrate the complexity of the regulations, their impact on potential treatment and disposal options and the lack of commercially available hazardous waste management facilities which are permitted to accept these wastes. The various RCRA hazardous waste classifications for soil, water and debris containing pentachlorophenol and 2,4,5-trichlorophenoxy-propanoic acid (2,4,5-TP, Silvex) are reviewed. These waste classifications yield three different treatment and disposal situations which are based on knowledge of the origin of the waste materials, even though the presence and concentration of the constituents are similar:

- Waste materials which cannot be commercially treated or disposed as hazardous waste
- Waste materials which can be treated and commercially disposed as hazardous waste
- Waste materials which are classified as solid waste or which can be treated and disposed as solid waste

This case history illustrates the application of RCRA classification of "listed" waste, "characteristic" waste by EP Toxicity and "characteristic" waste by the new TCLP test for soil, water and debris. It also addresses wastes classified by the "derived from" rule and the "mixture" rule. It examines the impact to treatment and disposal options, including delisting, brought about by the regulatory approach to hazardous waste classification on the basis of waste origin as well as constituent concentrations.

INTRODUCTION

The site is located in what is currently a combined residential and commercial area of a major city. It was used previously for the manufacture, formulation, storage and distribution of a wide variety of agricultural herbicides and pesticides. A preliminary assessment of the site indicated the presence of residual organic compounds associated with the past activities in the structural members of the buildings, in the soil above the groundwater and in the groundwater. The geology of the site is essentially low permeability clay soil to a depth of approximately 15 feet, underlain by strata of sand, silt and clay of varying thickness. The water table is at a depth of approximately 4 to 6 feet below the surface. The ground surface at the site is flat and nearly horizontal with building floor slabs at grade. Because of the low permeability clay soil and topography, lateral gradients are almost nonexistent, except for localized lateral flow toward the storm drains surrounding the site. Organic compounds which had been released during past facility operations are essentially confined to the upper few feet of the soil, shallow groundwater within the upper clay soil and backfill around the storm drains.

The site was voluntarily remediated and there was an agreement with the state regulatory agency to document the proposed remedial actions. Since the site is within a metropolitan area, is not on the NPL and could be valuable for future commercial or light manufacturing use, the selected remedial action was removal of hazardous and solid waste materials for off-site commercial treatment and/or disposal. Land disposal was selected for a majority of the soil and debris, but provisions were made for incineration of some materials as required because of high constituent concentrations in localized areas. The essential elements of the program consisted of:

- Demolition and disposal of one building
- Decontamination of one building
- Excavation and disposal of soil containing pesticide, herbicide and other organic chemical compounds
- Investigation of the groundwater to confirm the lack of migration of the site-related compounds

The remedial action was developed and implemented on a fast-track basis; the project involved sampling and analyses of the soil and building materials concurrent with the remedial activities. The analytical data were used to determine the specific areas of the site which required remedial excavation. They also were used to determine the applicable waste coding of the excavated soil and debris, to determine the appropriate method of soil and debris disposal and to complete the waste manifest forms. Because of the wide variety of organic compounds present at the site and the timing of the project, the California list restrictions and the soft hammer provisions of the first third land disposal restrictions were applicable.

RCRA WASTE CLASSIFICATION

Because the constituents detected were judged to have been caused by releases from past manufacturing and formulation activities at the

site, the waste materials containing hazardous constituents were subject to the hierarchy of RCRA hazardous waste classification. The contaminated soil and below ground debris were judged to be listed wastes by the "cleanup of a spill into or on any land or water" provision of 40 CFR Subpart D, Section 261.33(d). Thus, the "P" and "U" waste codes were applicable to most of the constituents detected. Determination of whether building demolition debris was hazardous waste was made pursuant to the "characteristics" provisions of 40 CFR 261.24.

Pentachlorophenol

During the program, samples of soil and debris from below ground were reported to contain pentachlorophenol and 2,4,5-TP. Although these compounds are listed with the "U" waste codes in 40 CFR 261.33, they are not given a "U" code number. Instead, they are referenced to waste code F027 in 40 CFR 261.31. Because of past site operations, the waste materials containing these constituents could also be classified as waste code F020. The distinction between F020 and F027 is not critical since both codes are considered as a dioxin class waste which includes codes F020 through F023 and F025 through F028. It is noted that there is no requirement to determine if waste containing pentachlorophenol actually contains dioxin, it is simply coded as a dioxin waste by association. These dioxin code waste materials are subject to the land disposal restrictions and treatment standards of 40 CFR 268.41 and 268.42.

The 40 CFR 268.42 treatment standards require incineration as the specified treatment technology if the total constituent concentration in the waste (CCW) of halogenated organic compounds (HOCs) is greater than 1,000 mg/kg (California restriction for HOCs). For concentrations less than 1,000 mg/kg total HOCs, treatment standards have been established by incineration for specific dioxin compounds in 40 CFR 268.41, but the regulations do not mandate incineration as the required treatment technology. The treatment standard for pentachlorophenol is 0.01 ppm based on constituent concentration in the waste extract (CCWE) from the TCLP test. Land disposal of dioxin class waste containing pentachlorophenol is permitted for concentrations below this treatment standard.

In addition to being included as a constituent within the F020 and F027 "listed" waste codes, pentachlorophenol is also included as a hazardous waste constituent within "listed" codes F039, K001 and U050. The F039 waste code is for multisource leachate and the treatment standard for pentachlorophenol is 0.089 mg/L (CCW) in wastewater and 7.4 mg/kg (CCW) in nonwastewater. The K001 code is applicable only to the disposal of bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol. Pentachlorophenol is also regulated as a constituent in creosote within waste code U050. The treatment standards for pentachlorophenol as a K001 and U050 waste constituent are 0.18 mg/L (CCW) for wastewater and 7.4 mg/kg (CCW) for nonwastewater (40 CFR 268.43). Wastes with pentachlorophenol concentrations below the treatment standards can be land disposed. These "listed" waste codes did not apply at the example project site because wood treating was not performed at the site. They are included in this discussion to indicate the different land disposal treatment standards which are applied to the same constituent for different "listed" waste codes.

If a waste is not able to be classified as "listed" waste, the determination of whether the waste is hazardous is made by the "characteristics" of reactivity, ignitibility, corrosivity or toxicity. The recent revisions to 40 CFR 261.24 implementing toxicity characteristic (TC) by the TCLP test now include pentachlorophenol as a regulated "characteristic" hazardous waste constituent. By these TC revisions, solid waste which contains pentachlorophenol, but which is not a "listed" waste, is hazardous by "characteristic" if its leachate concentration by TCLP is greater than 100 mg/L. The hazardous waste code for pentachlorophenol by "characteristic" is D037. If the leachate concentration is less than 100 mg/L, the waste is not a hazardous waste and may be managed as a solid waste; consequently, it is permitted to be land disposed as a solid waste.

In summary, waste containing pentachlorophenol may be a "listed"

hazardous waste which can be land disposed at concentrations below the various treatment standards for the "F," "K" and "U" codes. Alternatively, it may be a D037 code "characteristic" hazardous waste which may be land disposed at concentrations at or above the established "regulatory level," but which is not a hazardous waste below the "regulatory level." It should be noted that the "regulatory level" is not a land disposal restriction level, but is a level which has been established solely to determine if a waste is hazardous. The applicable "F," "K" and "U" "listed" hazardous waste treatment standards and the D037 "characteristic" hazardous waste "regulatory level" are as follows:

Waste Code	Waste Form	Standard/Level	Basis
F020 et. al.	All	0.01 ppm	CCWE
F039	Wastewater	0.089 mg/L	CCW
F039	Nonwastewater	7.4 mg/kg	CCW
K001, U050	Wastewater	0.18 mg/L	CCW
K001, U050	Nonwastewater	7.4 mg/kg	CCW
D037	All	100 mg/kg	CCWE

2,4,5-TP

The compound 2,4,5-TP is no simpler to deal with. Although it is included as an F020 and F027 "listed" waste constituent, there is no treatment standard established in 40 CFR 268.41. Thus, as a dioxin "listed" waste it cannot be land disposed at any concentration according to 40 CFR 268.31. It also is included within multisource leachate "listed" hazardous waste code F039 with a treatment standard of 0.72 mg/L (CCW) for wastewater and 7.9 mg/kg (CCW) for nonwastewater. This compound was previously included as "characteristic" hazardous waste code D017 in the 40 CFR 261.24 regulations and also is included in the revised 40 CFR 261.24 regulations as a "characteristic" waste by the TCLP test. As a "newly regulated" waste by revised 40 CFR 261.24 regulations, it has a "regulatory level" of 1.0 mg/L by TCLP (CCWE) for wastewater and nonwastewater. However, because it was previously regulated under 40 CFR 261.24, it also has a land disposal treatment standard of 7.9 mg/kg (CCW) for nonwastewaters. Thus, as a "characteristic" waste, if the total concentration of 2,4,5-TP is less than 7.9 mg/kg, the material is hazardous and can be land disposed, but if the concentration is less than 1.0 mg/L in a TCLP extract, the material is not hazardous waste. It is noted that a primary drinking water standard of 0.01 mg/L has been established for 2,4,5-TP. Thus, even though solid waste material with this compound cannot be accepted for land disposal at a commercial hazardous waste disposal facility, it can be consumed in drinking water.

Proper disposal of waste containing pentachlorophenol, 2,4,5-TP and other dioxin class constituents is a complex matter based on the waste code (waste origin specific) and the constituent concentration. As a K001 or U050 waste code, pentachlorophenol may not be land disposed at a concentration above 7.4 mg/kg. As an F020 or F027 waste code, pentachlorophenol may not be land disposed at a concentration above 0.01 ppm in the TCLP extract, but it is not even a hazardous waste up to 100 mg/L in the extract as code D037. It is arguable that a compound should be regulated on the basis of its total concentration and on the basis of its TCLP leachate characteristics. However, in the author's opinion it makes no technical sense that a compound be regulated at different levels on the basis of its total concentration. Furthermore, it is ridiculous that a compound is not considered to be a hazardous waste at a leachate concentration 10,000 times greater than its hazardous waste land disposal leachate concentration restriction. It is also ridiculous that a compound cannot be accepted for disposal at a commercial disposal facility, but is permitted to be in drinking water.

TREATMENT AND DISPOSAL OPTIONS

The technically available treatment options for waste containing pentachlorophenol vary depending on concentration and waste form. As is

the case with other organic compounds, treatment by incineration or biologic processes is technically feasible, particularly at higher concentrations. Wastewater can be treated by a variety of means such as UV Peroxide oxidation and carbon adsorption. However, the practical treatment and disposal options are a nightmare because of RCRA regulation waste classification and the lack of commercial RCRA disposal facilities which accept dioxin class wastes.

At present, there are no commercial treatment or disposal facilities permitted to accept pentachlorophenol as a "listed" dioxin class waste, waste codes F020 and F027, even though a land disposal treatment standard has been established. Industry representatives have indicated that a special permit is required along with a separate public comment period. Apparently, those commercial facilities which did apply were denied a permit, but most did not apply for fear of jeopardizing their existing permits because of potential emotional issues about dioxin raised during the public comment process. It is understood that there are commercial facilities intending to apply for permits to incinerate dioxin class wastes, but as of September 1990, none have been permitted. The only available commercial disposal option is for disposal of liquids at a few deep injection well sites which recently received "no migration permits."

Although there are no commercial treatment or disposal facilities for solid materials, there is one commercial facility which is permitted to accept dioxin class waste for containerized storage. Even though commercial facilities cannot accept waste containing pentachlorophenol as a dioxin class waste, they are permitted to accept pentachlorophenol with the other "listed" and "characteristic" waste codes. It is interesting to note that the pentachlorophenol concentration permitted to be land disposed under these other codes is significantly higher than the concentration permitted under the dioxin codes.

At the example site, some of the soil from the cleanup contained pentachlorophenol and/or 2,4,5-TP. This soil was judged to be an F020/F027 waste, a "listed" dioxin class waste. This classification was deemed appropriate since the remedial action at the site was a cleanup of a spill "into or on any land or water" (40 CFR 261.33(d)) from the formulation and manufacture of pesticides containing these and other, compounds. The facility did not produce, manufacture or otherwise deal with creosote or wood preserving products so the K001 and U050 codes were not applicable. The detected compounds were not from multisource leachate so the F039 code was not applicable.

The site is not on the NPL, so the cleanup could not take advantage of the on-site remediation preference of CERCLA or the waiver of RCRA regulations as ARARs under CERCLA. At CERCLA sites, soil containing pentachlorophenol is often treated and placed back in the ground at the site. In most of these cases, the "placement" provisions of RCRA are considered to be not applicable or appropriate. Even though the majority of the soil which did contain pentachlorophenol was determined to have concentrations well below the applicable land disposal restrictions, it could not be commercially landfilled because the commercial disposal facilities do not have permits to accept the dioxin class wastes. Because the soil was classified as a "listed" waste, on-site treatment would not eliminate the off-site commercial disposal problem because the "derived from" rule would cause the treated soil to continue to be a "listed" waste.

On-site biologic treatment or soil washing may have been technically feasible and on-site incineration certainly would have been technically feasible as treatment options to deal with the soil which contained pentachlorophenol. On-site incineration as a treatment option was discounted because it was judged essentially impossible to obtain an incinerator permit for this site because of its location within a residential neighborhood of a large city. More critical, however, was that all technically feasible treatment options require excavation of the soil for treatment. Consequently, after treatment the soil would have to undergo "placement." Such "placement" has to be in a RCRA permitted landfill, but the soil would continue to be an F020/F027 "listed" waste by the "derived from" rule provisions of 40 CFR 261.3(c).

Since there are no commercial landfills to accept the F020/F027 dioxin class wastes, there was no commercial means of disposing of the soil after treatment. The option of constructing a landfill on-site and ob-

taining a RCRA permit for soil disposal or storage was considered to be infeasible because of the site location and characteristics. Delisting of the treated soil is theoretically possible, but practically impossible. To even consider delisting, the treatment option would likely have to be incineration in order to reduce the pentachlorophenol and other chemical constituent concentrations to extremely low or nondetectable levels. Unfortunately, the option cycle returns to the probable impossibility of obtaining a permit for an on-site incinerator and the lack of permitted off-site commercial incinerators. Since there was insufficient space at the only commercially permitted storage facility for the estimated volume of soil which contained pentachlorophenol and because of the enormous cost of storage (approximately $5.00/day/drum) for an unspecified time, any remedial option requiring excavation and later placement was considered to be not viable.

In the absence of a commercial facility to accept the soil which contained pentachlorophenol, the majority was left in the ground. Because of the inability to commercially handle dioxin class wastes under present regulations and permit conditions, such materials remain in the ground at many sites. The small amount of soil which was excavated or removed by investigation drilling and sampling and a small volume of soil which was excavated in very limited areas, are presently warehoused at the only available commercial facility. By RCRA regulations, this material must remain in storage until it can be transported to a different facility with a RCRA treatment, storage or disposal permit.

The building debris from the site did not require a "listed" waste classification since the constituents which were present in the building materials were not from the cleanup of a spill "into or on any land or water." The structural building materials in the building which was decontaminated were analyzed for both total concentration and TCLP extract concentration of pesticides and herbicides to determine if they would be hazardous waste by "characteristic" in the event the building was demolished in the future. Both analyses were employed because it was presumed that if the building were demolished in the future the new toxicity characteristics would be in effect and both analyses would be required for pentachlorophenol as previously noted. The analytical results indicated such building debris would be solid waste.

It was decided to dispose of the debris from the building which was demolished as part of the remedial program at a permitted hazardous waste landfill, even though it could have been disposed at a solid waste facility. There was a slightly higher cost for disposing of the debris at a hazardous rather than solid waste landfill, but disposal at the hazardous waste facility was selected as a more responsible means of dealing with the debris which contained hazardous constituents.

As part of the remedial action, precipitation and groundwater which accumulated in the excavations on the site and precipitation which could have potentially come into contact with materials containing site related constituents (contact water) were collected for treatment and/or disposal. A small carbon treatment unit was installed on-site to treat approximately 200,000 gallons of collected contact water and a temporary permit was obtained to discharge the treated water to the storm drain system. The collected contact water was judged to be "listed" hazardous waste by the "mixture" rule in 40 CFR 261.3(a)(2)(iv) for a variety of site related constituents. However, some of the contact water contained very low concentrations of 2,4,5-TP and was segregated from the remaining contact water.

About half of the treated water met the constituent specific discharge requirements; the other half failed to meet the requirements for constituents other than the 2,4,5-TP. Because there were no commercial disposal facilities available at the time for the contact water containing the listed dioxin class waste, the on site treatment provided a mechanism to reduce the F020/F027 waste from thousands of gallons to a few drums of solids residue. During the course of the project a deep injection well disposal facility received a "no migration" permit and it was decided to dispose of the contact water which did not initially meet discharge requirements at this facility rather than provide additional treatment. This decision was primarily based on schedule considerations even though it was slightly more expensive than additional treatment.

The solids from the water treatment were filter pressed to reduce

their water content and also mixed with lime to further solidify them. The solids were analyzed for the F020/F027 constituents and they were not detected. Even so, by the "derived from" rule and the "mixture" rule these solids were also "listed" F020/F027 waste. Due to the F020/F027 compounds, these solids could not be commercially land disposed. Delisting the solids was considered so they could be disposed of rather than stored. However, there is no regulatory mechanism to delist a material for a specific constituent or set of constituents. If there were, the residual solids could have continued to have been classified as "listed" waste without F020/F027 constituents and could have been land disposed. However, because of concentrations of other "listed" waste constituents in the solids, and because of the tremendous time and expense involved in a delisting petition, it was decided to commercially store these drums of solids.

When the carbon unit was selected for treating the collected contact water, the carbon suppliers indicated the carbon could be regenerated, even with the F020/F027 compounds. They would not regenerate carbon containing 2,3,7,8-TCDD. The collected contact water was analyzed for this 2,3,7,8-TCDD at levels of 0.2 ng/L (ppt). None was detected at this level. However, near the completion of the project the suppliers of the carbon refused to regenerate the carbon because the regeneration ash would be considered a "listed" F020/F027 waste by the "derived from" rule and could not be disposed of. It is presently contemplated that the spent carbon will have to be drummed and commercially stored.

It is noted that if the soil at the site had been determined to have been hazardous by "characteristic" and not by "list," it could have been directly landfilled or could have been treated on-site. If it could have been treated to a level where the constituents causing it to be a "characteristic" waste cease to be detected, or were at concentrations below the TCLP levels for the newly identified waste, the materials would no longer be a hazardous waste. Also, the "derived from" and "mixing" rules would not have applied to the water or any treatment residue. Classification as a "characteristic" waste would have been appropriate if the origin of the constituents had been unknown. In this case, ignorance may have been more blissful.

COMMENTARY

The RCRA regulations were not initially contemplated to address the classification and disposal of soil and debris. The treatment standards have been set based on manufacturing and production waste streams, not for contaminated soil. Although the U.S. EPA has indicated they will deal with this issue, they have failed to do so thus far and it is not known when they will promulgate standards for soil and debris.

The present regulations and waste classification system are complex in themselves, but the system becomes irrational when the waste has different constituent treatment standards based on classification by its origin. The situation is exacerbated when one of the origin based classifications eliminates disposal of hazardous waste by accepted methods and at constituent levels below all of the established treatment standards. It is ridiculous that the regulations have yielded a situation where contaminated soil is left in the ground because of a regulatory inability to properly deal with it because of its origin, while it can be dealt with at similar and higher constituent concentrations because of a different origin or because of ignorance of its origin.

The regulations do not encourage proper disposal of hazardous waste; they inhibit it. When the cleanup of a site is more dependent on the origin of a constituent rather than its concentration, the system has failed. Knowing a constituent's origin does not enhance protection of the environment. The U.S. EPA and Congress need to be more aware of situations like this in order to develop actions which will foster voluntary cleanup of sites without having to resort to CERCLA in order to sidestep RCRA. RCRA and CERCLA are for environmental protection and need to be refocused to address this goal.

Land Ban Wastes: Pitfalls in Certification/Demonstration Submittal

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ABSTRACT

The HSWA include specific restrictions on the land disposal of RCRA-defined hazardous wastes. The Land Disposal Restrictions "soft hammer" regulations prohibited the disposal of wastes in surface impoundment or landfill units unless the receiving unit met the RCRA minimum technology requirements and generators certified that they had made a good-faith effort to locate and to contract with treatment and recovery facilities for treatment that was practically available.

The generator was required to submit to the Regional Administrator a demonstration and certification that the requirements of 40 CFR 268.8(a)[1] had been met. The demonstration had to include a list of facilities contacted, each facility official's name, facility addresses, telephone numbers and each contact date. The correct certification to be submitted depended on whether the generator determined that there was or was not practically available treatment. The certification statement had to be signed by the generator prior to submission.

The Agency has identified several treatment technologies that are generally considered appropriate for handling soft hammer wastes. Those technologies that are deemed appropriate for the non-wastewater forms of soft hammer wastes include: metal recovery, leaching/oxidation, metals stabilization, ash stabilization, chemical oxidation, biodegradation, incineration and PCB incineration. Technologies generally considered for wastewater soft hammer wastes include: aqueous metal recovery, chromium reduction, metals precipitation, steam stripping, carbon adsorption, oxidation/reduction, chemical oxidation, biodegradation, incineration and PCB incineration. The actual choice of a particular treatment technology would depend on the physical and chemical characteristics of a specific waste.

For soft hammer wastes that were to be land disposed or treated off-site, generators had to comply with the Land Disposal Restrictions notification, certification and demonstration requirements. This paper presents an overview of land disposal restrictions with particular emphasis on soft hammer certification/demonstration submittals and pinpoints the EPA review process to evaluate the validity of the certification.

INTRODUCTION

The HSWA[1] to RCRA[2], signed on Nov. 8, 1984, prohibited the land disposal of specified RCRA hazardous wastes beyond statutory dates established by Congress unless: (1) the wastes are treated to a level or by a method specified by the U.S. EPA, (2) it can be demonstrated there will be no migration of hazardous constituents from the land disposal unit for as long as the wastes remain hazardous or (3) the wastes are subject to an exemption or variance from meeting the treatment standards.

HSWA directed the U.S. EPA to establish treatment standards for each of seven groups of RCRA hazardous wastes by specific dates[3] These

dates are referred to as statutory deadlines and will eventually restrict land disposal of all RCRA hazardous wastes as follows: spent solvent- and dioxin-containing wastes (Nov. 8, 1986), California List Wastes (July 9, 1987), First Third Wastes (Aug. 8, 1988), spent solvent-, dioxin-containing and California List Soil and Debris from CERCLA/RCRA Corrective Actions (Nov. 8, 1988), Second Third Wastes (June 8, 1989), Third Third Wastes (May 8, 1990) and newly identified wastes (within six months of identification as a hazardous waste).

HSWA provided that if the Agency failed to set treatment standards for First or Second Third Wastes by their statutory deadline, then the wastes would become restricted under the soft hammer provisions until the U.S. EPA set treatment standards for them, or until May 8, 1990. The soft hammer provisions specified certain restrictions that would have to be met before the wastes could be land disposed in landfills or surface impoundments.

Generators of soft hammer wastes had to comply with the Land Disposal Restrictions (LDR) certification and demonstration requirements as well as the notification requirements for all LDR wastes. Notification requirements (40 CFR 268.7) include name and address of facility, the U.S. EPA hazardous waste number, the U.S. EPA I.D. Number, manifest associated with shipment of waste and waste analysis data, where available. The required language for certification statements may be found in 40 CFR Part 268.8. Prior to disposal, the generator had to demonstrate that he had made a good-faith effort to locate and contract with treatment and recovery facilities practically available, which provided the greatest environmental benefit. The demonstration had to include a list of facilities, facility officials contacted, addresses, telephone numbers and contact dates. The generator also should have provided information on the chosen treatment technology selected or why treatment/recovery was not practical for the waste.[4]

To help the U.S. EPA expedite its evaluation of certifications/demonstrations, certain pitfalls should be avoided. An examination of some of these pitfalls and a discussion of effective submittals are presented below.

OVERVIEW OF LDR

For purposes of the LDR program, the statute specifically defines land disposal to include, but not be limited to, any "placement" of hazardous waste in a land, fill, surface impoundment, waste pile, injection well, land treatment facility, salt dome, salt bed formation, underground mine or cave. The LDR Rule of Nov. 7, 1986, added to this definition the placement of waste in a concrete bunker or vault intended for disposal.[5] The LDR apply only to RCRA hazardous wastes that are land disposed or placed after the effective date of the restrictions.

LDR contained in RCRA Section 3004 and 40 CFR Part 268 will eventually prohibit land disposal of all RCRA hazardous wastes that

do not meet LDR treatment standards. LDR treatment standards were established by the U.S. EPA on the basis of the best demonstrated available technology (BDAT) rather than risk-based or health-based standards. The LDR treatment standards may be expressed as constituent concentration levels (which must be attained before the waste or treatment residuals may be land disposed) or specified technologies (which must be applied to waste before the residuals may be land disposed).[6]

Most of the LDR treatment standards are expressed as constituent concentration levels and compliance with LDR is achieved by meeting the numerical performance standards established for each constituent. Any technology that can achieve the required levels may be used unless the technology is otherwise prohibited: the BDAT used by the U.S. EPA to set standards need not be used.[4]

"SOFT HAMMER" REQUIREMENTS FOR NOTIFICATIONS, CERTIFICATIONS AND DEMONSTRATIONS

"Soft hammer" provisions fell on those First Third and Second Third Wastes for which the U.S. EPA did not set treatment standards by the statutorily-mandated date (Aug. 8, 1988 and June 8, 1989, respectively). The soft hammer provisions specified certain restrictions that had to be met before the wastes could be disposed in landfills or surface impoundments. As of May 8, 1990,[3] "soft hammer" provisions are no longer in effect.

Under soft hammer, generators, treatment and disposal facilities were required to meet special restrictions if the wastes or residues were to be disposed in a surface impoundment or landfill unit. Prior to disposing of the untreated wastes, generators had to determine if treatment was "practically available." If treatment was "practically available," generators had to send these wastes to a facility that would provide the "best" type of treatment. Whether the wastes were treated or not, they had to be disposed in a unit that is in compliance with the RCRA minimum technology requirements. Facilities also had to complete soft hammer certifications and demonstrations to show whether treatment was practically available and submit these to the Regional Administrator.[7]

Cost factors were allowed in the soft hammer determination of "practicable." If the cost of transporting and treating the waste was more than twice the pretreatment cost of disposal by whatever practice the generator was using previously, then that treatment could have been considered not to be "practically available." Generators had to provide a one-time demonstration, certification and notification if wastes were to be disposed in a landfill or surface impoundment and as long as the waste stream did not change or some other major aspect of the demonstration did not change before the waste was shipped off-site. The demonstration, which showed whether treatment was practically available, had to be sent to the treatment facility with the initial shipment and to the Region in which the generator was located. Generators also had to prepare and sign a certification, a copy of which had to be sent with each shipment to the treatment facility. The exact certification language depended on whether practically available treatment existed.[7]

In some cases, soft hammer wastes could have been California List Wastes (HOCs or PCBs) and should have been considered as such under treatment standards that were promulgated for California List wastes. The statutory California List levels represent the minimum level of treatment for these wastes. If there is overlap between the requirements, the waste must meet the most stringent requirements before being land disposed.[8]

THIRD THIRD SCHEDULED WASTES

All remaining listed hazardous wastes and all wastes identified as of Nov. 8, 1984, by one or more of the characteristics as defined in 40 CFR Part 261 were identified as Third Third scheduled wastes. On May 8, 1990, Third Third Wastes became restricted and were therefore subject to a number of land disposal restrictions. However, the effective date for compliance with treatment standards for these waste codes was extended to Aug. 8, 1990, by granting a three-month national capacity variance. The effective date is being delayed because the Agency realizes that even where data indicate that sufficient treatment capacity exists, it is not immediately available.[9] This delay also would provide adequate time needed by generators to adjust existing treatment

systems, segregate waste streams in accordance with the dilution prohibition to enter into contracts with commercial treaters.

The Agency has the authority to grant national capacity variances from the statutory effective dates, not to exceed two years, if there is insufficient alternative protective treatment, recovery or disposal capacity for the wastes. In order to make capacity determinations, the U.S. EPA compares the nationally available alternative, treatment, recovery or protective disposal capacity at permitted and interim status facilities, which will be in operation by the effective date, with the quantity of restricted waste generated. If there is a significant shortage of such capacity nationwide, the U.S. EPA will establish an alternative effective date based on the earliest date such capacity will be available.[9]

PITFALLS IN CERTIFICATION/DEMONSTRATION SUBMITTAL

The U.S. EPA's evaluation of certification/demonstration submittal involved many parameters. Pertinent information had to be supplied in order to determine whether the certification was valid, invalid or incomplete. The Regional Administrator could invalidate a certification for two reasons: (1) practically available treatment existed where the generator certified otherwise; or (2) some other method of practically available treatment which yields greater environmental benefit existed. In many instances, additional information was needed to evaluate the validity of the certification.

Evaluation of a submittal was conducted in four parts: (1) general information—generator's name, address, the U.S. EPA I.D. Number, waste code, submission of both certification and demonstration; (2) certification—[correct certification statement (treatment vs. no treatment), wording of certification as specified in 40 CFR Part 268.8 and certification signed by generator]; (3) demonstration—adequate description of waste or waste residue, waste quantity, frequency of generation, waste analysis, treatment previously used, treatment technologies considered, including recovery/recycling, name of treatment facility, individual contacted, telephone number, date contacted, treatment method selected (if treatment rejected; justify and if treatment based on cost; justify) and (4) conclusion,—was certification valid and was additional information needed. The majority of pitfalls can be summarized as a lack of information needed to review the submittal efficiently.

CONCLUSION

This paper has discussed a general overview of land disposal restrictions and pitfalls observed in certification/demonstration submittals. It is apparent that the Land Disposal Restrictions place important new constraints on how owners and operators can close and/or cleanup their facilities. Any generator who treats, stores or disposes of hazardous wastes on- or off-site should have a working knowledge of the types of wastes that he has in his inventory. This knowledge should include maintaining accurate files pertaining to manifests, biennial reports on generator activities, test results, waste analyses and reports concerning the quantities and disposition of wastes.

The Third Third Final Rule imposes new waste analysis requirements on generators who treat in tanks or containers in a 90-day accumulation area. This Rule promulgates LDR treatment standards for almost all RCRA hazardous wastes not previously addressed and expands the restrictions of earlier rules, particularly with respect to the dilution prohibition. To summarize, LDR treatment standards are in effect for solvents and dioxins (Nov. 8, 1986); California List Wastes (July 8, 1987); First Third Wastes (Aug. 8, 1988); Second Third Wastes (June 8, 1989); and Third Third Wastes (including First and Second Third soft hammer wastes) [May 8, 1990].

The U.S. EPA granted a three-month national capacity variance until Aug. 8, 1990, for Third Third Wastes because sufficient treatment capacity was not immediately available.

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The In Situ Vitrification of Subsurface Containment Barriers-An Overview

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ABSTRACT

In situ vitrification (ISV) is an environmental engineering process in which soil or soil/waste mixtures are melted through the direct application of electrical current and subsequently cooled to a glassy solid. The technology was developed by Pacific Northwest Laboratory (PNL) in the 1980s and has been tested on transuranic, mixed-hazardous and PCB/organic waste similar to that found at U.S. Department of Energy (DOE) and other facilities nationwide. These tests have led to endorsements of ISV from DOE, the National Association of Professional Engineers and the U.S. EPA. PNL is conducting a wide range of field tests, expanding the scientific basis of ISV and assessing its extension into new applications. One such project is ISV—Selective Barriers, an investigation into the construction and performance of ISV-generated, vertical and/or horizontal subsurface barriers to groundwater flow and biogenic intrusion. In some situations, it may be impractical or unnecessary to either excavate or vitrify an entire waste site. Vitrified barriers could minimize the diffusive or fluid transport of hazardous components with either a groundwater diversion wall or an in situ, "box-like" structure.

During the first year of this project, engineering-scale tests are being conducted between graphite electrodes within a 1.8-m diameter, 2.4-m high test cell. The experiments are designed to investigate the initiation of melts within the subsurface and the control of melt size and shape and to evaluate the performance of the resulting ISV structures. Several methods are being tested, including passive metal electrodes, electrode feeding systems, fluxed soil and fluxed boreholes. In addition, basic data have been collected on the thermal and material properties of ISV melt and solidified glass.

These experimental and analytical studies will support a series of field-scale melting experiments, refinements to ISV theory and computer modeling. This work was performed by PNL operated by Battelle Memorial Institute for the DOE under Contract number DE-AC06-76RLO 1830.

INTRODUCTION

The U.S Department of Energy (DOE) requires technical options for the cleanup and long-term isolation of variably contaminated subsurface structures, soils and groundwaters at a number of sites nationwide. These sites are diverse in geology, hydrology and design. Generic technical solutions or methods that are easily adapted to local conditions remain the most appealing, and solutions that can isolate waste sites through the use of hydrologic or geotechnical barriers are particularly important. The purpose of the Selective Barriers project is to research, develop, evaluate and demonstrate the most promising new concepts in subsurface barriers to fluid migration.

The Selective Barriers project was funded for FY 1990 by DOE and

is managed by the Pacific Northwest Laboratory (PNL), a multiprogram DOE national laboratory operated by Battelle Memorial Institute. For the first two years the project will focus on barriers formed through in situ vitrification (ISV). The five technical project tasks are

- Conceptual, Computational and Laboratory-Scale Studies
- Engineering-Scale Testing and Performance Assessment
- Pilot-Scale Testing and Performance Assessment
- Field-Scale Testing and Performance Assessment
- Technology Transfer and ISV Coordination

Following a brief discussion of general ISV science, each of the technical task will be presented in detail.
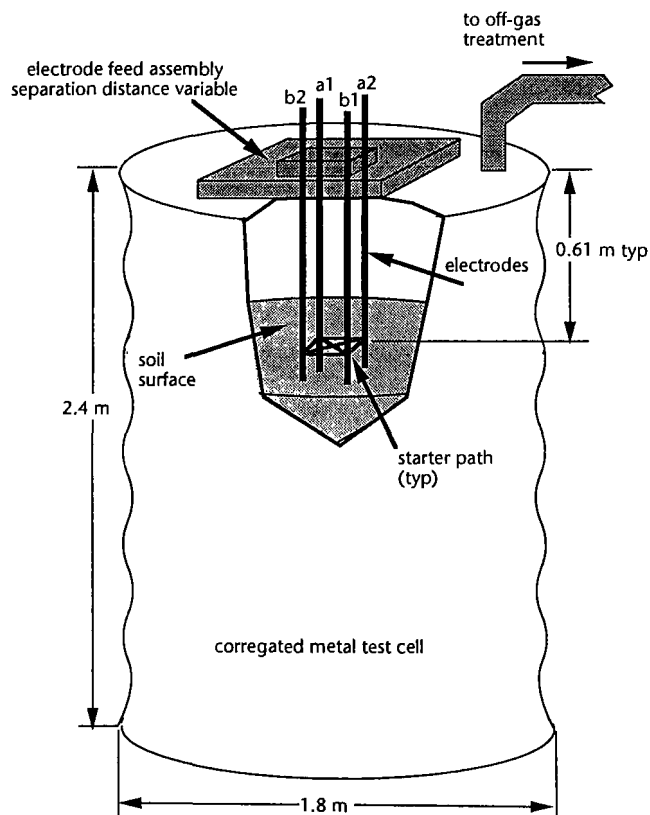
Figure 1
Typical ISV Engineering-scale Layout.

GENERAL ISV METHODOLOGY

In situ vitrification is a waste/soil treatment process that grew out of PNL's long-term research efforts in nuclear waste vitrification (glass formation). The technology has enjoyed strong national regulatory support, great interest among state agencies and several engineering awards. For a typical ISV application (Fig. 1), electrodes are inserted in the ground in a desired array (depth and spacing). A mixture of flaked graphite and glass frit is placed between the electrodes to act as a conductive starter path. An electrical potential is then applied to the electrodes, establishing an electrical current in the starter path. The current generates resistive heat along the starter path and the temperature of the surrounding soil is raised to between 160 and 2000° C.

A working relationship between resistivity and melt/electrode geometry is given by:[1]

$$R_{e,d} = \rho \, \frac{\ln \left(2 \frac{S_{e,d}}{D} \right)}{\pi \, D_g}$$ (1)

where,

$R_{e,d}$ = resistance across edge (e) or diagonal (d) electrodes
$S_{e,d}$ = electrode separation distance
D_g = depth of melt
D = electrode diameter
ρ = electrode resistivity of the glass

A mean resistivity combined with Ohm's Law gives a general idea of the heat available to dissipation during current flow. A more physically explicit expression is derived[2] from Gauss's Law using an analogy to electrodynamic theory,

$$\oint E \cdot dA = \frac{Q}{\varepsilon_0}$$ (2)

where

E = the electrical field
A = area of the plate
Q = charge on the plate
ε_0 = permittivity constant

given parallel plates and a constant field. The scaler product of the E field and the current density results in

$$E \cdot J = \frac{QJ}{A\varepsilon_0}$$ (3)

with, J = current density or charge density over unit time. If the work done by the moving charge is dissipated as heat (herein called H, to avoid confusion with charge) over the separation distance, L, then,

$$H = \Delta W = QEL$$ (4)

and

$$E = \frac{\sigma}{\varepsilon_0}$$ (5)

therefore,

$$\frac{H}{V} = \frac{\sigma Q}{A\varepsilon_0}$$ (6)

and Equations 3 and 6 are equivalent and

$$H = \int_v E \cdot J \, dV$$ (7)

which is the electrodynamic description of Joule heat. Using Joule's Law,

$$J = \sigma E$$ (8)

and some algebra, one can derive

$$J \cdot E = \sigma E^2 = \frac{J^2}{\sigma}$$ (9)

where σ now represents electrical conductivity.

Since the conductance is explicitly not homogeneous in an ISV melt, any thermomechanical model of the process must account for or simplify the coupled variation in current density and the electrical field. Because of the strongly nonlinear, probably chaotic nature of a turbulently convecting, current-carrying fluid, an analytical description of the temperature or velocity field is not available. The code TEMPEST is being adapted to give an improved numerical solution to this problem (see below). Equation[7] also demonstrates the requirements for directing melt progression. If a designed spatial deviation of the mean current density or electrical field can be produced, heat can be spatially focused and melt progression can be directed.

The graphite starter path eventually is consumed by oxidation and the current is transferred to the molten soil. The melt is maintained at temperatures between 1450 and 2000° C. Between the electrodes, the temperature greatly exceeds the liquidus and turbulent convection homogenizes the melt. Organic material pyrolysizes at the melt front and is swept upward to the off-gas hood where it combusts or is captured by the off-gas filtering system. Mass balance calculations[3] suggest that retention of 99.999% of strontium and 99.88% of cesium within the glass monolith are attainable. Under ambient cooling, the melt becomes a monolithic, vitreous mass. Varied cooling rates and compositions result in crystallization, often spherulitic in habit. Observed mineral phases include anorthite, pseudowollastonite and silica minerals.[4]

After cooling, the resulting ISV product is composed of glassy and crystalline phases, superficially resembling volcanic glass. Unweathered ISV glass has a higher leach resistance than granite or marble, approaching Pyrex glass.[5] For typical soils, final ISV block density varies from 2.3 to 2.65 g/cm^3.[5] This material is approximately 3 to 19% more dense than concrete. The tensile and compressive strength of unfractured ISV product is an order of magnitude greater than unreinforced concrete. Power requirements for the ISV process can be met by local distribution lines or portable generators. Total power requirements are less than 0.8 kwh/kg of solidified mass. The presence of water in the soil increases the power requirement to less than 40% for fully saturated soils.

The process is operated at four scales. Bench- and engineering-scale experiments use a 1.8-m diameter by 2.4-m deep, corregated-metal test cell. The PNL facility is located in a high-bay, engineering-development laboratory. Pilot- and field-scale applications occur outdoors in natural soil and require one to three trailers for process and power equipment. Figure 2 shows a typical pilot-scale operation. The dimensions of the four scales are listed in Table 1.

CONCEPTUAL AND COMPUTATIONAL STUDIES

In situ vitrification is still an emergent technology and many of the modifications required for the Selective Barriers project are untested. For this first year, our objective is a survey of methods that can be applied to the project goal: the construction of vertical and horizontal, planar ISV monoliths. The three methods under review are

• Controlling melt geometry
• Starting melts at depth
• Constructing multiple-melt welds

If absolute isolation is essential or if a specific subsurface design must be met, then it will be important to control the melt size and shape in a predictable fashion. The presence of active underground facilities, pipelines and/or storage tanks must be assumed; therefore, the con-
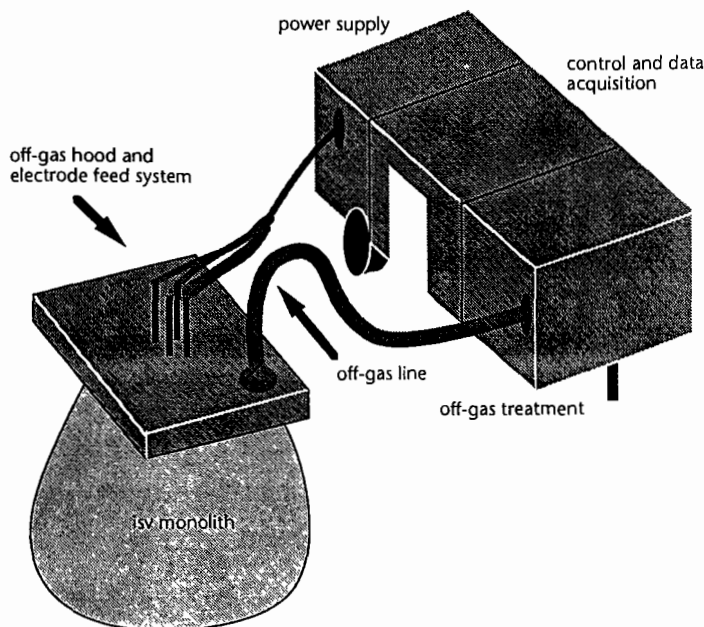
Figure 2
Typical ISV Pilot-scale Layout. Field-scale Similar with
Separate Trailers for Power, Control and Processing Operations.

Table 1
Application Scales for In Situ Vitrification

Test Scale	Electrode Separation, m	Block Size	Tests Completed
Bench	0.11	1 to 10 kg	19
Engineering	0.23 to 0.36	0.05 to 1.0 t	33
Pilot	0.9 to 1.5	10 to 50 t	17
Large	3.5 to 5.5	400 to 800 t	5

struction and use of barrier structures must not degrade preexisting site facilities. Finally, QA, environmental and safety concerns require the barrier technology to be as controlled and predictable as is practical.

Work during FY 1990 has uncovered three key methods of melt control that will be tested through computer simulation and experimentation. These are:

- Fluxes and other low melting temperature materials
- Passive electrodes
- Changes in current phase

In general, these three methods all shift the melt isotherms such that the steepest temperature gradient is collinear to the direction of melt progression. This results in a concentration of heat in that direction and an equivalent distribution of melt. In an ideal ISV melt, free convection is maintained between turbulent "hot spots" near the electrodes and the cooler sides, walls and surface of the melt. The melt along the margins is more viscous than the core and buoyancy is insufficient to overcome the high drag. For this reason, heat exchange across the walls is dominated by conduction across a stagnant boundary layer. If material has been placed (backfilled boreholes, buried trenches, saturated zones and/or buried layers) that can melt and convect at a lower temperature than the melt core, a change in melt-front geometry will occur. Presumably the convective cell would disturb the stagnant boundary, allow a spike in the isotherms to develop and focus heat transfer in the direction of interest.

One can evaluate this effect[6] through the Rayleigh number (Ra), where

$$Ra \equiv \frac{g\beta\Delta TH^3}{\alpha\nu} \tag{10}$$

g = gravitational acceleration
β = coefficient of thermal expansion
ΔT = temperature differance
H = length scale
α = thermal diffusivity
ν = kinematic viscosity $\left(\frac{\mu}{\rho}\right)$

When the temperature difference, ΔT, over length scale, H, exceeds a critical value (set by the geometry and boundary conditions), the system becomes unstable and begins to convect. At a nominally subcritical ΔT, a drop in viscosity or an increase in thermal expansion will increase the Rayleigh number for the fluid.

For this reason, it is important to choose a flux that changes not only the melting temperature of the soil, but also the mechanical properties of the molten soil (i.e., increases the Rayleigh number). Numerous fluxes and viscosity reductants are used by the glass industry, including soda ash, borax and sodium or potassium metasilicate. Figure 3a is an equilibrium phase diagram for the system $SiO_2-CaO-Na_2O$ taken from Morey and Bowen.[7] Plotted on Figure 3a is an average composition for Hanford Formation alluvium and the composition of sodium metasilicate (Na_2SiO_3). A tie line between these compositions comes very close to the minimum melting cusp in the liquidus line. Figure 3b, also from Morey and Bowen,[7] is similar except that isokoms of equal log viscosity are given for 1100°C. The same tie line is superimposed upon the diagram and indicates a 1 to 1.5 log unit decrease in viscosity resulting from the addition of sodium metasilicate. These results are supported by Buelt et al.[5] showing that the addition of sodium causes a greater than 2 log unit decrease in the viscosity of melt derived from Hanford Formation alluvium (700 to 6 poise). Unfortunately, there is a limit to this effect in ISV (approximately 35 wt% in Na_2O). Increased sodium also increases the electrical conductivity of silicate melts, resulting in less efficient Joule heating.

Passive electrodes in electric glass melters have been used by the glass industry and investigated at PNL during ISV testing of soils with high metals concentrations. The idea relies upon the relationship between current density, J and heat indicated in Equation.[9] If δ, electrical conductivity, is not constant but is distributed in space, then the current density and E field and the thermal profile will vary. Because of the high electrical conductivity of most metals, any concentration of metals in the soil will increase current density and Joule heat in the adjacent soil. Further, because most metals are significantly more dense than silicate melt, they will stably stratify in the lower part of the melt. In ISV practice, the metal sublayer does form and the electrode array is lowered such that no direct "short" occurs across the sublayer. The electrodes are slowly fed downward, following the descending melt and metal sublayer and concentrating current and heat at the base of the melt.

Variations in the electrical field can provoke "hot spots" in the melt, as shown by results of numerical simulations. These results appeared when current phase was varied in a nonstandard fashion. The ISV power supply system has been designed to optimize the load balance such that Joule heat is evenly distributed over the space between the four electrodes and the power factor approximates unity, the most energy-efficient arrangement. If the load balance was unevenly distributed and the mean voltage varied with position, the current density would be altered and "hot spots" would grow in the melt. The details of this plan are yet to be worked out. In FY 1991, numerical modeling will be used in conjunction with E-field theory to determine the most appropriate electrical design to explore these ideas.

The ISV barriers technology must include some method for initiating melting at depth (< 7 m). Although it may be possible to "weld" vertical walls to a relatively impermeable, natural or treated substratum, such a requirement would severely limit the application of ISV barriers. A more useful plan would begin with an ISV-generated horizontal subbase, created with minimal disturbance. The problem lies in the melt startup process, developed and optimized to surface conditions. Surface starting of an ISV melt requires a fixed, square array of graphite elec-
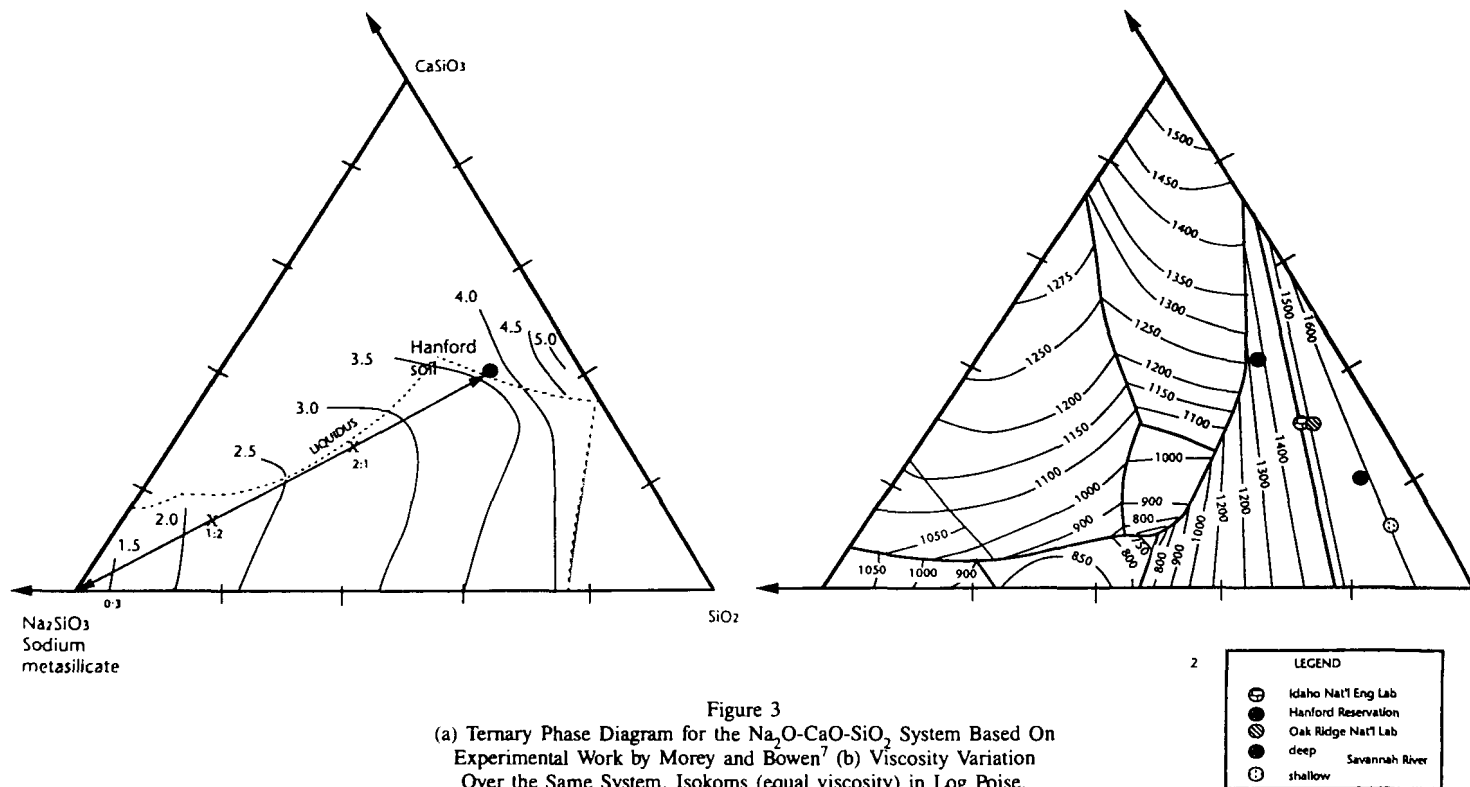
Figure 3
(a) Ternary Phase Diagram for the Na$_2$O-CaO-SiO$_2$ System Based On Experimental Work by Morey and Bowen[7] (b) Viscosity Variation Over the Same System. Isokoms (equal viscosity) in Log Poise.

trodes inserted into the ground. Without an initially conductive starter path, which will elevate temperature in the soil to its melting point, the process cannot begin. Further, the starter must be consumed so that current and Joule heat are initiated within the melt.

One scenario would begin with large diameter (approximately 50-cm) boreholes drilled on a line (Fig. 4). Special electrode arrays would be mounted on the end of a drill string and lowered to the base of the hole. The electrodes would be seated within a graphite starter layer and a melt would be formed at the bottom of the hole. Meanwhile, a second melt would be started in the neighboring hole. Because of the two adjacent melts, the intervening soil would experience relatively high temperatures and the "septum" between the melts would preferentially melt. The two melts would grow until they joined. Similar melt pairs could be started within other holes and joined and so forth, extending the melt in any direction or geometry desired.

Another possible solution would begin with the subsurface injection of a nonhazardous metal salt or other conductive solution (Fig. 5). If circulation could be achieved between adjacent holes, it might be possible to use the solution as a subsurface starter path. If natural permeability was not sufficient, hydrofracing could be used. As current is conducted along the path, the solution would heat up and water would be driven off. Thus it is important that the dry salt have a low melting temperature (< 500 °C, approximate temperature of the off-gas) for melting to begin and current to continue to flow once the solution has completely devolatilized. One possible candidate is salt sodium carbonate and/or borax (Na$_2$B$_4$O$_5$(OH)$_4$• 8H$_2$O).

Finally, perhaps the least exotic, deep startup method would use a buried graphite/frit starter path (Fig. 6). The path would be injected at the desired "floor" depth as a slurry or paste injected through horizontal boreholes located directly beneath the electrodes. The electrodes would access the buried starter path through vertical boreholes. These vertical electrode access holes would also allow the direct discharge of induced soil vapor and combustion products to the off-gas hood. Given adequate room for an angled drilling mast, such a geometry and directional precision is well within reason.

Results from tests at the Savannah River Laboratory indicate that

accuracies within 0.1% are possible at a minimum depth of 18 ft. The graphite/frit slurry could be pumped into either the vertical wells or the horizontal boreholes, whichever resulted in a more uniform path. If four starter path boreholes were drilled, the standard, single-phase, two-electrode circuit would be logical. Drilling only two horizontal boreholes would clearly be less difficult. Melts would start as independent, single-phase circuits between each pair of electrodes until melting began. Continued heating would result in propagation of the melt front toward the center of the square. At this point, a standard circuit would be initiated.

A major effort has begun to modify the PNL, TEMPEST, finite difference, fluid mechanical and heat transfer computer code to simulate ISV melting. Several traditional ways of solving the moving boundary/phase change condition at the melt front are being evaluated, including the possibility of including a melting range, or "mushy zone." A related project will improve the ability of TEMPEST to operate over rapid viscosity variations. TEMPEST currently is capable of determining the electrical field; however, the nonlinearity, suggested by the E-field formulation, Equation 9, demonstrates that this problem will require thermal boundary conditions that are challenging. Scaling and code verification/sensitivity analyses will be used to test all idealizations and simplifications.

These efforts will be guided by investigations into the physics of melting and cooling at the University of Washington geophysical fluid dynamics laboratories. Work on the fundamental aspects of partial melting using similitude analysis and bench-scale experiments will elucidate the geometry of the melting front. Parallel development of silicate-melting models applicable to geophysical problems will be a side benefit of this project. At PNL, residual stress analysis of a cooling, infinite slab will determine the viscoelastic behavior of an ISV-generated barrier wall. Current efforts include one-dimensional simulations and a development of appropriate mechanical parameters for silicate liquids.

In FY 1991 to 1993, other concepts will be tested and refinements to the modeling capability are planned. The problem of multiple ISV melts will be a major concern. Specific investigations of nonstandard electrical configurations, hydrologic testing of barrier walls and materials properties of glassy slabs are all planned.
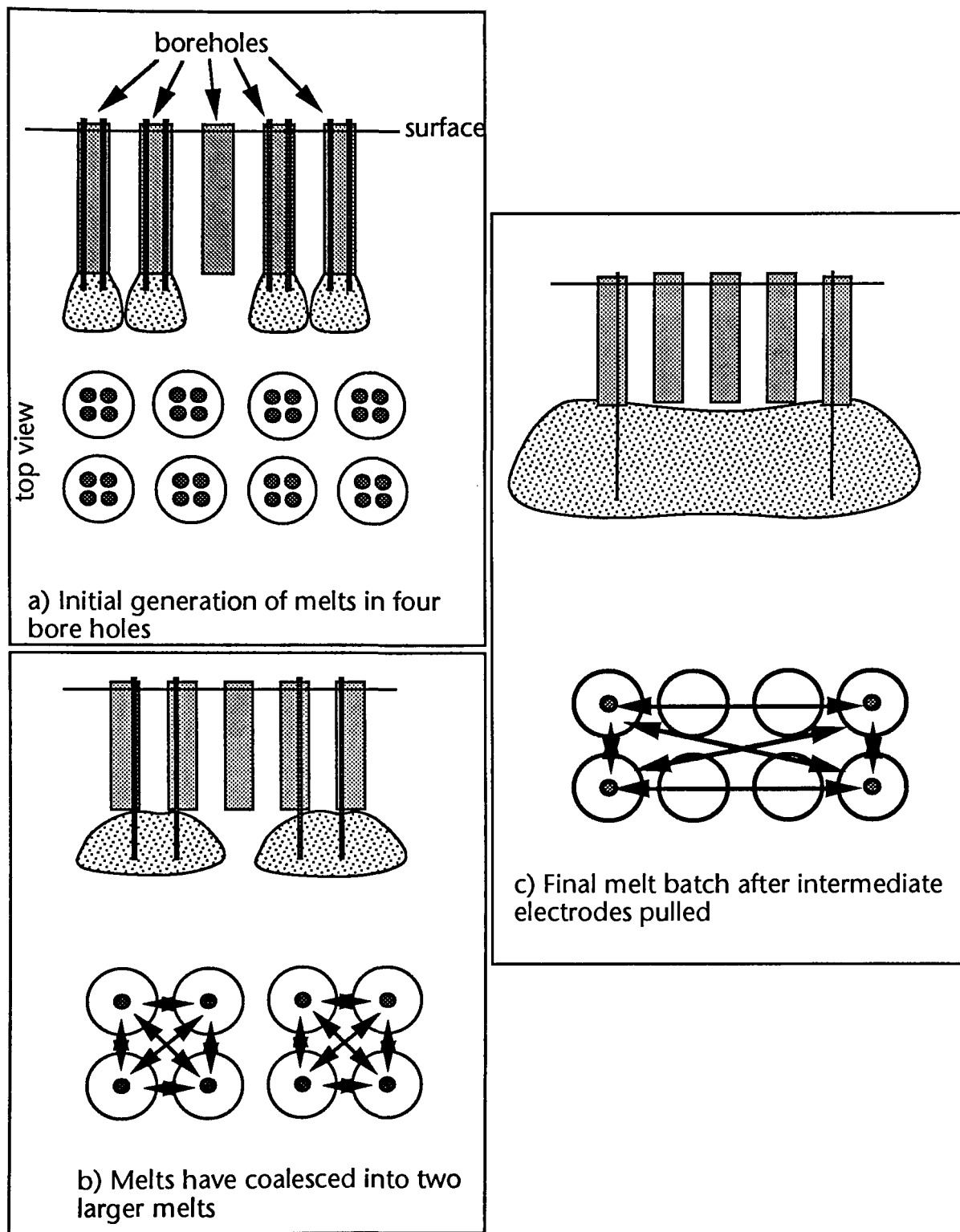
Figure 4
"Borehole Startup" Concept for Deep Startup of ISV Melts.
Arrows Indicate Current Path. Melting is Initiated in
Adjacent Boreholes and Grows Together.
Electrodes Follow the Evolving Melt Volume.

ENGINEERING- AND PILOT-SCALE
EXPERIMENTAL PROGRAM

The purpose of the engineering-scale program is to test concepts. Pilot-scale testing, on the other hand, will verify/demonstrate the most promising barrier generation concepts identified at the engineering scale.

Engineering-scale testing will be continuous over the life of the project as different conceptual questions are raised; however, pilot-scale experiments will be fewer in number and more tightly focused. Wall and floor tests will be a key part of the pilot-scale program, with innovative hydrologic testing (verification) an important part of the program.
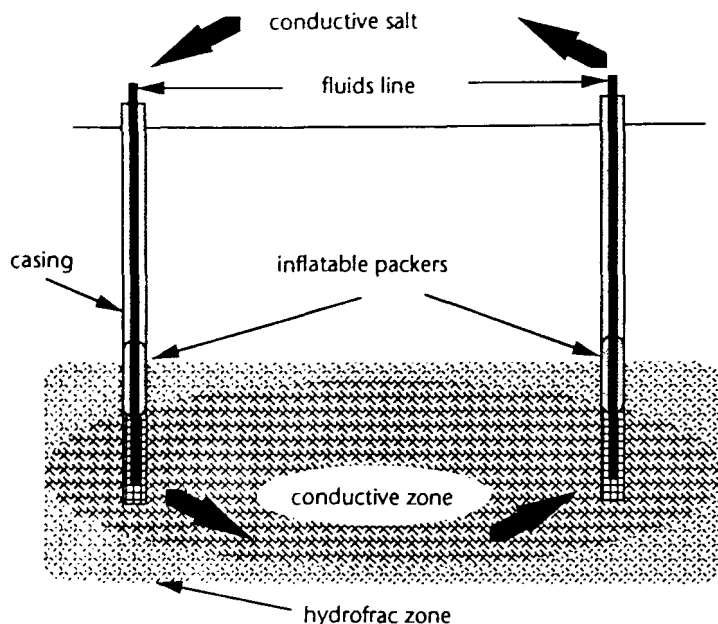
Figure 5
"Conductive fluid" Concept for Deep Startup of ISV Melts.
Hydrofracing Develops a Permeable Zone Between Adjacent Wells. A
Low-melting-temperature, Conductive-salt Fluid is Circulated
Between the Holes. Electrodes are Placed Within the Conductive
Fluid.
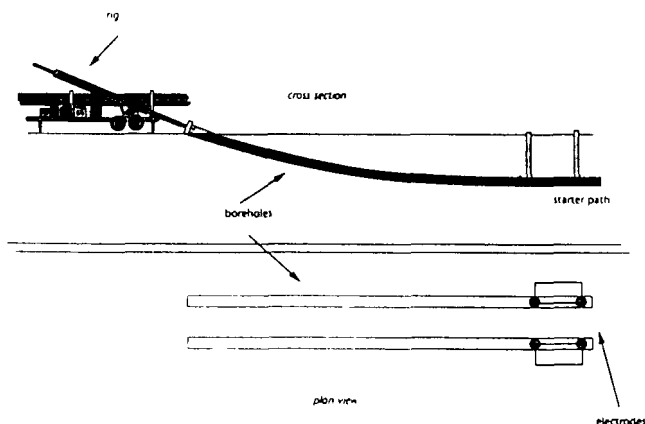
Figure 6
"Buried Path" Concept for Deep Startup of ISV Melts.
Rectilinear Boreholes are Drilled Parallel to the Sides of the
Electrode Grid and Backfilled with Starter Material. Vertical
Boreholes are Drilled at the Corners of the Grid and Electrodes
are Placed in the Starter Material.

A major objective of the pilot-scale testing will be the production of multiple, welded or contiguous melts, resulting in a laterally extensive, vitrified barrier wall. Previous work at PNL has suggested that the fusion of equidimensional melt monoliths is possible; however, it has not yet been demonstrated that planar wall components can be assembled into a "tight" structure. The pilot-scale program will also test our ability to create large horizontal base layers. Investigation of the ISV melt interaction with natural or vitrified base material liners will provide important information relative to sealing volumes of soil from water infiltration and biotic or human intrusion.

Field techniques developed independently by the drilling, well testing and measurement industries and the DOE Subsurface Science Program and Horizontal Wellbore Research Program will be an important part of the pilot-scale program as the project planning narrows in on a full field-scale configuration.

FIELD-SCALE VERIFICATION AND TESTING

The objective of this project is to demonstrate, calibrate and verify the most promising ISV barrier system at an actual DOE waste site. The anticipated scope includes:

- Design and procurement of large-scale processing equipment
- Testing of barrier installation under DOE field site conditions
- Monitoring the barrier performance
- Final reporting and recommendations

At the field-scale stage of the project, decisions will be made on the specific barriers technology that best satisfies remedial needs. A final site will be chosen and testing plans will be prepared by PNL for DOE approval. The candidate barrier technology will be tested by the production of field-scale barrier walls joined to a natural or ISV-generated layer as the base. A full hydrogeologic investigation of the site will be conducted, including site characterization, well testing and groundwater monitoring. All barriers produced will be nondestructively tested and sampled for petrographic, chemical and geotechnical analysis and partially exhumed for visual inspection and examination. A site monitoring project, including equipment installation, will be established to provide long-term performance assessment information.

Project researchers will provide an economic assessment of the developed barriers technology. Also, in conjunction with the other ISV projects, it is anticipated that the modified version of TEMPEST would be available to predict vitrified barrier viability, performance and cost at the selected DOE site. This assessment and computer model would include a parametric-type presentation, which would allow DOE to estimate characteristics for specific applications of vitrified barriers as they occur.

TECHNOLOGY TRANSFER AND ISV COORDINATION

Each major DOE site now plans to use ISV for remediation of certain wastes. Programs to develop ISV are being funded individually from each site's environmental remediation budget and from DOE research and development funds. Because of the unique yet widely applicable nature of the ISV barriers concept, special attention has been paid to the technology transfer process. To ensure that duplication of effort is minimized and that these emergent applications of ISV are disseminated, PNL will prepare an overall ISV program plan for review by interested parties. In FY 1990, a workshop was convened to provide interested persons the opportunity to present their needs and plans in order to sharpen and refine the overall ISV technology development plan. Future ISV workshops are being planned.

CONCLUSION

Admittedly, this is a very ambitious project. The basic ISV technology is still young and significant advances in design and application could emerge during the Selective Barriers project life. On the other hand, unforeseen problems are to be expected in emergent technologies. Despite these uncertainties, the ISV barriers concept could represent an enormous savings over either "pump-and-treat" environmental remediation or "conventional" ISV treatment of buried waste. In a time of decreasing technical options and increasing programmatic costs, the great practical advantage of a successfully developed ISV barrier technology is a reward worthy of such risk.

ACKNOWLEDGEMENTS

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Simulation of Subsurface Barrier Wall Performance Near a River

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ABSTRACT

Subsurface barriers (including slurry walls, diaphragm walls and grout curtains) have been widely used to contain groundwater contaminant plumes or control their movement by placing the low-permeability wall either upgradient, downgradient or surrounding the plume. In addition to containing a plume, barrier walls often are used in conjunction with groundwater extraction systems to minimize the volume of uncontaminated water withdrawn from an aquifer. A combined barrier/extraction system is particularly advantageous when the contaminant plume is located near a surface water body; in this case, the barrier serves to reduce greatly the volume of surface water drawn into the extraction system. When a barrier/extraction system is placed near a river or other body of water, care must be taken to minimize the volume of water that is drawn around the edge of the barrier from the water body while continuing to contain the contaminated water. Additional reduction of inflow to an extraction system located near a river may be possible by altering the geometry of the barrier wall ends.

A finite-difference model is used to investigate the performance of a combined subsurface low-permeability barrier and groundwater extraction system adjacent to a river. Various geometries of barrier wall ends are simulated in order to evaluate their ability to minimize the withdrawal of river water while providing adequate plume containment and allowing for efficient and timely aquifer restoration.

INTRODUCTION

Subsurface barriers have been widely used to control the movement of groundwater either into or out of waste sites and are often used in conjunction with other groundwater control systems. In general, there are three common barrier wall configurations with respect to the contaminant plume:[1]

- Upgradient wall placement
- Downgradient wall placement
- Circumferential wall placement

While the circumferential wall placement is most common and greatly reduces the amount of uncontaminated groundwater passing through the contaminated site, it is also the most expensive to construct.[1] Upgradient wall placement serves to divert uncontaminated groundwater away from the contaminated area and downgradient wall placement prevents further downgradient migration of contaminated groundwater.

Downgradient walls are commonly used to enhance the performance of an active groundwater recovery system by preventing further migration of the contaminant plume and reducing the amount of uncontaminated groundwater drawn into the extraction system. This is particularly true when the groundwater recovery system is located adjacent to a surface water body. Under the induced stress of a groundwater recovery system, infiltration from this surface water body can greatly increase the amount of uncontaminated water mixing with the captured contaminant plume and increase the total volume of recovered groundwater that must be treated. In this case, the barrier wall can be used to minimize the amount of surface water drawn into the recovery system.

The basic operation of a combined barrier/extraction system involves maintaining a lower groundwater level on the upgradient side of the barrier wall to capture the contaminant plume and to prevent the movement of contaminated groundwater around the wall. However, when such a system is placed near a river or other surface water body, care must be taken to minimize the volume of uncontaminated water that is drawn around the ends of the wall from this water body. The amount of surface water inflow depends on the length of the barrier wall in relation to the extraction system, the shape of the barrier wall ends and the effective drawdown created by the extraction system.

To quantify the effects of barrier wall shape and length and of effective drawdown on the amount of surface water drawn into a groundwater recovery system, a series of groundwater model simulations has been performed using several combinations of wall configurations and drawdowns. The length and shape of the barrier wall were varied for three drawdowns in the recovery system. The results of these simulations have been evaluated in terms of the aquifer restoration time and the total inflow from a nearby surface water body versus total volume of recovered groundwater.

GROUNDWATER MODEL SIMULATIONS

A hypothetical groundwater flow system and contamination scenario were defined to evaluate the performance of a combined barrier/extraction system operating near a river. The groundwater flow was simulated as a steady-state system using the Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) computer model.[2] The following guidelines were assumed for defining the scenario to be modeled:

- The contamination fully penetrates the aquifer
- The barrier wall is keyed into the impermeable base of the aquifer
- The river has a constant head
- Aquifer restoration is achieved when 5 times the initial contaminant plume pore volume is removed
- The hydraulic conductivity of the barrier wall remains constant over time
- The groundwater flow field is two-dimensional

Model Scenario

The scenario simulated for this evaluation, shown in Figure 1, assumed that a groundwater contaminant plume had been detected in the shallow unconfined aquifer underlying an industrial facility. This shallow aquifer
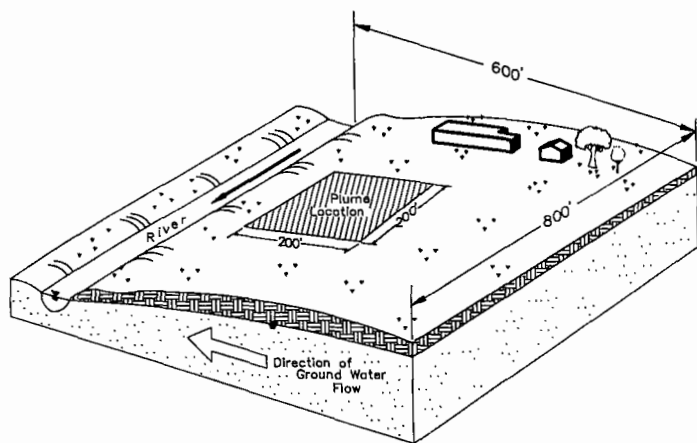
Figure 1
Model Scenario

discharges to the river immediately adjacent to the facility. The contaminant plume is 200 ft by 200 ft with its leading edge located less than 100 ft from the river. The unconfined aquifer underlying the site has a hydraulic conductivity of 10^{-3} cm/sec and an average saturated thickness of approximately 29 ft. An impermeable layer is present immediately below this shallow aquifer. The average groundwater flow gradient across the site is 0.013 ft/ft and the river gradient is 0.001 ft/ft.

Due to the expected low yield of this aquifer unit, it was decided that an interceptor trench would be used to collect the contaminated groundwater for treatment. In addition, a slurry wall with a hydraulic conductivity of 10^{-7} cm/sec was selected to minimize the volume of river water drawn into the system. To evaluate possible barrier/extraction system configurations, a series of groundwater flow simulations was performed. The goal of these simulations was to determine if the length of the barrier wall could be kept to a minimum while maintaining an adequate upgradient capture zone and a timely aquifer restoration period.

Model Simulations

The groundwater domain defined above was simulated using the MODFLOW computer model. The discretized domain is shown in Figure 2. The model grid, 600 ft by 800 ft, is composed of one layer with 70 rows and 70 columns of model cells. Cell size was varied to reduce the overall number of cells while allowing sufficient detailed

Figure 2
Discretized Domain with Interceptor Trench
and Slurry Wall Placement

discretization in the area where the barrier/extraction system is to be placed.

Two types of boundary conditions were used in these simulations (Fig. 2). The cells representing an upgradient groundwater boundary, the cells representing the river and the cells representing the interceptor trench were defined as constant head boundaries. The cells along the two sides of the domain perpendicular to the river were defined as no flow boundaries.

Initially, the groundwater recovery system was simulated without a barrier wall. An interceptor trench aligned perpendicular to the direction of groundwater flow and having a length of 220 ft was placed immediately downgradient of the contaminant plume. Four simulations using the trench alone were performed, each having a different defined drawdown (percent drawdown as measured from the original water table elevation at the trench location). The constant head defined in the cells representing the trench for each simulation was, respectively, (1) the average river stage level (approximately 32.1 ft), (2) 30% drawdown, (3) 50% drawdown and (4) 70% drawdown.

Three slurry wall shapes were then simulated in conjunction with the interceptor trench defined above. The first shape evaluated was a straight wall extending past both ends of the interceptor trench (parallel to the trench). The second shape evaluated was a wall that angled around the end of the trench away from the river at an angle of approximately 30 degrees. The third shape evaluated was a wall that angled away from the ends of the trench toward the river at an angle of approximately 30 degrees. Wall shapes were simulated with overall lengths varying from 220 to 340 ft. Each configuration of wall length and shape was simulated using drawdowns in the interceptor trench of 30, 50 and 70%.

RESULTS AND DISCUSSION

Performance of Interceptor Trench without a Slurry Wall

The simulation results obtained from four different water levels (Fig. 3) maintained at the interceptor trench are summarized in Table 1. The drawdown values given in Column 2 represent the percentage of the total available drawdown at the trench. The total flow in Column 3 represents the amount of flow contributed from the river (Column 4) plus the flow from the upgradient region (Column 5). The percentage of the total flow contributed from the river (i.e., Column 4 divided by Column 3 multiplied by 100) is given in Column 6. The time required to remove five times the initial contaminant plume pore volume is given in Column 7. Assuming a total porosity of 0.3, the five pore volumes of the 200 ft by 200 ft plume was estimated to be 1,410,000 ft^3. This pore volume was divided by the flowrate contributed from the region upgradient of the trench (Column 5 multiplied by 365 days) to obtain the cleanup time given in Column 7.

As shown in Figure 4, the percentage of the total flow contributed from the river depends on the drawdown level prescribed at the trench. The entire effluent flow from the trench was drawn from the upgradient region only when the drawdown at the trench was maintained equal
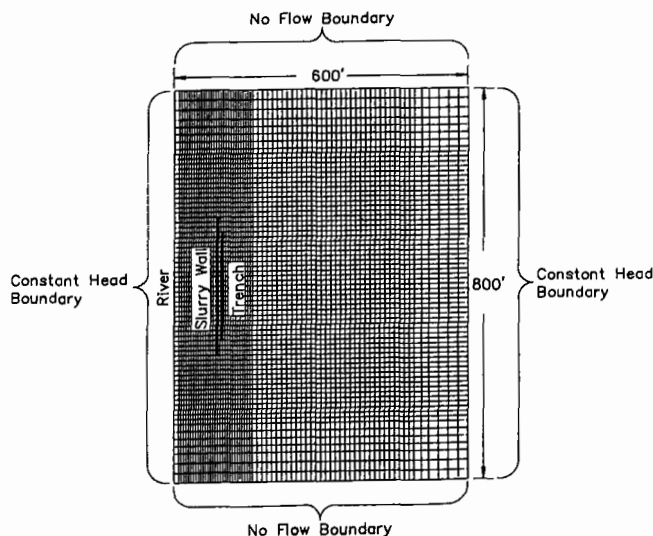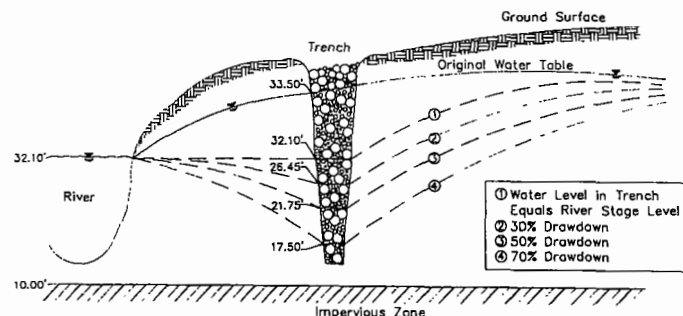
Figure 3
Simulated Interceptor Trench Water Levels

Table 1
Results for Simulations of an Interceptor
Trench without a Slurry Wall

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Simulation No.	Drawdown' in Trench (%)	Total Effluent Flow from Trench (ft.³/day)	Inflow from River (ft.³/day)	Inflow from Upgradient Region (ft.³/day)	Inflow from River (%)	Time to Remove 5 Plume Pore Volumes (years)
1	River Level²	433.32	0	433.32	0	8.91
2	30%	1886.46³	898.30	988.16	47.62	3.91
3	50%	2767.62	1567.03	1200.59	56.62	3.22
4	70%	3348.86	2033.55	1315.32	60.72	2.93

' Percent drawdown from the original water table elevation at the trench location.

² Water level at the trench maintained equal to the river stage level adjacent to the trench.

³ 1886.46 = 898.30 + 988.16
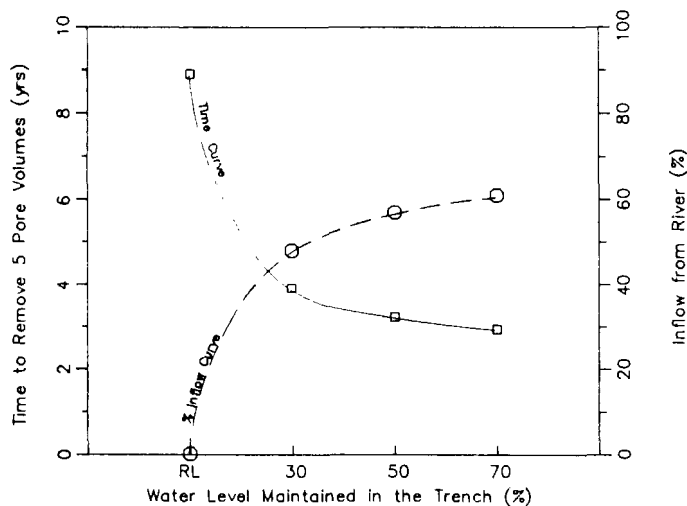
Figure 4
Results for Simulations of an Interceptor
Trench Without a Slurry Wall

Figure 5
Flow Pattern for Simulation of Interceptor Trench
with Drawdown Set at the River Stage Level
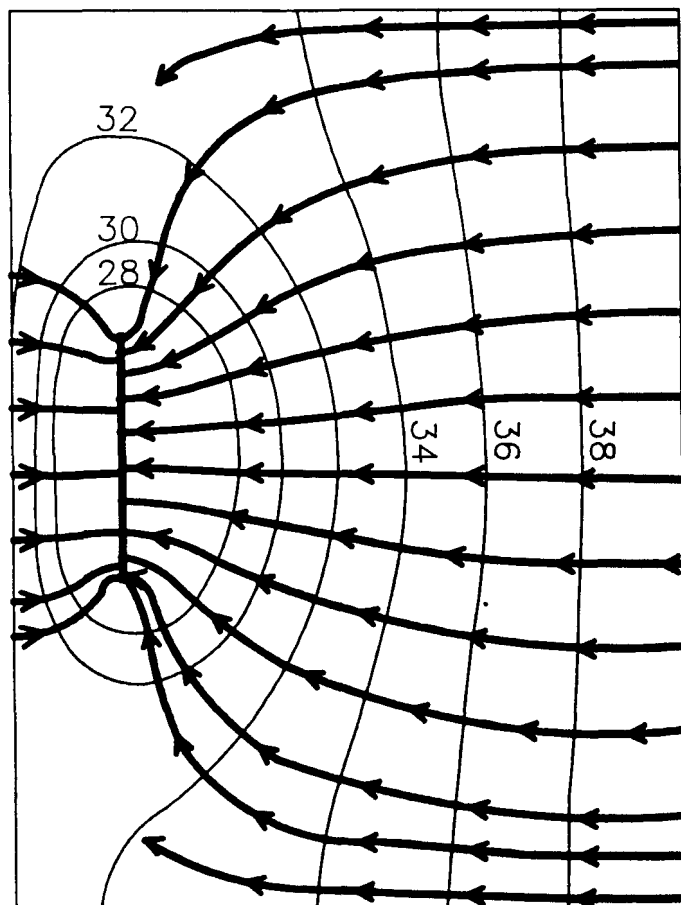
Figure 6
Flow Pattern for Simulation of Interceptor Trench
with 70% Drawdown

to the river stage level (RL). However, this resulted in the longest cleanup time of approximately 9 years. When the drawdown is increased to 70%, the cleanup time is drastically decreased (2.9 years), but approximately 61% of the total effluent flow from the trench would be uncontaminated water drawn in from the river.

A significant decrease in cleanup time can be achieved by lowering the head maintained in the trench from the RL to 30% drawdown (i.e., reduction from 9 to 4 years, respectively). It is apparent that further reductions in the cleanup time resulting from drawdowns beyond 30% are relatively insignificant. Even at 30% drawdown, however, the amount of uncontaminated river water that must be treated with the contaminated water from the upgradient region is about one half of the total effluent outflow from the interceptor trench.

The above simulations indicate that a subsurface barrier wall should be used in conjunction with the trench system in order to reduce the cleanup time while minimizing the induced inflow from the river. The flow patterns generated by simulation No. 1 (trench water level equal to RL) and simulation No. 4 (70% drawdown) are shown in Figures 5 and 6, respectively.

Performance of Interceptor Trench with a Slurry Wall

The results obtained from a total of 12 simulations simulated with

a combined straight slurry wall and interceptor trench system located downgradient of the contaminant plume are summarized in Table 2. It was assumed that a 5-ft thick keyed-in slurry wall was placed 5 ft downgradient of the trench. All 12 simulations were performed with the slurry wall downgradient and parallel to the trench. For the first three simulations (Nos. 5, 6 and 7), the length of the slurry wall was set equal to the length of the interceptor trench. Subsequent simulations (Nos. 8 through 16) were performed with the slurry wall extending beyond both ends of the interceptor trench.

Table 2
Results for Simulations of an Interceptor
Trench and Straight Slurry Wall

Simulation No.	Slurry Wall Length (ft.)	Drawdown in Trench (%)	Total Effluent Flow from Trench (ft.³/day)	Inflow from River (ft.³/day)	Inflow from Upgradient Region (ft.³/day)	Inflow from River (%)	Time to Remove 5 Plume Pore Volumes (years)
5		30	1140.61	190.99	949.62	16.74	4.07
6	220	50	1584.92	423.32	1161.60	26.71	3.32
7		70	1866.58	588.09	1278.49	31.31	3.02
8		30	1036.32	89.09	947.23	8.60	4.08
9	260	50	1413.89	252.09	1161.80	17.83	3.32
10		70	1659.91	378.80	1281.11	22.82	3.01
11		30	993.41	39.90	953.51	4.02	4.05
12	300	50	1336.43	165.21	1171.23	12.36	3.30
13		70	1562.43	269.05	1293.38	17.22	2.98
14		30	968.63	14.12	954.51	1.46	4.04
15	340	50	1292.19	107.96	1184.23	8.35	3.26
16		70	1504.56	196.06	1308.51	13.03	2.95

The effect of the slurry wall length on the percent inflow from the river was evaluated at three different drawdown levels (30, 50 and 70%) and is shown graphically in Figure 7. The aquifer restoration time computed for each slurry wall length and corresponding drawdown level are illustrated in Figure 8.

It is apparent that the percent inflow from the river can be significantly reduced by placing a slurry wall downgradient of the interceptor trench. For example, with 30% drawdown in the trench, the placement of a 220-ft slurry wall can reduce the percent inflow from the river from approximately 50% (simulation No. 2, without a slurry wall) to 17% (simulation No. 5). When the length of the slurry wall is increased to 340 ft, the percent inflow from the river is further reduced to less than 2% (simulation No. 14). However, the performance of the slurry wall becomes less effective with increasing drawdown levels in the trench. At 70% drawdown level, the percent induced flow can be reduced from 61% (simulation No. 4, without a slurry wall) to 32% by placing a 220 ft slurry wall. Increasing the slurry wall length to 340 ft, however, still allows 13% of the total interceptor trench effluent flow to result from river inflow. The total reductions in the induced river flow resulting from the increase in slurry wall length from 220 ft to 340 ft are 91, 69 and 59% for 30, 50 and 70% drawdown levels, respectively; i.e.,

30% Drawdown: (16.74 - 1.46)/16.74 $\approx$ 90% reduction
50% Drawdown: (26.71 - 8.35)/26.71 $\approx$ 69% reduction
70% Drawdown: (31.51 13.03)/31.51 $\approx$ 59% reduction

As indicated in Figure 8, the length of the slurry wall does not appear to affect the cleanup time because the wall length controls the amount of inflow from the river, but has little influence on the flow from the region upgradient of the trench. However, the cleanup time is still affected by the drawdown levels in the trench. In particular, the cleanup time is reduced from approximately 4 to 3 years by increasing
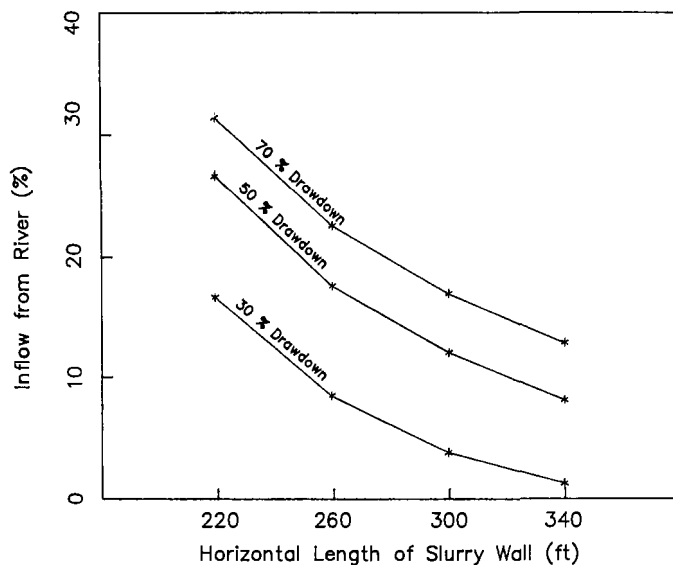
Figure 7
Effect of the Length of a Straight Slurry
Wall on the Percent Inflow from the Paper
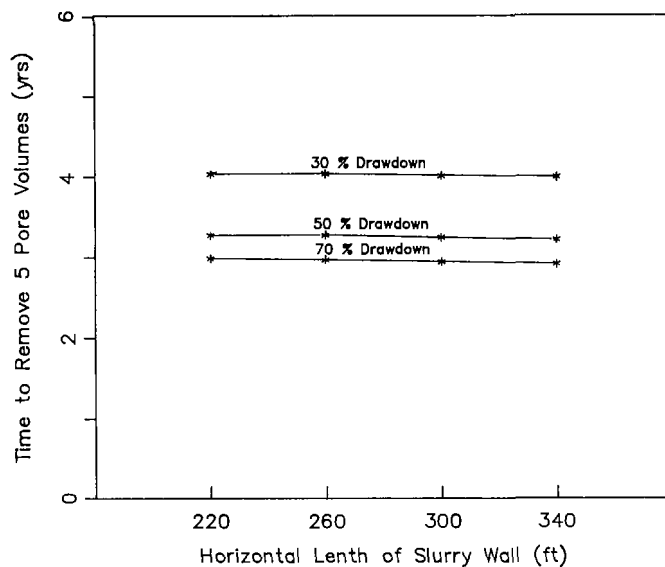
Figure 8
Effect of the Length of a Straight Slurry
Wall on the Aquifer Restoration Time

the drawdown levels from 30 to 70%. Such a reduction is nearly identical to the results for the simulations without a slurry wall present [3.91 years at 30% drawdown (simulation No. 2) compared to 2.93 years at 70% drawdown (simulation No. 4)].

The above simulation results indicate that conjunctive use of a slurry wall with an interceptor trench can be highly effective in minimizing the inflow from a river, provided that a relatively low drawdown level is maintained in the trench (i.e., 30% of the total available drawdown). The flow patterns generated from simulations No. 14 and No. 16 are shown in Figures 9 and 10, respectively.

Effect of the Slurry Wall End Configuration

Six additional simulations were performed to evaluate the performance of a slurry wall with an angled end configuration. Both ends of the slurry wall which extend beyond the ends of the interceptor trench (with the trench length remaining constant) were either angled away from the river or towards the river as shown in Figure 11. The Type A con-

figuration has both ends angled 30 degrees upgradient (away from the river) and the Type B configuration has both ends angled 30 degrees downgradient (toward the river). Table 3 summarizes the results obtained from the above simulations and provides a comparison to those simulations for a straight slurry wall (simulation Nos. 8, 11 and 14). All of the above simulations were performed with a 30% drawdown level in the interceptor trench. The above results are presented graphically in Figure 12.
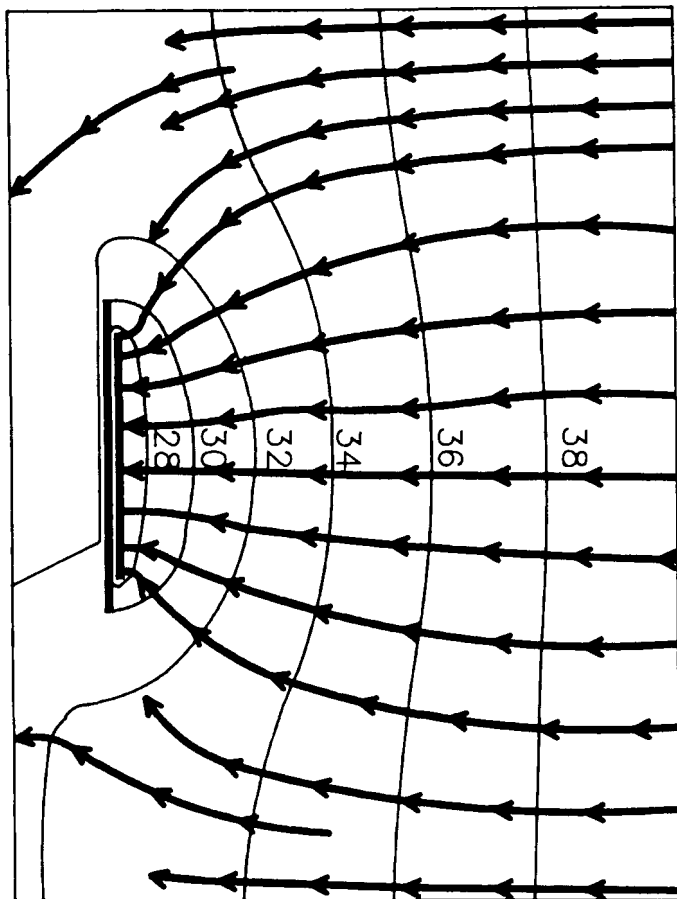
Figure 9
Flow Pattern for Simulation of a Straight Slurry
Wall (Length=340 ft) and Interceptor Trench with
30% Drawdown (Simulation No. 14)

Figure 10
Flow Pattern for Simulation of a Straight Slurry
Wall (Length=340 ft) and Interceptor Trench with
70% Drawdown (Simulation No. 16)

The results indicate that the performance of the slurry wall can be further improved with a proper end design. In particular, bending both ends of the slurry wall away from the river can provide additional hydraulic impedance to the induced river inflow drawn around the ends of the slurry wall. For example, a 340-ft slurry wall angled away from the river (simulation No. 19) resulted in zero percent inflow from the river. On the contrary, a noticeable reduction in the performance can be observed when the barrier wall ends are angled toward the river; this guides the induced river inflow around the ends of the wall.

CONCLUSION

A series of model simulations was conducted to evaluate the performance of a slurry wall/interceptor trench system for recovering a groundwater contaminant plume near a surface water body (e.g., a river). The simulation results indicate that a barrier wall will not fully perform

its intended function of eliminating the induced inflow from the river unless the drawdown from the original static level at the interceptor trench is maintained relatively low (i.e., 30% of the available drawdown at the trench). High drawdown levels at the trench will result in uncontaminated surface water being drawn around the ends of the slurry wall and into the trench.

The increase in the length of the slurry wall beyond both ends of the trench reduces the induced inflow from the river, provided that the drawdown level at the trench is maintained relatively low. With low drawdown levels, the performance of the system can be further improved by angling the ends of the barrier wall away from the river. A properly designed end configuration provides additional hydraulic impedance to the induced river inflow. The increase in the wall length would only contribute a slight reduction in the induced river flow when the drawdown is greater than 30%. The only advantage to having a high drawdown level in the interceptor trench is that the time required for aquifer restoration to occur would be reduced. However, a significant portion of the total effluent volume recovered from the trench would be uncontaminated water from the river.

The sensitivity of the system's performance (i.e., aquifer restoration time and reduction of induced flow) to the physical geometry of the barrier wall as well as the drawdown level at the trench can be evaluated via model simulations. For a given set of design criteria (extraction and treatment capacities) and constraints (total project cost and duration), a linear programming approach can be employed to obtain an optimum design of a barrier/interceptor trench system.

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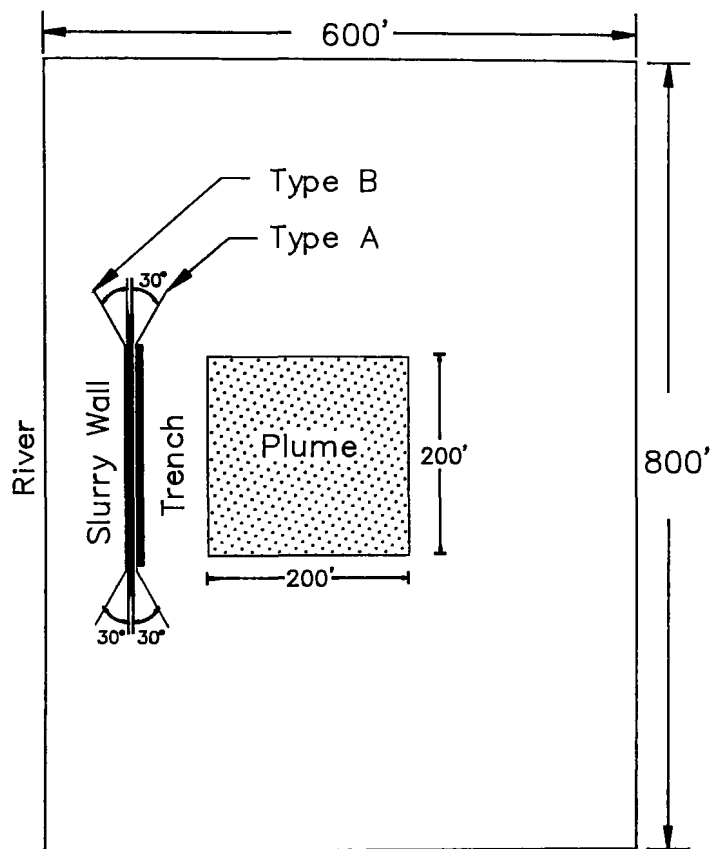
Figure 11
Alternative Slurry Wall End Geometries
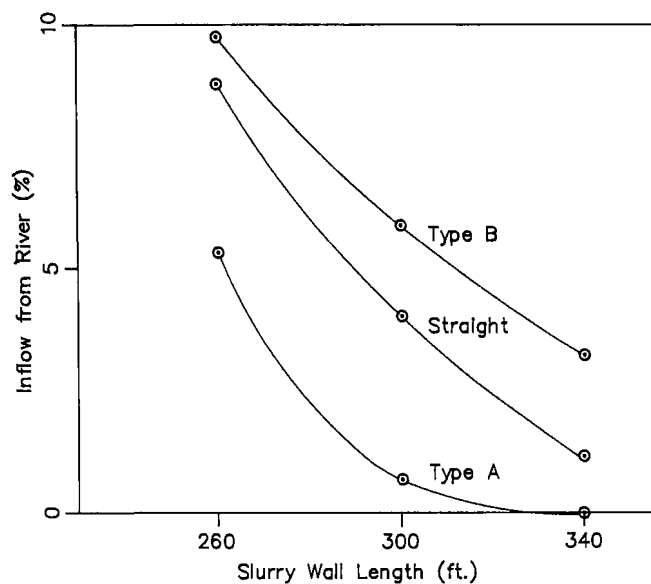
Figure 12
Effects of the End Configuration of Slurry Wall Performance

Table 3
Results for Simulations of an Interceptor
Trench and Angled Slurry Wall

	TABLE 3		
	Results for Simulations of an Interceptor Trench and Angled Slurry Wall		
Simulation No.	Edge Configuration	Slurry Wall Length (ft.)	Flow From River* (%)
17		260	5.20
18	Angled 30° away from River	300	0.72
19		340	0.00
20		260	9.78
21	Angled 30° toward River	300	6.04
22		340	3.55
8		260	8.60
11	Straight Slurry Wall	300	4.02
14		340	1.46
* 30% Drawdown in trench.			

Closure of the Industrial Waste Lagoon at Tooele Army Depot

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ABSTRACT

The Industrial Waste Lagoon (IWL) was an unlined evaporation pond, measuring approximately 400 feet by 200 feet, into which an average of more than 140,000 gallons of industrial wastewater and stormwater were discharged daily via 15,000 feet of unlined ditches from the mid-1960s until November 1988.

The closure plan for the IWL and wastewater ditches consisted of removing the most highly contaminated soil from the wastewater ditches and placing it in the IWL where it was covered with a multilayer cap. The wastewater ditch excavations were backfilled with clean material and also were capped. Soil and sludge in the IWL was mixed with clean soil to absorb free moisture and then compacted to create a firm foundation for the overlying cap. The IWL sludge did not yield hazard constituents when subjected to laboratory leach tests. Consequently, the sludge did not require treatment except to reduce its free moisture content.

The multilayer cap was designed according to U.S. EPA guidelines for closure under the Resource Conservation and Recovery Act (RCRA). After the sludge/soil mixture had been emplaced and compacted, it was covered with soil excavated from the wastewater ditches followed by a 2-foot layer of clay. A synthetic membrane was placed on top of the clay layer followed by a 6-inch thick, permeable drainage layer composed of uniformly sized sand. Finally, the drainage layer was covered with 3.5 feet of clean backfill and 6 inches of topsoil. Native vegetation was established in the topsoil to minimize erosion. The surface of the cap was mounded to promote run-off, and benchmarks were installed in the surface for periodic monitoring to detect settlement that would allow water to accumulate on the cap.

INTRODUCTION

The Industrial Waste Lagoon (IWL) received an average of more than 140,000 gallons of industrial wastewater and stormwater run-off daily from the maintenance area of Tooele Army Depot (TEAD) in Utah from the mid-1960s until discharges were discontinued in 1988. It was closed by the U.S. Army in 1989 under the terms of a Consent Decree with the State of Utah. This paper describes how the IWL and its associated wastewater ditches were closed using a design prepared by James M. Montgomery, Consulting Engineers, Inc. (JMM) under contract to the U.S. Army Corps of Engineers, Huntsville Division.

Description of Tooele Army Depot

The Tooele Army Depot (TEAD) is located approximately 35 miles southwest of Salt Lake City, Utah, in the southern portion of the Tooele Valley. The Tooele Valley covers approximately 250 square miles and is bounded by the Oquirrh Mountains, South Mountain and the Stansbury Mountains on the east, south and west, respectively. To the

north, the valley opens to the Great Salt Lake. Tooele Valley is sparsely populated and land is used primarily for agriculture and ranching. Principal population centers include the City of Tooele, approximately one mile east of the Depot, the City of Grantsville, approximately two miles to the northwest, and Erda, approximately three miles to the northeast.

The primary activities of TEAD are storage and demilitarization of conventional and chemical munitions and rebuilding of military equipment. TEAD consists of two areas: (1) the north area, which occupies approximately 39 square miles in Tooele Valley; (2) and the south area, which occupies approximately 30 square miles in Rush Valley, located approximately 10 miles south of the north area (Figure 1). Hazardous materials are or were used, generated or disposed of in the north area at the demolition grounds, the maintenance area, the IWL and the trinitrotoluene (TNT) washout ponds. In the south area, hazardous materials are present in the demilitarization area/disposal pits, the chemical agent storage areas and the demolition grounds.

Physical Setting

The Tooele Valley is bounded on the north by the Great Salt Lake at an elevation of approximately 4,200 feet. The eastern border of the valley is the north-south trending Oquirrh Mountains which rise sharply from the valley floor at an elevation of approximately 5,200 feet to a maximum height of 10,350 feet. The western border of the Tooele Valley is formed by the Stansbury Mountains which reach a maximum altitude of 11,031 feet at Deseret Peak. South Mountain, a relatively low-lying east-west trending structure, bounds the valley on the south.

The topography of the valley floor is shaped by coalescing alluvial fans formed by erosional debris washed from the mountains. The IWL is situated on the bajada formed by alluvium derived from the southern portion of the Oquirrh Mountains. The alluvial fans which form the valley floor slope gently toward the north at a gradient of approximately 40 feet per mile near the Great Salt Lake. The TEAD site is characterized by a gently rolling surface intersected by a series of shallow gullies.

The Tooele Valley is typical of Basin and Range physiography in which fault-block mountains rise above flat, intermontane valleys. The Oquirrh Mountains to the east and South Mountain to the south are composed mainly of alternating quartzite and limestone beds of late Mississippian, Pennsylvanian and early Permian age. The Stansbury Mountains to the west contain similar formations in addition to quartzite of Cambrian age. The rocks in all three mountain ranges bordering the valley have been extensively folded and faulted.

The Tooele Valley is filled with a thick sequence of unconsolidated sediments of Tertiary and Quaternary age. The older Tertiary sediments comprise the Salt Lake Group and consist of moderately consolidated sand, gravel, silt and clay with an abundance of volcanic ash (Everitt

Figure 1
Vicinity Map

ranged up to approximately 8 feet deep. Wastewater in the IWL was alkaline and contained elevated levels of chromium, lead and organic solvents such as 1,1,1-trichloroethane, trichloroethene, toluene, carbon tetrachloride, and other organic compounds. However, the composition of wastewater was highly variable due to the many industrial processes that contributed to the flow. Sludge from the IWL yielded similar inorganic and organic contaminants.[3]

Description of the Wastewater Ditches

Four parallel wastewater outfall ditches extended from the vehicle maintenance area 1,200 to 2,700 feet to the northwest where they terminated into a single wastewater ditch. The single ditch extended to the north approximately 6,000 feet to the IWL. The ditches were constructed in gravelly soils and were unlined with broad U-shaped cross-sections. The ditches ranged from 1 to 3 feet deep with the bottoms 1 to 3 feet across. The ditch widths at the top ranged from approximately 10 to 20 feet.

CLOSURE ACTIVITIES

The IWL was closed in place by removing the liquid, stabilizing the sludge, placing contaminated soil from the wastewater ditches into the IWL and installing a multilayer cap. Closure activities are briefly described below, and the design parameters are presented in detail in the next section.

Liquid Removal and Disposal

Liquid remaining in the IWL after wastewater discharge ceased was pumped into tank trucks and discharged into the industrial wastewater treatment plant (IWTP) in the TEAD maintenance area that was constructed to replace the IWL. Most of the wastewater in the IWL was lost to infiltration when discharges ended before closure activities began, and the remaining liquid was taken to the IWTP.

Sludge Treatment, Backfill and Compaction

Sludge samples from the IWL subjected to the Toxic Characteristic Leaching Procedure (TCLP) yielded concentrations of metals and organics below their toxic thresholds. Consequently, it only was necessary to mix clean, fine-grained soil with the IWL sludge to absorb any free liquid. The sludge/soil mixture was placed in the IWL and firmly compacted to construct a strong foundation for the cover.

Wastewater Ditch Excavation, Backfill and Cover

Sludge and contaminated soil from the wastewater ditches were excavated and placed in the IWL on top of the sludge/soil mixture. The objective of the wastewater ditch excavations was to remove the majority of contaminated materials and to generate adequate volumes of soil to construct the final cover on the IWL. After the wastewater ditches were excavated, they were backfilled with clean soil and covered with a synthetic membrane.

IWL Cover

Soil excavated from the wastewater ditches was placed in the IWL and graded and compacted to form the slope of the final cover. The cover, in ascending order from the wastewater ditch soil, consisted of a 2-foot low-permeability layer, a synthetic membrane, a protective geotextile, a 1-foot drainage layer, a geofabric filter and 2 feet of natural fill and topsoil covered with a geofabric to prevent erosion. The cover also was constructed with run-on/run-off control and subdrains to receive water transmitted by the drainage layer.

CLOSURE DESIGN PARAMETERS

This section describes how closure design parameters were developed for stabilizing the IWL sludge, for compacting the cover foundation and for installing the cap.

Summary of Bench Tests on IWL Sludge

Laboratory bench tests were conducted on various sludge mixtures to select the design admixture. The objective of the bench test was to identify a mixture of sludge and additive that met the following requirements:

and Kaliser, 1980). The younger Quaternary sediments consist of interlayered and unconsolidated sand, gravel, silt and clay including sediments deposited before, during and after the existence of Lake Bonneville. The thickness of the valley sediments ranges from a feather edge at the margins of the valley to more than 8,000 feet in the north central part of the valley.

Description of the Industrial Waste Lagoon

The IWL is an unlined evaporation pond, measuring approximately 400 feet by 200 feet, into which an average of more than 140,000 gallons of industrial wastewater and stormwater were discharged daily until November 8, 1988. It was originally excavated for gravel borrow material and began receiving wastewater about 1965, according to TEAD personnel. However, the total amount of wastewater discharged to the IWL is unknown. Wastewater generated by the boiler plant, metal parts cleaning, degreasing, steam cleaning and dynamometer test cells flowed into the IWL through four unlined ditches.

The results of a study by the U.S. Army Environmental Hygiene Agency[1] conducted between March 15 and September 26, 1982, showed that of the 139,800 gallons per day (gpd) of wastewater discharged to the IWL during that period, 96% or 134,000 gpd infiltrated from the ditches and the IWL and the remaining 4% evaporated. On October 8, 10, 11 and 15, 1985, the USAEHA measured the discharge to the ditches and IWL at 161,100 gpd.

A limited amount of information was collected regarding the volume and composition of liquid and solid waste in the IWL. It contained approximately 2,000 cubic yards of sludge and approximately 2,000,000 gallons of liquid as of December 1984.[2] The sludge accumulated primarily in the south end where it was up to 3 feet thick, and wastewater

- Contains no free water
- Can be classified as non-toxic when subjected to the TCLP (Toxic Characteristic Leaching Procedure)
- Minimizes the increase of the volume of the mixture
- Makes use of readily available, non-proprietary additives
- Is the least expensive of the additives that meet the other criteria

The selected mixture was subjected to geotechnical tests to identify the optimum moisture and density at which it should be emplaced in the IWL to resist settling. Complete details of the bench-testing program can be found in JMM's 1987 Report.[4]

The materials for the bench-testing consisted of sludge and various materials for mixing with the sludge. Approximately 5 gallons of sludge were collected from the IWL from several points in the south end. The additives for the bench tests included fly ash, type I portland cement, a 60/40 mixture of fly ash and type I portland cement, hydrated lime and imported soil from an approved borrow area.

Several sludge/additive mixtures were subjected to the Paint Filter Liquids Test (U.S. EPA Method 9095) to determine when the mixtures contained no free liquids. The test for free liquid consists of placing a predetermined amount of sample in a paint filter. If any portion of the sample passes through and drops from the filter within the 5 minute test period, then the test sample is considered to contain free liquids. The test results indicated that a 1:1 ratio of sludge and any of the additives was the approximate minimum dosage to eliminate free liquid from the mixture. Mixtures containing twice as much additive as sludge were tested to evaluate the ability of the larger dosage of additive to stabilize any mobile chemical species. Samples of raw sludge were subjected to the TCLP to evaluate the degree to which the additives stabilized the sludge.

The raw sludge sample yielded low concentrations of five volatile and three semivolatile organic compounds and three metals at concentrations greater than laboratory detection limits. None of the identified compounds exceeded their respective TCLP regulatory levels and, consequently, the raw sludge did not exhibit the toxic characteristic. Similarly, all the sludge mixtures were nontoxic on the basis of TCLP testing. In addition, the analyses indicated that there were not large differences in the abilities of the five additives to treat the IWL sludge; each of the mixtures was nontoxic according to the TCLP and produced a stable solid containing no free liquid. The differences among the analyses of the mixtures were not considered to be significant from the standpoint of admixture design. The alkaline sludge apparently immobilized the hazardous constituents so the additives were necessary only to absorb free liquid. There was no need for the additives to chemically bind the metals and organic compounds.

Table 1 lists the percentage increases in the sludge mixtures for each additive. Table 2 presents estimated costs for each additive, taking into consideration the material costs, volume increase and handling costs. The unit costs for materials were obtained from a Salt Lake City supplier and include delivery to TEAD. TEAD soils were assumed to be excavated from within 2 to 3 miles of TEAD and hauled to the IWL. A handling charge for mixing the sludge and additives was assumed to be $5.00 per cubic yard for each additive. The estimated total cost for TEAD soil was the lowest among the mixtures and was highest for lime. Lime must be transported from South Dakota, which added considerably to its cost. TEAD soil was selected as the most appropriate additive because its use was least expensive, and the volume increase of the sludge/soil mixture was similar to the other mixtures.

Sludge/soil mixtures were subjected to compaction tests to determine moisture-density relationships of the mixture and a one-dimensional compression test to estimate long-term settlement of the mixture under its own weight plus the weight of overlying cover. The compaction test determined that the optimum moisture content of the sludge/soil mixture would be 22.8% with a maximum dry density of 96.3 pounds per cubic foot (pcf). At 95% of this compaction, the sludge/soil mixture can support the maximum load of the IWL cover, which was estimated to be approximately 3,000 psf, with a total differential settlement of less than 0.3 feet.

Table 1
Increase in Stabilized Sludge Volume

Additive	Increase in Volume (% of Unstabilized Sludge Volume)[a]
Fly Ash	26
Portland Cement	36
Lime	30
TEAD Soil	42
Fly ash/Portland cement mixture	46

[a]Average of three replicate tests.

Table 2
Estimated Costs of Additives

Additives	Unit Cost ($/cy)	Material Cost[*]	Mixture Volume (cy)	Handling Cost ($5/cy)[**]	Total	$/cy
Fly Ash	27	$ 54,000	2520	$ 12,600	$ 66,600	$ 26
Type I Portland Cement	94	188,000	2720	13,600	201,600	74
60% Fly Ash/40% PC	54	108,000	2920	14,600	122,600	42
Lime	150	300,000	2600	13,000	313,000	120
TEAD Soil	5	10,000	2840	14,200	24,200	8.50

* 2000 cy for a 1:1 mixture.
**The unit handling cost is assumed to be the same for all additives for comparison purposes.

Material costs are from the Resource Materials Corporation, Salt Lake City, and include delivery to TEAD.

Mixture volume includes the 2,000 cy of IWL sludge (JMM, 1986) and the increase in volume due to each additive is shown in Table 1.

IWL Cover Design

The cover design for the IWL meets the requirements of RCRA Guidance Documents[5,6] and the U.S. Army Corps of Engineers.[7] In addition, the cover meets the design requirements in Utah Hazardous Management Regulations (UHWMR) Section 7.21.4(a) which include the following:

- Provide long-term minimization of migration of liquids through the closed IWL
- Function with minimum maintenance
- Promote drainage and minimize erosion or abrasion on the cover
- Accommodate settling and subsidence so that the cover's integrity is maintained
- Have a permeability less than or equal to the permeability of any bottom liner system or natural subsoils present.

The cover was designed to meet the following post-closure responsibilities of the Owner or Operator as specified by UHWMR 7.21.4(b):

- Maintain the integrity and effectiveness of the final cover, including making repairs to the cover as necessary to correct the effects of settling, subsidence, erosion or other events
- Maintain and monitor the groundwater monitoring system and comply with all other applicable requirements of 7.13 of these regulations
- Prevent run-on and run-off from eroding or otherwise damaging the final cover
- Protect and maintain surveyed benchmarks used in complying with 7.21.3

On the basis of these regulations, the cover design consists of three layers. The lowermost layer is constructed from low permeability material to prevent infiltration from precipitation and surface water to enter the waste. The middle layer is relatively permeable to allow infiltrating water to flow along the top of the lowermost layer to the perimeter of the cap. The upper layer consists of native fill and topsoil to sustain vegetation and resist erosion.

The lower permeability layer consists of 2 feet of clay or clay-amended soil with a recompacted permeability less than or equal to 1 x 10-7 centimeters per second (cm/sec) which is covered with a synthetic membrane (Figure 2). The synthetic membrane is covered by a protective geotextile. The middle drainage layer consists of 12 inches of relatively permeable, uniformly graded sand or fine gravel with a permeability of at least 1 x 10-3 cm/sec. The purpose of this layer is to carry infiltrating water to the perimeter of the cap for collection and discharge. This layer is covered by a geofabric filter to prevent infiltration and clogging by soil from the upper soil layer. The upper layer consists

of 6 inches of topsoil and 3.5 feet of fill to sustain native vegetation for erosion control and to protect the underlying layers from frost penetration. The vegetation will consist of persistent but shallow-rooted plant species whose roots will not extend into the drainage layer.

The shape of the cover was based on providing run-on/run-off control and creating an adequate slope on the surface of the cover (Figure 3). The perimeter of the cover is approximately 2 feet above the existing grade to prevent surface water from running onto the cover. Run-on ditches surrounding the cover were sized for the 100-year storm based on precipitation events using Richardson's data.[8] The surface of the

Figure 2
IWL Cap Profile

Figure 3
IWL Cap Design

EXISTING GROUND SURFACE

LIMIT OF CONTAMINATED SOIL EXCAVATION (20" BELOW BOTTOM OF DITCH)

ADDITIONAL EXCAVATION FOR CONSTRUCTION OF COVER (3'- 5' BELOW EXISTING GROUND)

EXCAVATION DESIGN

TOPSOIL AND VEGETATIVE COVER

COMPACTED COVER MATERIAL

COVER MATERIAL FOR SYNTHETIC MEMBRANE

40mil. THICK SYNTHETIC MEMBRANE WITH PROTECTIVE GEOFABRIC COVER

COMPACTED BEDDING MATERIAL
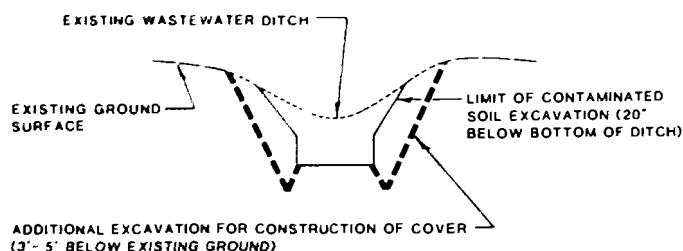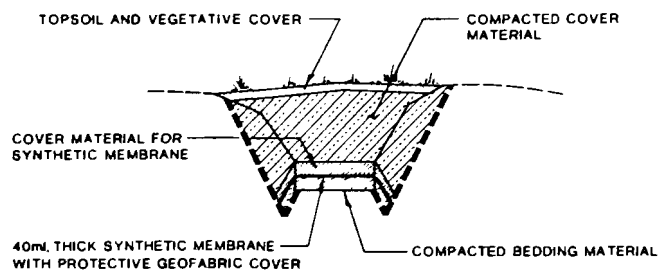
BACKFILL DESIGN

NOTE. DETAILS ON EXCAVATION AND BACKFILL PROCEDURES AND COVER MATERIALS ARE PRESENTED IN DESIGN ANALYSIS AND TECHNICAL SPECIFICATIONS, JMM 1988.

Figure 4
Wastewater Ditch Cover Construction Design

cover was designed with a 3.8% slope to promote drainage without erosion and to fall within the 3 to 5% slope recommended by the U.S. EPA[9] even if settlement occurs. Water running off the cover on the top of the synthetic membrane will be intercepted by 6-inch diameter, perforated Schedule 40 PVC subdrains along the edges of the cover. The collector subdrains discharge to an 8-inch PVC drain on the downhill side of the cover. The volume of fill in the cover was calculated from cross-sections drawn at 25-foot intervals over the entire length of the IWL.

The composition of the synthetic membrane was specified to meet the requirements of the National Sanitation Foundation (NSF) Standard Number 54 for flexible membrane liners. The NSF standard is widely accepted, and it is endorsed by the U.S. EPA.[5] The membrane material must also withstand the organic compounds that may be present in the sludge/soil mixture and wastewater ditch soil.

The thickness of the membrane was specified at 40 mils to ensure that it has sufficient tensile and elongation strength to withstand the effects of the gravelly and cobbly soil at TEAD.

Cover Design for the Wastewater Ditches

The purpose of excavating the wastewater ditches is to remove sludge and contaminated soil to a depth of 20 inches and to obtain foundation material for the IWL cover. At least 6,000 cubic yards of material were excavated from the ditches under the assumption of 1:1 slopes of the sides of the excavation and a 15% shrinkage rate.

The wastewater ditch excavations were backfilled with material from TEAD borrow pits or other locations and were free of roots and other organic matter, trash, debris, frozen materials, stones larger than 2 inches and materials classified as Pt, OH, OL, MH or ML (Unified Soil Classification) The backfill was compacted to 95% of the maximum dry density obtained in the laboratory by the test procedure presented in ASTM D-698. Although the wastewater ditches were not loaded to the extent of the IWL, the backfill was compacted firmly to resist settling.

The purpose of the wastewater ditch covers is to prevent infiltrating run-off and precipitation from contacting soil that may still contain contaminants (Figure 4). The cover consists of the same material selected by the contractor for the IWL cover. The tops of the covers were 2.5 to 5 feet below grade, and the edges were anchored 4 to 6.5 feet below grade. This depth of burial was designed to provide protection from frost. The finished grade of the covers will be 2% from the centerline to the edges to direct precipitation and surface drainage away from the ditches and to allow for settlement. The covers will range from 10 to 20 feet wide.

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In Situ Vitrification Treatability Study

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ABSTRACT

The Denver Radium Site consists of 31 properties contaminated by low level radioactive waste that could endanger public health, welfare and/or the environment. The soil from Operable Unit (OU) VIII of the Denver Radium Site contains both radioactive and nonradioactive contaminants and thus may not meet the acceptance criteria of existing commercial facilities. During the remedial investigation, in situ vitrification (ISV) was identified as a technology which could provide a permanent solution to the waste types on-site. A bench-scale test was conducted to determine if the ISV process is appropriate to the specific soil-waste mixture present at the site. At the time of this publication, the test results were still in draft, preliminary form. Because this site involves enforcement of actions directed to potentially responsible parties, the results cannot be released in draft form. The results of this test will be used to determine if a full-scale ISV field test will be conducted on-site.

INTRODUCTION

The Denver Radium Site was placed on the National Priorities List in September 1983. The site was divided into 11 Operable Units (OU) which contain both open areas, some paved areas and structures. The contaminated soils from all but one of the OUs are being excavated and hauled by rail to a permanent disposal facility.

OU VIII of the Denver Radium site is currently in the Remedial Investigation/Feasibility Study phase. It was the site of metal processing activities beginning in the early 1920s. Throughout the 1930s vanadium ore, uranium ore and radium salts were received at the site. From 1939 to 1941, this property was one of two radium producers in the United States. In 1942, radium production stopped and emphasis shifted to the production of molybdenum; however, the plant continued to receive shipments of vanadium ore until 1943. The plant was actively producing uranium compounds in the 1960s and ceased operations in 1984 due to a decrease in the market price of molybdenum.

Processing involved dissolution of the ores with acids and caustics and extraction using various processes, some involving organic compounds now considered hazardous or potentially hazardous. Because of the nature of the production process, wherein reagents, solvents and processing solutions were stored in vats and pumped to different reaction vessels, the chance of spills and leaks was high and spills resulted in soil and possibly groundwater contamination.

Studies of the radiological conditions on the site have identified radiation fields and radionuclide concentrations in various media due to the presence of uranium, radium and associated decay products.

Metals used on the property include, but are not limited to:

Arsenic	Lead	Selenium
Barium	Magnesium	Nickel
Manganese	Iron	Uranium
Cobalt	Mercury	Vanadium
Copper	Molybdenum	Zinc

Chemicals or other materials that were either used in the ore processing, used in the laboratories on the property, or stored on the property include:

Inorganic Reagents	*Organic Reagents*
Ammonia	Acetic acid
Ammonium hydroxide	Chloroform
Ammonium nitrate	Methyl isobutyl ketone
Barium carbonate	Tributyl phosphate
Calcium hydroxide	1,1,1-trichloroethane
Hydrochloric acid	Tertiary amines
Hydrogen peroxide	
Hydrogen sulfide	*Others*
Nitric acid	Asbestos
Sodium hydroxide	Propane gas
Sodium sulfate	Kerosene
Sulfuric acid	

IN SITU VITRIFICATION

ISV was developed in 1980 by Battelle Memorial Institute and Geosafe Corporation. ISV is a thermal treatment process involving electrical melting of soil. A square array of four electrodes is inserted into the ground to the desired treatment depth. In order to establish a path of conductance, a mixture of flaked graphite and glass frit is placed around the electrodes. An electrical potential of more than 12,000 volts is applied to the electrodes which establishes an electrical current in the graphite and glass frit. The resultant power heats the path and surrounding soil to above fusion temperature. The melt advances at a rate of 1 to 2 inches per hour.

Most contaminants in the soil typically exist in a solid or liquid phase. During processing, most undergo a change of state to a liquid or gaseous phase. The physical state of contaminants is directly related to their movement during ISV processing. Many organic components vaporize during processing. Organic vapors increase in temperature to their pyrolysis temperature where they break down into successively smaller chains of molecules and eventually reach the state of elemental or diatomic gases. Upon pyrolysis, the concentration of the original compound vapor is diminished, resulting in a concentration gradient of the original vapor toward the melt. Some of these gases may dissolve into molten mass; the remainder may be expected to escape the treatment volume. Such vapors are collected and treated to below air emission requirements in an off-gas treatment system.

Inorganic compounds may thermally decompose or otherwise enter into reactions with the melt. Nitrates and sulfates yield decomposition products which may dissolve into the melt or may evolve through it and be collected at the surface. Some volatile or semi-volatile inorganics (i.e., Pb and Hg) are removed from the treatment area and recovered in the off-gas system. Pyrolytic destruction of hazardous inorganic elements (CN, for example) is possible; however, destruction of heavy metals is not possible. Heavy metals ultimately are dissolved and incorporated or encapsulated in the residual product. Radioactive elements cannot be destroyed, but are incorporated (immobilized) into the final product.

The processing area is covered by an octagonal shaped off-gas collection hood which is much larger than the treatment area. Flow of air through the hood is controlled to maintain a negative pressure. Air provides oxygen for combustion of pyrolysis products and vapors. Off-gases, combustion products and air are drawn from the hood by an induced draft blower into a treatment system. Unit processes within the treatment system include quenching, pH controlled scrubbing, dewatering, heating, particulate filtration and activated carbon adsorption.

A self-controlled cooling system is utilized to cool the quenching/scrubbing solution. The filters and carbon adsorption columns are utilized as secondary or backup stages to ensure safe air emissions. After processing for a time, the scrubber solution, filters and activated carbon likely contain sufficient contaminants to warrant treatment or disposal themselves. Typical treatment may include passing the scrubber water through a diatomaceous earth filter and activated carbon. The water may be recycled or discharged to a sanitary sewer, and activated carbon filters may be placed in a subsequent ISV setting for reprocessing. In this way, the only secondary waste resulting from the ISV processing is that contained in the off-gas treatment system after the last setting at a site.

Upon completion of the ISV processing, the cooling time of the molten mass affects the relative extent of glassy phase and crystalline phase present in the residual product. Typically, the mass solidifies into a silicate glass and microcrystalline product which is physically and chemically equivalent to natural obsidian.

BENCH-SCALE TEST: MATERIALS AND METHODS

The performance objective of the bench-scale ISV test was to identify the effectiveness of this treatment alternative for the radioactive and heavy metal soil contaminants at this site. The contaminants of primary concern are Ra-226, Th-230, natural Uranium, As, Se, Pb, Hg, Cd and Ba. The bench-scale test was conducted on April 12, 1990. Several different types of materials were involved in the test. They included: (1) bore hole soils (BH) - soils located on-site with high concentrations of radionuclides, (2) surface soils (SS)- soils located on-site with high concentration of heavy metals and (3) background soils-noncontaminated soils collected from an off-site location.

The physical properties of these soils were evaluated prior to the bench-scale test. The results of these analyses are presented in Table 1.

Table 1
Physical Characteristics

	Moisture wt%	Dry Density	Wet Density
Surface Soil	10	1.3 g/cm³	1.44 g/cm³
Borehole soil	41	0.72 g/cm³	1.23 g/cm³
Background soil	8	1.48 g/cm³	1.60 g/cm³

Compositional analysis of these soils was also performed. Whole rock analyses, using x-ray fluorescence, were performed on the soils used in the test to determine their bulk chemistry. These analysis quantified the concentration of glass-forming ions, electrically conductive ions and other ions which serve as fluxing agents during ISV melting.

A bench-scale vitrification unit was used to conduct the treatability test. The levels of radioactivity in the test soils prevented the performance of the test at the Geosafe laboratory located at the University of Washington without a license; therefore, the test equipment was transported to OU VIII.

The test was conducted in an 85-gallon drum which was placed inside a steel box for double containment safety purposes. The four 0.5-inch diameter by 24-inch long molybdenum electrodes were sheathed by 1.5-inch diameter by 20-inch long graphite collars to prevent oxidation of the molybdenum and to induce subsidence of the melt zone. The molybdenum and graphite electrodes were placed in the soil to a depth of 16 inches. The electrode assemblies were designed to have a center to center spacing of 8 inches in a square array. Due to the unexpected high iron content of the contaminated soils, this spacing array was moved out to a 10-inch center to center square array to reduce the potential for molten iron to form at the bottom of the melt. This molten pool, if formed, could serve as a path for the electric current, thus short circuiting the vitrification process.

The bench-scale tests are designed to challenge the vitrification process with the highest contaminant concentrations on-site. Because the highest radioactive and nonradioactive soil concentrations are not coincident with each other, the contaminated soil was placed in two distinct layers in the test drum. The contaminated soil was stratified and placed in an 8-inch square area in the center of the drum. The first contaminated zone consisted of the surface soils (SS), which were primarily contaminated with heavy metals, and had a height of 5 inches. The second contaminated zone consisted of borehole (BH) soils, which were primarily contaminated with radionuclides, also to a height of 5 inches. The contaminant zone had a height of 10 inches and was covered with 3 inches of clean soil. The clean soil was added to ensure that a full vitreous zone was established prior to encountering any contaminants. The ISV boundaries (adjacent to and beneath the contaminated soils) were surrounded by clean soils.

In order to monitor processing depth, type K thermocouples were installed in the center of the test drum extending from the surface down to the bottom of the drum (32 inches) in 2-inch intervals. In addition, three type K thermocouples were installed on a horizontal axis, 10 inches below the surface grade at 2-inch intervals to measure horizontal melt dimensions and the temperature isotherms in the surrounding uncontaminated soil. Geosafe continued to vitrify the soil until the thermocouple located at the 16-inch depth reached the 2192°F temperature.

A flaked graphite/glass frit mixture was placed in a 1-inch by 1-inch path laid in an "X" and square pattern on the surface of the soil to provide direct electrical conductive path between the electrodes. This spacing is consistent with full-scale remediation operations. Approximately 2 hours after the startup of the test, it was evident that a melt was not being established. The vitrification process was stopped and an additional layer of graphite and glass frit was added to promote electrical conductance. A melt was established, and the test was completed in six hours and eight minutes.

During the ISV testing, the vitrification zone was covered with a 2-inch kaowool insulation blanket, leaving a small gap around the electrode for venting. The insulation helps promote subsidence of the molten surface and improves the melting efficiency of the operation. This technique is consistent with full-scale operations.

The power system consists of a 30 kW capacity Scott-Tee transformer. The transformer is equipped with 12 voltage taps and two silicon controlled rectifiers for controlling power input to the melt. The test was run at a target control power of 15 kW to closely simulate full-scale operations (power density). The transformer was equipped with metering on the secondary side (output to the electrodes) for power, voltage and amperage. Electrical and thermocouple data were recorded at 0.5 hour intervals.

The off-gas stream from the test unit is equipped with a condensate collection tank for the collection of water and particulates released from the melt. This tank simulates the performance of the quencher and scrub tank in the Geosafe large-scale system. In addition, the system contains a desiccant, HEPA filter and activated vapor phase column to remove any particulate or gaseous emissions from the melt. Off-gases generated from the melt were sampled continuously during the test. Three side stream samples were drawn through 2-inch ports located

in the off-gas line. U.S. EPA Methods 1 and 2 were used to determine stack gas velocity, temperature and volumetric flow rate. U.S. EPA Methods 3 and 3A were used to determine the molecular weight of the stack gas. U.S. EPA Method 4 was used to determine the moisture content of the stack gas. U.S. EPA Methods 108, 12 and 101A techniques were employed to collect the multiple metals screen sample.

The pretest measurements include various physical, nonradioactive nuclide and radionuclide measurements of the background soil and of the contaminated soil. The physical measurements include moisture, dry density, fusion temperature, 100 poise temperature, electrical conductivity at 100 poise temperature, melting temperature and test sample mass. Chemical measurements include HSL metals, Al, Cu, Fe, K, Li, Na and Si by modified U.S. EPA method 6010. The radiochemical measurements include isotopic U, Ra-226, Th-230, Pb-210, gross alpha and gross beta/gamma radiation.

The test measurements which were conducted with the bench test include gas pressure at three points in the test apparatus, air flow at one point in the test apparatus, temperature at 18 points in the test matrix and one point in the test apparatus, electrical power, voltage, and amperage supplied to the electrodes, and total organic vapors in the off-gas effluent control discharge.

The post-test measurements which were conducted on the vitrified block and surrounding soils include: one physical measurement, bulk density; chemical measurements, including HSL metals; and radiochemical measurements, including isotopic U, Ra-226, Th-230, Pb-210, radon flux on the full block and gross alpha, beta and gamma.

Leaching tests and associated analyses were performed on the pretest soils and vitrified product using the Extraction Procedure Toxicity Test (EP Tox). The laboratory tests and analyses were performed to meet the Level III analytical category requirements.

RESULTS

Post-test sampling of soils adjacent to and beneath the vitrified mass were taken by a combination of driving a PVC sampling tube into the soil and by compositing representative grab samples at appropriate depths. These two sampling procedures were used because the large rocks in the soil limited sample recovery when driving a sampling tube.

Upon completion of the adjacent background soil sampling, the remaining adjacent soil was removed to allow examination and removal of the glass monolith. During the test, a solidified layer of glass formed on the top of the melt (cold cap). The cold cap (approximately 1.5 in. thick) was broken, and when it was removed, a large void measuring approximately 8 in. X 8 in. X 6.5 in. deep was observed under the cold cap. This void indicated that volume reduction had occurred during treatment. The base of the treatment zone consisted of a vitrified mass approximately 8 in. thick and 15 in. wide. Based on measurements of the void volume and the vitrified mass, the volume reduction appeared to be approximately 25%. All samples taken of the vitrified mass were subjected to radiation scans prior to packaging for transport to the laboratory for analysis.

Retention efficiencies for each contaminant of concern were calculated based upon the following equation:

$$RE \quad \frac{W \text{ in } - W \text{ out}}{W \text{ in}} \quad X \text{ 100} \tag{1}$$

Where
W in = mass of contaminant in the pre-test container
W out = mass of contaminant in the off-gas
RE = retention efficiency

CONCLUSIONS

The results of this treatability test will be used to determine whether ISV is a viable treatment alternative at the site. Specific data to be gathered and evaluated include:
(1) the effects of ISV on soil radiation/radon gas emissions;
(2) effects on contaminant immobilization and leachability;
(3) levels of contaminants in the off-gas system; (4) performance of a mass balance for contaminants of concern; and (5) cost estimates for full-scale remediation.

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Design and Construction of Soil Caps Over Sludge Ponds

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ABSTRACT

Most existing sludge ponds are either being capped or being proposed for capping due to tighter regulations and a growing serious concern over the environment. Capping is necessary to inhibit rainfall penetration, protect migratory waterfowl and shore birds, to prevent escape of gases, to control odors and in some cases for land reclamation. Most sludge deposits have very low shear strength which prohibits conventional construction equipment and even construction personnel from accessing the site. This paper describes design considerations and construction techniques that have been successfully used to place soil covers over soft sludge deposits.

Placement of soil over soft subgrade requires a careful balance between the fill thickness required to support construction equipment and the overburden weight that may cause excessive consolidation and/or bearing failure of the sludge, i.e. mudwaving. With stiff polymer geogrids, the amount of fill required to support construction equipment can be significantly reduced, making it possible to place the initial fill lift without exceeding the bearing capacity of the soft foundation. In many cases, the thickness savings of fill can mean the difference between successful construction using conventional equipment and having to resort to very costly and time consuming specialized construction techniques.

INTRODUCTION

With the growing concern for the environment, the stringent rules and regulations are now considered as standards needed to keep the pollution problems in balance with nature. To comply with the new regulations, several sludge lagoons that have been in operation for more than 20 years have to be closed and capped. Capping is necessary to inhibit rainfall penetration, to keep migratory waterfowl and birds out, to prevent escape of gases, to control odors and, in some cases, for land reclamation. Most sludge materials are very soft, highly compressible and have shear strength values rarely exceeding 200 lb/ft² These characteristics create serious construction and bearing capacity problems.

Due to the inherent very low shear strength of most sludge material, it is extremely difficult, and in some cases impossible, for construction equipment and manpower to access the site. Construction of a soil cover over soft sludge requires a careful balance between the fill thickness required to support construction equipment and the overburden weight that may cause excessive consolidation and/or bearing failure of the sludge, usually occurring in the form of mudwaving. With the use of stiff polymer geogrids, the amount of fill required to support construction equipment can be significantly reduced, making it possible to place the initial soil lift without exceeding the bearing capacity of the soft foundation. This paper describes the design procedure and con-

struction techniques that have been successfully used to place the soil covers over soft sludge deposit without creating bearing capacity failures. The paper also address the important geogrid properties required for such applications.

EMERGING TECHNOLOGY

The concept of designing a reinforced soil platform to allow access on top of soft materials is not new. This particular application started in Canada, in conjunction with oil drilling operations. The existing material referred to as "Muskeg" and the heavy weight of oil drilling equipment necessitated placing a geogrid directly on top of the existing material. A 3-foot thick soil layer was then placed on top of the geogrid. This reinforced soil platform provided a means for the heavy equipment to access the site without failing the subgrade.

When dealing with very soft subgrade and/or sludge materials, the primary objective of the engineer is to design an access system without having the subgrade fail. An indication of failure of the existing material is heavy rutting and creation of uncontrollable mudwaves. Rutting can slow down construction operation and substantially increase the cost and the construction time. Once a mudwave develops, it is extremely difficult to control and contain. Failure of the subgrade can lead to catastrophic failures endangering both loss of life and/or heavy equipment.

Stiff (as defined by the Geosynthetic Research Institute Test Methods GRI-GG3 and GG4)[8,9] biaxially oriented geogrids are used to distribute the loads and prevent overstressing and punching shear failure of the subgrade. The use of geogrid allows the existing sludge material to remain undisturbed and maintain its original design strength.

MATERIAL PROPERTIES

Geogrids were first introduced into North America in the early 1980s. According to The American Society for Testing of Materials definition, a geogrid is any planar structure formed by a regular network of tensile elements with aperture of sufficient size to allow interlocking with the surrounding soil, rock, earth or any geotechnical material to perform the functions of reinforcement and/or segregation.

Geogrids are produced in biaxial and uniaxial load carrying configurations, as illustrated in Figure 1 and were specifically developed for long-term reinforcement of critical structures. Biaxially oriented geogrids typically are used as access tools on top of sludge materials. Geogrids are prestressed during the manufacture to provide high tensile modulus and high tensile strength at very small elongation. A geogrid must be strain compatible with the medium it reinforces, i.e, a geogrid must generate high tensile strength at very low strains.[1,2] The geogrid tensile strength is defined based on GRI Standard Test Method GG1.[6] Again the primary goal is to get access to the site without failing the subgrade.

If the reinforcing structure does not provide high tensile strength at very small elongation, the existing soft material will have to undergo excessive deformation prior to mobilizing the tensile strength of the reinforcing element.[2,3] Excessive deformation can lead to catastrophic failures.

(a) Tensile Strength in MD Direction Only

LEGEND
MD   Machine Direction
     (i.e. Along Roll Length)
CMD Cross-Machine Direction
     (i.e. Across Roll Width)
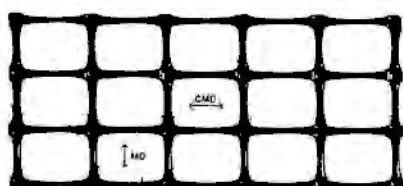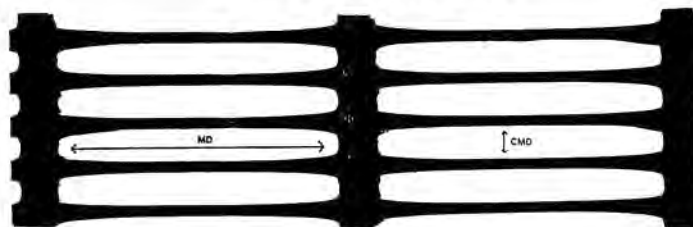
(b) Tensile Strength in both MD and CMD Directions.

Figure 1
Typical Uniaxial and Biaxial Geogrids
(a) Uniaxial Geogrid (b) Biaxial Geogrid
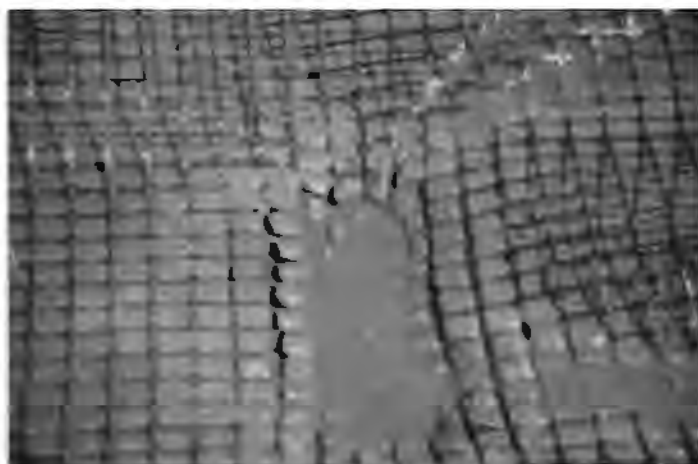
Figure 2
Effect of Geogrid Interlocking with Surrounding Material

Biaxially oriented geogrid structures should possess sufficient stiffness to enable them to resist shear stresses and deformation under load.[5,8] The geogrid should have a high interlock capacity. It is this interlocking capacity that enables the geogrid to rigidly confine, the surrounding material to its structure. Figure 2 illustrates the interlocking capacity of a biaxial geogrid. Another important property of the geogrid is its high junction strength (as defined by GRI-GG2)[7] that allows full load transfer from one rib to the adjacent rib. Thus the geogrid can distribute concentrated loads over a wider area of the weak underlying material. Figure 3 illustrates the ability of the geogrid to distribute a concentrated load. Notice that the laborer is standing at the edge of the geogrid layer, yet he is not sinking into the material. The consistency of the surrounding material is close to that of water. If the laborer was to step away from the geogrid he could sink in up to 3/4 of his height. It is this ability of the geogrid to distribute concentrated loads that prevents overstressing and bearing capacity failure of the underlying soft material, thus allowing the sludge to remain undisturbed and maintain its original

Figure 3
Surveyor Standing on Geogrid Placed on Top of
Existing Material which has Consistency of Water

strength. To ensure adequate load transfer from one rib of the structure to the adjacent rib, the geogrid must have high junction strength,[7] high interlock capacity and high resistance to construction induced damages. Table 1 outlines typical biaxial geogrid specifications.[1]

DESIGN CONSIDERATIONS

With the poor consistency of sludge materials, the fundamental question is the feasibility of constructing a stable platform or base layer suitable for construction of the final closure capping system and/or other specific operational needs like wick drain placement. An important design consideration is the determination of the maximum initial soil cover thickness required to support construction loadings without creating bearing capacity failures. Using classical soil mechanics principles one can determine the required fill material thickness to prevent overstressing of the underlying sludge.[1] If a very thick soil layer is used, the bearing capacity and the allowable shear strength of the sludge material can be exceeded which can result in a localized rotational deep seated failure that could lead to loss of equipment and life. Knowing the sludge shear strength, one can determine the allowable initial soild lift thickness and the maximum allowable contact pressure for placement of the initial life.[1]

The properties of the initial soil lift are important to ensure the stability and integrity of the cover system.[1,2,3] The initial soil layer to be placed directly on top of the biaxial geogrid should possess good filtration and drainage properties.[2,3,5] This soil layer should allow for pore water pressure dissipation and/or collection of the leachate material. Mixing of the sludge with the new fill material can be prevented with adequate selection of the appropriate fill material.[5] Finally, the geogrid and the initial soil layer will provide the stable platform for construction of the final cap. Most sludge material have very low solids content varying between 3 and up to 10%. The composition and the mode of deposition of highly compressible material can result in total settlement magnitudes in excess of 8 to 10 feet depending on the maximum weight of the closure fill material.[2] If a leachate collection zone is designed to be located below the final cap cover, design and construction of a stable platform are required to protect the integrity and the survivability of the leachate and gas collection systems.

CONSTRUCTION REQUIREMENTS

Adequate design should be complimented with good construction practice to ensure successful installation at a particular site. Several construction details should be carried out very carefully to avoid developing an uncontrollable mudwave or a bearing capacity failure. The geogrid can be unrolled easily by one or two laborers. The geogrid is installed directly on top of the existing sludge material. The width and length of the area to be covered prior to placement of the initial

Table 1
Typical Biaxial Geogrid Specifications

The geogrid shall be a regular grid structure formed by biaxially drawing a continuous sheet of select polypropylene material and shall have aperture geometry and rib and junction cross-sections sufficient to permit significant mechanical interlock with the material being reinforced. The geogrid shall have high flexural rigidity and high tensile modulus in relation to the material being reinforced and shall also have high continuity of tensile strength through all ribs and junctions of the grid structure. The geogrid shall maintain its reinforcement and interlock capabilities under repeated dynamic loads while in service and shall also be resistant to ultraviolet degradation, to damage under normal construction practices and to all forms of biological or chemical degradation normally encountered in the material being reinforced.

The geogrid shall also conform in all respects to the property requirements listed below.

PROPERTY	TEST METHOD	UNITS	VALUE
Interlock			
o aperture size[1]	I.D. Calipered[2]		
o MD		cm	2.5 (nom)
o CMD		cm	3.3 (nom)
o open area	COE Method[3]	%	70 (min)
o thickness	ASTM D 1777-64		
o ribs		mm	1.27 (nom)
o junctions		mm	4.06 (nom)
Reinforcement			
o flexural rigidity	ASTM D1388-64[4]		
o MD		mg-cm	750,000 (min)
o CMD		mg-cm	1,000,000 (min)
o tensile modulus	GRI GG1-87[5]		
o MD		kN/m	270 (min)
o CMD		kN/m	437.9 (min)
o junction strength	GRI GG2-87[6]		
o MD		kN/m	15.33 (min)
o CMD		kN/m	27.6 (min)
o junction efficiency	GRI GG2-87[6]	%	90 (min)
Material			
o polypropylene	ASTM D 4101 Group 1/Class 1/Grade 2	%	98 (min)
o carbon black	ASTM 4218	%	0.5 (min)
Dimensions			
o roll length		m	50
o roll width		m	3 & 4
o roll weight		kg	46.3 & 61.3

Notes:

1 MD dimension is along roll length. CMD dimension is across roll width.
2 Maximum inside dimension in each principal direction measured by calipers.
3 Percent open area measured without magnification by Corps of Engineers method as specified in CW 02215 Civil Works Construction Guide, November 1977.
4 ASTM D 1388-64 modified to account for wide specimen testing as described in Tensar test method TTM-5.0 "Stiffness of Geosynthetics".
5 Secant modulus at 2% elongation measured by Geosynthetic Research Institute test method GG1-87 "Geogrid Tensile Strength". No offset allowances are made in calculating secant modulus.
6 Geogrid junction strength and junction efficiency measured by Geosynthetic Research Institute test method GG2-87 "Geogrid Junction Strength".

Figure 4
Height of Leading Edge Initial Lift Should
be Maintained Relatively Uniform

Figure 5
Geogrids Do Not Need to be Anchored at Roll Ends

soil lift will vary based on the consistency and shear strength of the underlying sludge material.[5] Figure 4 shows several adjacent geogrid rolls placed on top of the existing sludge material. The adjacent layers of geogrid can be overlapped to prevent lateral spreading, as illustrated in Figures 3 & 4. The amount of overlap is directly related to the shear strength of the sludge material and can vary from a minimum of 1 foot and up to 3 feet. Plastic ties can be used to secure the adjacent rolls. The geogrid is stiff, has a high modulus, high tensile strength,and excellent junction strength. Thus, the sludge material does not have to undergo excessive deformation prior to mobilizing the tensile strength of the structural element. The ability of the geogrid to interlock with the surrounding material provides high shear stresses thus developing the tensioned membrane effect which allows a man's weight to be supported on materials that have consistency close to that of water.[2]

Once the appropriate area is covered with geogrid, the first soil lift

is placed using low ground pressure dozers with wide width track. Figures 4 and 5 illustrate the sequence of construction. A front-end dozer with rubber tires should be avoided, due to high loads concentration which could lead to catastrophic failures. The first layer should be placed in one lift. A well-graded sand layer can provide a stable platform, yet at the same time allow for pore water pressure dissipation and provide the base for a gas or leachate collection zone prior to placement of the final cap. The initial soil lift can be compacted by several passes of the dozer and/or by the weight of water used to keep the initial soil lift at an appropriate moisture content. Another advantage to the sand layer is that it can be used as a filtration medium and prevent mixing of the new fill with the sludge material. If other types of materials are used, care should be given to insure proper filtration and drainage, in order to avoid mixing with the sludge and/or pressure buildup. The thickness of the initial lift is critical and should be kept to the maximum allowable which can vary between 2 and 3 feet.[2] The leading edge of the initial lift should be maintained relatively uniform with no section advancing more than the initial lift thickness ahead of the remainder of the leading edge.[2]

CONCLUSION

For a successful closure of a sludge lagoon, it is extremely important to insure that construction techniques and sequences are carried out in such a manner as to prevent development of mudwaves and

eliminate potential for catastrophic failures. Each project should be designed and constructed based on the site-specific information. To successfully construct the final cap system, one must first be able to access the sludge. The use of a biaxial geogrid provides the necessary foundation upon which the initial soil lift can be placed. This initial reinforced soil lift then becomes the required construction platform upon which one can build the final cap system and/or any other earthen structure without compromising the integrity of the cap or jeopardizing loss of life and equipment.

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A RCRA Clean Closure of a Unique Site—Kerr Hollow Quarry at the Y-12 Plant

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ABSTRACT

An abandoned rock quarry, named Kerr Hollow Quarry (KHQ), near the Department of Energy, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, was used from 1951-1988 as a site to treat RCRA wastes which were reactive, corrosive or ignitable and which posed major concerns for personnel safety. The wastes were generated from operations at the Y-12 Plant and Oak Ridge National Laboratory and were previously treated by allowing the wastes to react with the water in KHQ, which has a surface area of approximately 4 acres and is up to 65-feet in depth. Ample water quality monitoring data were available to show that the water of the quarry was not being degraded by the treatment operations.

When closure of the site was required by the RCRA regulations, a closure method was selected to allow for clean closure of the quarry without treatment or removal of the water in KHQ. The method proposed to and approved by the Tennessee Department of Health and Environment (TDHE) was one of surveying the containers in the quarry by a submersible Remotely Operated Vehicle (ROV) using sonar and visually inspecting the containers by camera to confirm that all containers are breached and empty. Any container found intact would be breached to allow the contents to react with water and form non-hazardous residue. The progress of this unique type of closure is presented along with a summary of the problems encountered, planning activities, equipment utilized and other information about the closure.

The containers range in nature from compressed gas cylinders to drums, buckets, pipe sections, small containers and glass bottles, many of which, it had to be assumed, still contained explosive material.

Work rules require all personnel to be out of line of sight (around the shoulder of a hill) during all survey, inspection and work activity. All work was therefore done with remotely operated equipment. Work tasks at the site include survey and mapping, handling explosives, removal of mud and stone overburden, reaction of any unexploded material, cleaning and detailed inspection of containers and fragments, transportation of empty containers and fragments to a staging area from which they can be removed to a landfill and final detailed site inspection to insure that all hazardous materials were removed. Remotely operated tools, instruments and work systems include a mobile work platform, a hoist, a remotely operated system to carry containers, acoustic and a video positioning systems, video surveillance system, tools to rupture, clean and inspect containers and a dredge system for removal and screening of mud.

Software includes an integrated four-function package running on interconnected PC compatible 386 computers for real-time tacking/navigation of mobile equipment, display of locations of containers, data base management and data logging for permanent records of disposition of each container or other hazardous item. This work is being per-
formed by Sonsub, Inc., under the direction of Martin Marietta Energy Systems, Inc., under Contract DE-AC05-84OR21400 with the U. S. Department of Energy.

This closure project showed the practicality and cost benefits of telerobotic systems for work on hazardous waste sites. In addition to the intangible benefit of reduced exposure of workers, insurance costs are much lower and efficiency is higher. Daily start-up time is reduced since there is no need to don protective suits or other gear. Productivity is higher since personnel work only in clean areas where they are not hampered by masks, breathing apparatus, gloves or other protective gear. Cleanup time at shift end is minimized since the remote equipment does not leave the hazardous area and personnel need not go through decontamination.

INTRODUCTION

KHQ, shown in Figure 1, was operated in the 1940s as a rock and gravel quarry but was abandoned when it filled with water. Between 1951 and 1988, the Department of Energy's (DOE) Oak Ridge Y-12 Plant and the Oak Ridge National Laboratory used KHQ to treat water-reactive materials, potentially explosive chemicals and pressure cylinders. Materials were defined as hazardous wastes only by virtue of being reactive, corrosive or ignitable. The KHQ facility was used for emergency treatment and was not intended as a waste storage or disposal facility.

Figure 1
Aerial View of Kerr Hollow Quarry

In 1989, a remotely operated vehicle was used to survey the quarry and determine container locations and types. Survey results were used to plan closure work, which began in July 1990. The closure plan required all work to be done remotely, including making each container safe.by breaching or shredding, recovering the containers for transport to a landfill and performing a final survey to document closure. It was determined that the closure of KHQ was to be comparable to a clean closure under the TDHE Hazardous Waste Management Rules. No unreacted materials or explosive compounds were to be left in KHQ.

PAST TREATMENT PRACTICES

KHQ was a permitted facility under NPDES for treatment of certain potentially explosive chemicals or water-reactive metals. The permit required monitoring of KHQ water after a treatment operation and results were reported quarterly to the Tennessee Department of Health and Environment. Treatment operations were not permitted when there was surface discharge at the outfall.

A chute was constructed on a bluff high above the water surface to deposit materials directly into the water. A separate area was cleared on the opposite bank where compressed gas cylinders were placed for venting by rifle fire. Prior to the early 1970s, gas cylinders were placed in the water after venting. Containers floating in the quarry were penetrated by rifle fire to initiate reaction. Rifle fire was provided by security guards who were protected by a special metal building on the bluff.

Water-reactive metals including lithium, potassium, calcium, sodium or sodium-potassium alloy were normally packaged in 5, 30, or 55-gallon containers, taken to the quarry, placed in the chute and dropped into the water. The floating containers were punctured by rifle fire so water could enter. Water reacts with these metals, releasing hydrogen gas and forming oxides and hydroxides with the alkaline metal. Complete reaction of the metals is assured by the violent nature of the reactions. A limited number of 500 gallon pressure vessels containing sodium were treated in the quarry.

Potentially explosive chemicals such as picric acid were taken to KHQ in special containers, suspended above the water, punctured with rifle fire and dropped into the water.

An estimated 50 tons of hazardous and nonhazardous materials, including the weight of the containers, were sent to KHQ after record-keeping began in 1962. Table 1 shows a listing typical of materials reacted or vented in the quarry. Use of the Quarry as a treatment site ended in 1988 and closure work began soon thereafter.

Table 1
Description of Typical Wastes Treated in Kerr Hollow Quarry

```
Alkali Metals and Metal Hydrides (water reactive):
    -    Lithium and Lithium Hydride
    Sodium and Sodium Hydride
        Potassium and Potassium Hydride
        Calcium and Calcium Hydride
        Zirconium Hydride
        Titanium Hydride
        Lithium Hydride
        Lithium Aluminum Hydride
        Sodium   Potassium (Nak) Metal

Unstable Organics (explosive):
        Picric acid and related compounds
        Ethers
        Peroxides
        Hydrazine

Metals (reactive):
    -    Phosphorous
        Magnesium

Mechanical Hazard (explosive):
        Stressed Steel Parts (shrapnel danger)
        Vacuum Tubes (implosive)
        Blasting Caps
        Gas Cylinders (with frozen/broken valves)

Miscellaneous Hazards:
        Ammonia (irritant)
        Inorganic Acids (corrosive)
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PRE-CLOSURE SURVEY

In 1989, a remotely operated vehicle was used to survey the KHQ site and map container locations. The X and Y coordinates and a description of each container were stored in a data base. Survey results were used as the basis for planning the closure, designing special tools and equipment and defining closure work.

Survey results were also used during closure work. The data base was linked to graphics software which displayed the location of each item on an overlay of the site plot plan. Each container in the data base was displayed as a single character, such as "D" for a drum or "G" for a gas cylinder. The color of each character showed whether the container was open (empty), closed or of unknown status. The real-time positions of the mobile vehicles also were superimposed on this display and used for navigation.

CLOSURE WORK

Two remotely operated vehicles were used for closure work at KHQ. All personnel were required to stay well back and around the shoulder of a hill during closure tasks to insure their safety. In addition to handling containers, the vehicles installed, operated, maintained, decontaminated and removed special purpose equipment including the metal shredder. The small remotely operated vehicle performed light work tasks such as handling empty 5-gallon buckets. The large remotely operated vehicle with its 15-ton lift capability installed the metal shredder, handled heavy containers and deployed the dredge system. Control consoles for the vehicles and other equipment were in a control van located approximately 300 feet from the hazardous area and around the shoulder of a hill.

Some of the more pertinent closure tasks are listed in Table 2. All tasks were done exclusively with remotely operated equipment. The job was made more difficult by the need to do much of the work underwater where visibility was poor, electrical equipment required waterproof containers and practical methods of sensing and telemetry are severely limited. Pressure compensation was needed for the hydraulic systems, and special precautions were needed to prevent leakage of hydraulic fluid and lubricants into the water. In most other regards, the work was similar to work on dry land.

Table 2
Closure Tasks

```
Breach and recover gas cylinders

Collect and shred drums and buckets

Clean and inspect containers

Breach large pressure vessels with explosive charges

- Remove and inspect all containers and materials

- Move containers to approved landfill

- Dredge and store sediment

Recover small containers exposed by dredging

Do a final inspection of site

Decontaminate and recover equipment

Prepare closure documentation
```

CLOSURE FACILITIES

Temporary facilities were installed to support closure work. Twenty-foot vans were set approximately 300 feet from the hazardous area to house the control consoles and provide work space and storage for supplies. An office van was parked near the gate in the security fence surrounding the site.

A PVC-lined sediment storage facility, shown in Figure 2, was built to hold approximately 150,000 ft^3 of sediment and dredge water. A

gravity flow pipeline was installed to return clarified dredge water from the sediment storage area

Figure 2
PVC-lined Sediment Storage Area
Shown During Construction

Five video cameras were used for fulltime surveillance of the restricted area. A public address system provided voice communication, and an alarm output of the gas monitoring system was connected directly to the public address system. Sensors for the gas monitor were installed on the large mobile vehicle and around the site perimeter.

EQUIPMENT

Use of existing designs and equipment made it possible to go from concept to full operation on-site in 4 months. Systems were assembled at Sonsub's Houston facility and delivered by dedicated trucks. The mobile vehicles were deployed first and then used to install freestanding equipment such as the acoustic transceivers and the metal shredder. Equipment used included:

- Small remotely operated vehicle
- Large remotely operated vehicle
- Dredge system
- Gas cylinder breacher
- Metal shredder
- Collection baskets
- Acoustic tracking system
- Data management system.

This equipment is described below.

Small Remotely Operated Vehicle

The small vehicle, shown in Figure 3, is one of several owned and operated by Sonsub. It is approximately 6 feet long and weighs about 1,000 pounds. It carries video cameras, lights, sonar, gyrocompass, instrumentation suite and a six-function manipulator. Table 3 is a partial list of manipulator tasks performed by the small vehicle.

The vehicle is operated from consoles in the control van, as shown in Figure 4. Vehicle motion is controlled by a helicopter type joy stick. The spatially correspondent manipulator is controlled from a master arm mounted on the console. Instrument dials, video displays and the acoustic tracking system display also are mounted in the console.

Large Remotely Operated Vehicle

The large remotely operated vehicle provided heavy lift capability and, as shown in Figure 5, deployed the dredge system. Table 4 shows typical tasks performed by the large vehicle. It can lift loads up to 15 tons. A 60-horsepower electrohydraulic unit provides power for

propulsion and lifting. Separate electric motors on the vehicle provide power for dredging.

Figure 3
Small Remotely-operated Vehicle

Table 3
Small Vehicle Manipulator Tasks

- Set and recovering acoustic navigation transceivers
- Take sediment samples
- Set shaped charges for breaching
- Recover 5-gallon buckets and smaller containers
- Set and release latches on shredder hopper
- Rig lines and connect slings for:
- Installation and recovery of shredder
- Placement and recovery of shredder hopper
- Routine recovery of chip collection basket
- Contingency control
- Recovery of 500 gallon containers
- Operate tubing cutter
- Latch/unlatch shredder modules
- Clear jams from metal shredder
- Decontamination
- Clean containers with water jet
- Clean dredge head before recovery
- Clean shredder before recovery

The large vehicle has a control console similar to that described for the small vehicle. Automatic control functions enable it to return to a specific location, such as a collection basket, upon command. The automatic station keeping feature overcomes load forces and keeps the vehicle on station while working. Lights and multiple video cameras make the vehicle suitable for 24 hr/day operation.

Its grapple type hand, shown in Figure 5, was used to lift and carry large steel containers, collection baskets and heavy tools such as the gas cylinder breacher. For dredging, the grapple tool was removed and a 60-foot boom with a dredging head was installed on the large vehicle.

Figure 4
Control Consoles for Remotely-operated Vehicle

Figure 5
Large Remotely-operated Vehicle Fitted with Dredge Boom

Table 4
Large Vehicle Lifting and Positioning Tasks

- Install shredder
- Transport shredder modules
- Assemble shredder modules
- Acquire and breach gas cylinders
- Lift and carry
- Large containers
- Container collection baskets
- Shredder chip collection basket
- Deploy dredge system
- Provide dredge power
- Position suction head
- Place restraint net in breaching area

Gas Cylinder Breaching Tools

All gas cylinders required breaching to vent any internal pressure before recovery. A freestanding tool was built to make a hole in each cylinder. The large remotely operated vehicle transported and installed the freestanding breaching device which accepted gas cylinders and punched a one inch diameter hole in them. The breaching function was incorporated into the grapple shown in Figure 5 when poor visibility made it difficult to recover gas cylinders from the freestanding breaching device.

Figure 6
Grapple Used by Large Remotely Operated Vehicle for Grasping and Carrying Large Containers

After being breached, gas cylinders were placed in a collection basket and lifted out of the quarry in batches. They were then examined by a health physics specialist and transported to approved landfills.

Metal Shredder

A 200-horsepower metal shredder reduced most containers to steel chips to help insure that any residual explosive materials in the containers would be fully reacted before recovery. The shredder was installed by the remotely operated vehicles. The vehicles prepared an area in the deepest part of the quarry by removing all containers and dredging down to rock. The large vehicle carried the shredder stand, set it in the prepared area, and leveled it. It then carried the 26,000-pound cutter assembly and set it on the stand, while the small vehicle provided observation and alignment. This procedure was repeated to set the hopper atop the shredder and place the hydraulic hoses.

The vehicles then gathered waste containers and placed them in collection baskets. The small vehicle gathered 5-gallon cans and smaller containers while the large vehicle gathered drums, steel boxes, pipe sections and other large items. Large containers were inspected to avoid introduction of large quantities of explosives into the shredder. When the collection basket was full, the large vehicle carried it to the shredder and dumped it into the shredder hopper. Chips from the shredder fell into a basket which the large vehicle periodically carried to a location

from which the basket could be recovered by crane.

When shredding operations were complete, the small vehicle cleaned and inspected the shredder and hopper and made it safe for removal. The large vehicle then carried each module to a location from which it could be recovered by crane.

PYROTECHNIC BREACHING PROCEDURE

The larger, heavy walled containers exceeded the shredder capability. The large vehicle carried these to a special breaching area and covered them individually with a restraint net. The small vehicle then placed explosive charges at several points on the container to burn holes through which the water could react with any contents. The small vehicle then inspected the containers and the large vehicle carried them to a location from which they could be recovered by crane. The small vehicle attached sling lines and engaged the slings to the crane hook.

ACOUSTIC POSITIONING SYSTEM

The size of the quarry and the poor visibility made it necessary to use an acoustic system to show the precise locations of the containers, freestanding equipment such as the shredder and the mobile vehicles. Transceivers, installed by the small vehicle, sent acoustic signals to each other and measured the transmission time. The acoustic system computer used the transmission times and the known speed of sound to calculate the relative positions of the transceivers. With this grid as a reference, the computer could then calculate the position of transceivers on each mobile vehicle twice per second and feed the coordinates to the displays and to the automatic control systems.

DREDGING

After the larger containers had been removed, the sediment was dredged away to expose small containers. The dredge system met three unusual requirements.

- Precision capability to clean around rocks and in cracks
- Fully remote operation
- Ability to exclude any item over 0.5 inches in diameter to insure that no small explosive items would be carried to the sediment storage area

Dredge pumps were set well below the water surface to increase the suction head. Pump intakes were connected to a self-cleaning intake grill with 0.5 inch openings, and the grill was mounted on an articulated boom on the large vehicle. Intake grill position was controlled by positioning the vehicle and moving the boom. An acoustic transceiver on the intake grill tracked its position and provided records to show 100% coverage.

Discharge hoses ran up to a temporary sediment storage facility on the hillside above the quarry. As shown in Figure 1, the storage facility was a specially constructed, PVC lined earthen berm with 150,000 ft³ capacity. Dredge water was clarified and returned to the quarry by gravity flow.

FINAL INSPECTION

Primary documentation required for closure is 100% video survey of the site with resolution adequate to detect any manmade item of 0.5 inch diameter or larger. This survey will be conducted in much the same manner as the 1989 preclosure survey, with three video cameras mounted vertically on the small vehicle with overlapping fields of view. When held 2 to 3 feet high, they provided an 8-foot wide composite view.

The vehicle moves slowly along parallel grid lines to perform the survey. The acoustic system provides real-time feedback of vehicle position as an aid to the operator and coordinates are recorded to the computer disk. These coordinates are traced onto a plot plan of the site to provide documentation of 100% coverage. The date and time also are recorded with each coordinate change. This survey technique provides convenient cross reference to the video tapes which were filed by date and time of recording.

Video tape records of all survey video were required as closure documentation. On-screen annotation shows the camera number, date, time and precise coordinates as the camera moves. This provides convenient cross reference to other records.

DATA MANAGEMENT AND GRAPHICS DISPLAYS

The system makes extensive use of high end personal computers for vehicle navigation, telemetry, alarms, automatic control, data management and efficiency enhancement.

As part of the survey work in 1989, a data base was created to show the location and description of piles and scattered containers. The data base was linked to mapping software which displays the site perimeter and the location of each container. The zoom feature can expand any sector to fill the screen.

The full data base record of any container is shown in a window on this display when the operator clicks the computer "mouse" on the corresponding item. When any work is performed on a container, the computer operator updates the data base by entering simple two character codes to show breaching, inspection, transport to collection basket, or recovery for transport to landfill. The computer then automatically updates the data base with date, time and, if appropriate, the new coordinates of the container. When a container is made safe and removed the computer prints its history on a certificate of removal.

All breaching was video taped. Annotation on the video recording shows the date, time, camera number and X,Y coordinates of the vehicle carrying the camera. All video tape was filed according to the date and time it was taken. The information in the data base (or on the removal certificates) can now be used to quickly locate any item of interest in the nearly two thousand hours of video tape.

SAFETY PLAN

A Safety Assessment, conducted by Y-12 during 1988 and 1989, evaluated whether containers in KHQ could be moved while ensuring the protection of human health and environment. The remote vehicle approach to closure work was selected partially as a result of this assessment. A more detailed safety assessment and safety plan were prepared after Sonsub was selected as the closure contractor and the details of closure work had been defined.

The work involved handling potentially explosive wastes, but the exclusive use of telerobotic equipment in the hazardous area greatly reduced the necessary scope of provisions for health and safety. Primary safety concerns were for construction site hazards common to operations in remote, wooded hillside areas. Other concerns included projectiles and gases released during neutralization of containers in the hazardous area.

A central gas monitoring system used sensors on the remotely operated equipment and at locations around the perimeter of the hazardous area. In addition, all personnel were required to be inside the steel control vans during routine breaching and shredding operations and all personnel were required to fall back to a remote area during breaching with explosive charges. Gas monitor alarms were connected directly to the sitewide public address system. Readings from each monitor were automatically logged at 5-minute intervals and more frequently in the event of an alarm condition.

FUTURE APPLICATIONS

The closure work at KHQ proved the practicality and advantages of using remotely operated systems for environmental restoration. The KHQ project was made more difficult by the need to perform much of the work underwater where visibility is poor, telemetry techniques are limited and special provisions are needed to insure reliability of equipment.

The principles and equipment used at KHQ are directly applicable to many other sites which present hazards to workers. Prime examples include sites with toxic chemical or toxic gas environments, radioactive wastes or explosive wastes.

DISCLAIMER

Sheet Pile Barrier Walls as an Alternative to Slurry Walls for Temporary Containment Actions at Hazardous Waste Sites

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ABSTRACT

A common technology for temporary waste containment and ground-water flow diversion at Superfund and other hazardous waste sites is the subsurface barrier wall. In most cases, the wall has been constructed from a soil-bentonite-concrete slurry. These walls are effective for most conditions, but sometimes are subject to constructability, cost and compatibility problems.

This paper presents a case study of the use of an interlocking sheet pile barrier wall for containment and demonstrates both the technical and economic advantages of this approach.

INTRODUCTION

Under certain site conditions, a sealed sheet pile barrier wall offers advantages over slurry walls for containment at uncontrolled hazardous waste sites. Such a wall was used at the Southern Maryland Wood Treatment (SMWT) Superfund site to contain soil and groundwater contaminated with creosote, pentachlorophenol and other wood preserving chemicals. The wall was used to overcome site constraints related to steep grades, structural considerations, dewatering, chemical compatibility and ultimate disposal/reuse of wall materials.

BACKGROUND

The U.S. EPA, Region III, performed a RI/FS at the SMWT site. The RI/FS identified remediation alternatives which were rated based on their applicability, implementability, cost-effectiveness and other criteria as defined in the U.S. EPA's NCP.

ROD, signed in June 1988, provided for on-site thermal treatment of contaminated soils and tank liquids; treatment of contaminated groundwater by ultraviolet radiation and ozone or carbon adsorption; demolition of existing process buildings and facilities; and installation of a barrier wall to limit contaminant migration and to facilitate dewatering.

In October 1988 it was determined that the project would be designed and implemented in two phases (operable units). Operable Unit 1 (OU1) consisted of the design and installation of the barrier wall and a vehicle decontamination facility. Under Operable Unit 2 (OU2), the contained area will be dewatered, and contaminated soil within the barrier wall will be excavated and incinerated at an on-site thermal treatment facility.

Remedial design for OU1 was initiated in December 1988 when the U.S. Army Corps of Engineers (USACE)—Omaha District, under a working relationship with U.S. EPA, developed a scope of work for remedial design. USACE—Omaha retained EA Engineering, Science and Technology to implement this work scope. Construction for OU1 was initiated in January 1990 and was scheduled for completion in September 1990.

SITE DESCRIPTION

Physical Conditions

The SMWT site is located off Route 235 in Hollywood, St. Mary's County, Maryland (Fig. 1). The site comprises approximately 25 acres in the northwest portion of a 96-acre property. Approximately 4 acres were previously devoted to a wood treatment operation. The site is surrounded by residential and agricultural areas. Site elevations range from approximately 119 to 154 ft above mean sea level and run-off is to tributaries on the east and west which discharge to the Potomac River via Brooks Run and McIntosh Run.
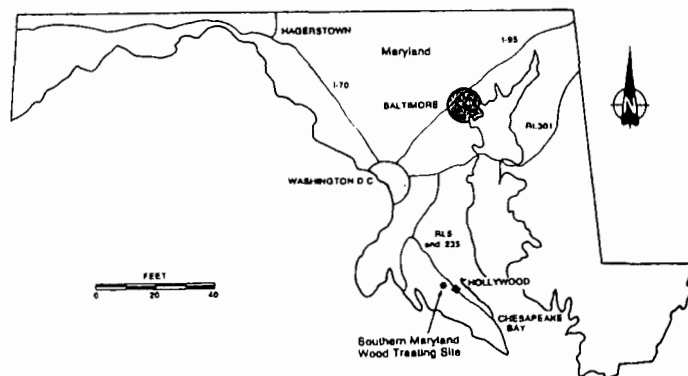
Figure 1
Location Map-Southern Maryland
Wood Treating Site

Site History and Use

The SMWT facility was owned and operated by Southern Maryland Wood Treating Co. from 1965 to 1978 as a pressure treatment facility for wood products. Locations of various features, structures and surface waterbodies, as well as the property boundary, are shown in Figure 2. Creosote and pentachlorophenol (PCP) were used as wood preservatives during the facility's active period. Wastes generated included retort and cylinder sludges, process wastes and material spillage. These wastes were placed in six unlined lagoons south of the process area.

Contamination of an on-site freshwater pond with VOCs, PAHs and other organic contaminants prompted legal proceedings by the Maryland Department of Health and Mental Hygiene. Pursuant to these pro-

ceedings, the PRP, L.A. Clarke and Sons, Inc., initiated cleanup actions in 1982. Liquids from the lagoons were spray-irrigated onto the nearby woods. The six waste lagoons were excavated, and the area was backfilled and graded. The freshwater pond was partially excavated. Excavated sludges were mixed with composted sludge, topsoil and grass seed, then spread in a level treatment area on the property.
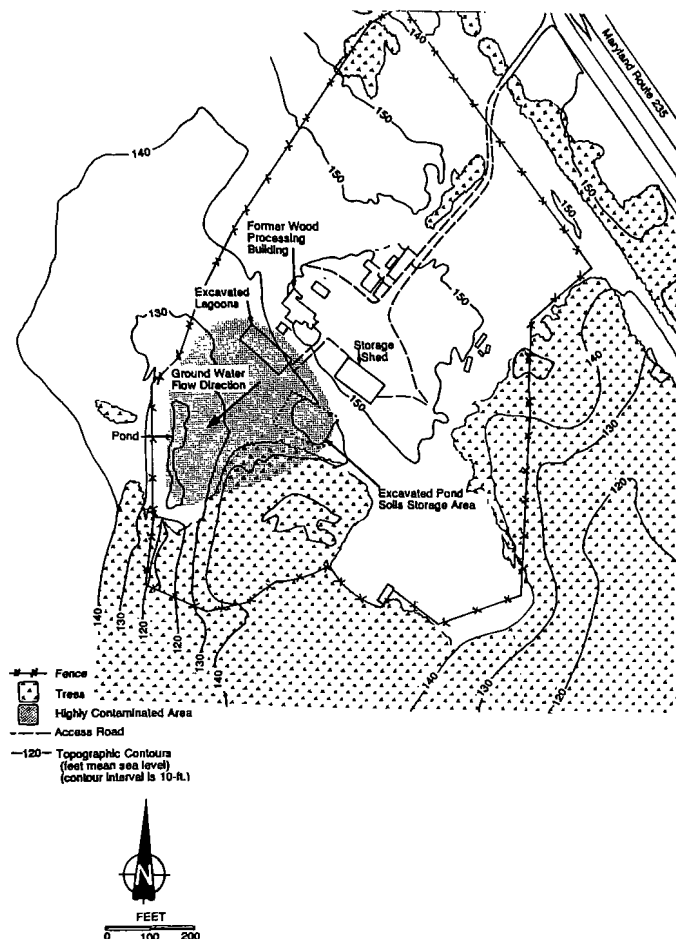
Figure 2
Existing Site Conditions (Sept. 1989)

Geology/Hydrology

The site lies within the Atlantic Coastal Plain physiographic province which consists of unconsolidated gravel, sand, silt and clay deposits ranging in age from Cretaceous to Holocene. The thickness of unconsolidated sedimentary deposits at the site is estimated to be 3,500 ft. Figure 3 shows the geologic profile at the SMWT site.

The region of primary interest with respect to OU1 is confined to the upper 30-60 ft of strata where saturated sandy Pleistocene and Holocene age Upland Deposits have been contaminated. The water-table aquifer in the Upland Deposits is a source of drinking water and provides recharge to streams and other surface waterbodies. The Upland Deposits are underlain by a 20-ft-thick blue clay layer known as the St. Mary's Formation. Physical testing of soil samples from this zone indicates that it functions as a competent confining layer between the Upland Deposits and the underlying Piney Point—Nanjemoy Formation with a permeability ranging from 3×10^{-8} to 1×10^{-7} cm/sec.

Contaminants/Pathways

Primary contaminants at the site include creosote and PCP in both the soil and groundwater within the Upland Deposits. Other soil contaminants include polyaromatic hydrocarbons (PAHs), acetone, benzene,

toluene, ethyl, benzene, xylene (BTEX) and dioxins. Other ground-water contaminants include BTEX, PAHs and phenols. On-site surface water also is contaminated, most notably in the drainage pond at the southwest corner of the site.

Contaminant transport is primarily via groundwater flowing laterally through the Upland Deposits in a southward direction. Vertical transport is impeded by the St. Mary's clay.
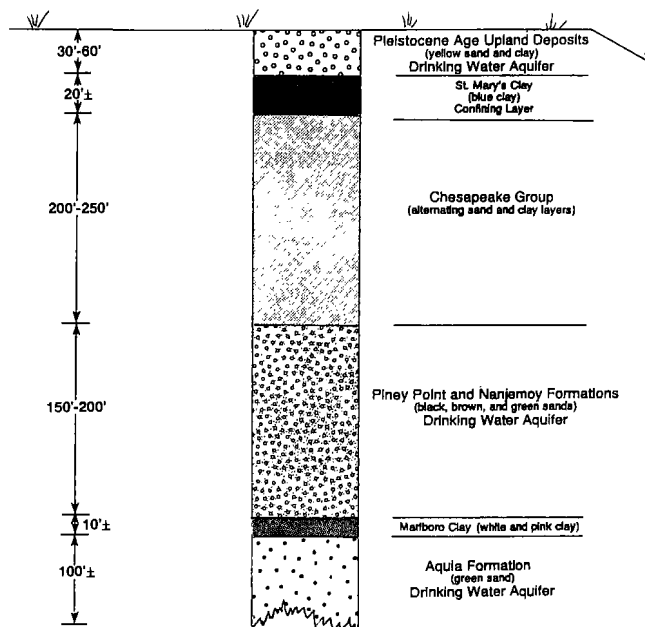
Figure 3
Geologic Profile at SMWT Superfund Site

GENERAL APPROACH

The General Approach to site remediation was predicated on consistency with the NCP and other state and local applicable or relevant and appropriate requirements (ARARs). Throughout the remedial process, the U.S. EPA, State of Maryland and local requirements were applied to site characteristics to formulate remedial action objectives and alternatives.

Value Engineering Considerations

Army Corps of Engineers regulations require the preparation of a Value Engineering (VE) Report to evaluate items in the design criteria that may result in cost savings. For this site, the major subject of the VE Report was the type of barrier wall to be implemented. While the feasibility study concentrated on various combinations of soil-bentonite-concrete slurry walls, the evaluation in the VE Report indicated various difficulties with such walls:

* Site slopes were not suitable for slurry wall construction without implementing significant benching and regrading activities
* For this project, the barrier would need to be a structural wall so that it could be free-standing during soil excavation activities planned for OU2
* Data indicated that soil-bentonite-concrete materials are particularly nonresistant to chemical attack by various site contaminants (creosote, PCP, etc.)
* Since the barrier wall would become contaminated prior to final remedial action, the cost of removal and disposal of the wall materials must be considered
* It was estimated that a structural slurry wall for this site would cost in the range of $7,000,000 to $8,000,000 and would still likely be subject to chemical attack

By comparison, interlocking "Z" section sheet piles offered the following advantages:

- Using tie-backs at selected locations, sheet piles can be utilized to produce a structural wall for excavation purposes
- Sheet piles can be installed on highly sloped surfaces and eliminate the concerns of bridging
- Sheet piles did not exhibit susceptibility to chemical attack inherent in slurry wall implementation
- Sheet pile walls can be easily removed after the completion of the final remedial action, decontaminated and reused
- Sheet piles are relatively more impermeable than slurry walls. (The vast majority of the sheet pile surface area is impermeable, with use of a joint sealant further minimizing potential for leakage through the wall. A slurry wall's entire surface area is permeable and will allow low-rate flow through a large surface area. Calculations indicated that the actual throughput volume of water penetrating the sheet pile wall will be less than through a low permeability slurry wall.)
- This site is particularly suited for sheet piles because a competent, consistent clay layer is available for embedment of the piles
- The cost of the sheet pile barrier wall/decontamination facility was estimated to be approximately $2,600,000 (a considerable savings over a structural slurry wall)
- Design and predesign costs are considerably lower utilizing a sheet pile wall

Based upon the above, the VE Report recommended a sheet pile barrier wall as a constructible, lower cost and technically appropriate alternative to a slurry wall for the site conditions at SMWT.

Regulatory and Statutory Considerations

Under SARA, the U.S. EPA was required to initiate remedial construction on 175 new sites between October 1986 and October 1989. This project was chosen as one these "SARA 175" starts, thus resulting in an extremely tight design and award schedule. Due to this schedule and since use of sheet piles as a hazardous waste containment system is relatively unique, it was essential that the U.S. EPA and State of Maryland concurrence be obtained at the earliest possible time. In numerous consultations with representatives of the U.S. EPA Region III and the Maryland Department of the Environment, design objectives, details and the merits of the sheet pile wall were discussed. Both the U.S. EPA and the State of Maryland were provided review copies of preliminary and final design documents and comments were received and incorporated as appropriate. A cooperative effort on the part of all regulatory agencies involved and general concurrence with the design rationale greatly aided in a successful design and award of a construction contract on Sept. 30, 1989, thus meeting both the Oct. 16, 1989 SARA mandate and the fiscal year 1989 deadline.

Design Considerations

The design of the sheet pile barrier wall system was driven by a number of variables. Important considerations included containment of the most highly contaminated portion of the site and design of a vertical perimeter barrier which would be consistent with final remedial action. The design phase included predesign site characterization studies and detailed engineering design. Since the project was conducted for the Army Corps of Engineers, design deliverables included construction plans and specifications, a Design Analysis report, a government cost estimate, a submittal list and a bid form. Three design submissions (30, 90 and 100 percent) were used to assure sufficient opportunity for review comments from interested parties.

DESIGN APPROACH

Many factors were major considerations in developing the final design for OU1 of the SWMT site. The following sections describe some of the key design considerations associated with this project.

Alignment

Several concerns were noted with respect to the wall alignment identified in the ROD. The first concern had to do with slope stability and

the foundations of existing structures. In order to protect foundations of existing structures, it was recommended that the wall alignment be moved north of the existing structures. This resulted in a relatively flat alignment (<4 percent) along most of the north section of the barrier wall and protection of the structures within the contained area. Another concern related to relatively steep grades (6-10 percent) encountered along the east and west sections of the barrier wall. Use of a slurry wall barrier in these areas would have required extensive regrading and benching to create the appropriately sloped work platforms needed for slurry wall construction. Driving sheet piles in these areas did not present similar problems.

Another alignment consideration was the proximity of contamination to other property owners west of the site and the location of the drainage pond in the southwest corner of the site. As a result, the barrier wall had to be located as close as possible to the property line to prevent contaminant migration to other properties. In addition, the wall needed to have structural integrity to remain intact during excavation activities to be conducted in OU2. This alignment consideration once again pointed toward a sheet pile barrier wall as a logical approach. The final wall alignment is shown in Figure 4.
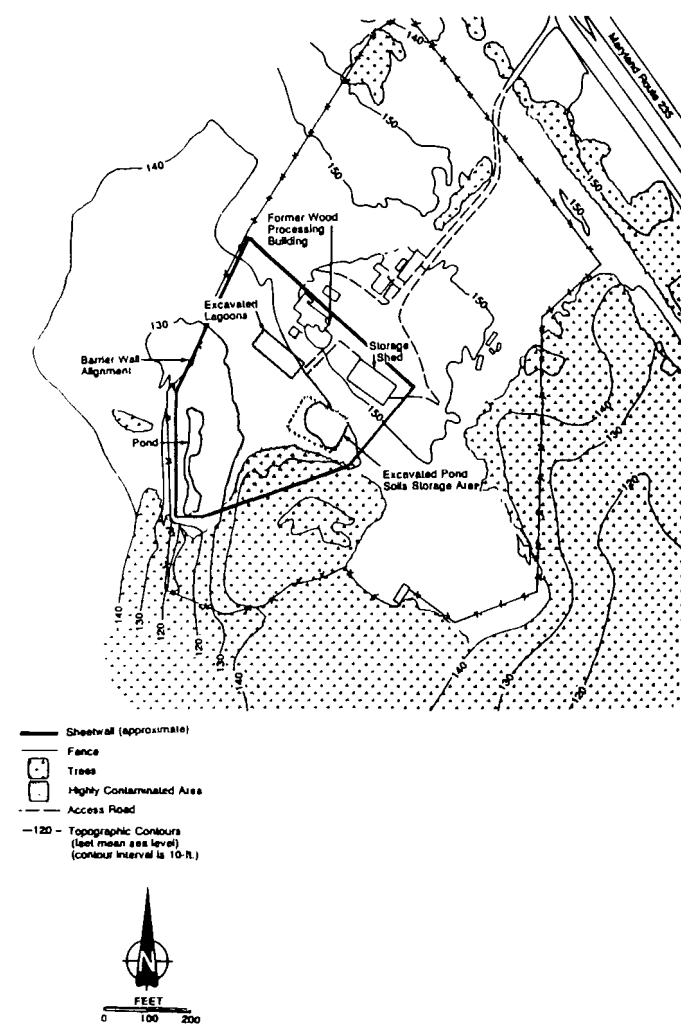
Figure 4
Sheet Pile Barrier Wall Alignment

Probably the most significant alignment consideration was the necessity to design a free-standing structural barrier wall. Excavation activities in the southern and western portions of the site will remove soil right up to the limits of the wall. In order to allow excavation up to this limit, the wall must be able to prevent soil or groundwater from

the other side of the wall from impacting the excavation. A sheet pile barrier wall will effectively satisfy these conditions. If a slurry wall was used, it would be necessary to relocate the wall alignment beyond the existing limits since slurry walls cannot withstand lateral soil pressures to as great a degree as sheet pile walls.

Materials

Once it was determined that a sheet pile barrier wall would be used, it was necessary to identify the size, shape and type of steel sections to be used and the approach to sealing the piles in place. The preliminary design indicated that interlocking steel "Z" section piles would be most appropriate for site conditions. The sizing of the "Z" sections required geotechnical characterization of the wall alignment and concern for wall integrity required that the steel be subjected to contaminated liquid from the site to determine chemical compatibility.

Interlock Sealing

The issue of interlock sealing was considered at length. Various approaches were considered including pressure injecting grout into the interlock, both during and after driving and coating the interlock with a sealant prior to driving. Based upon chemical contamination concerns, it was felt that a bentonite grout mixture would be most appropriate. The project specifications did not specifically identify a grout material or procedure, but left the selection to the Contractor as a submittal item to encourage creativity. In retrospect, it would have been preferable to clearly specify the grout material and procedure to be used.

Sizing of "Z" Sections

A geotechnical site characterization program was conducted in April 1989 to examine subsurface conditions along the proposed wall alignment. The program consisted of drilling boreholes every 200 ft along the wall alignment. Continuous samples were collected using a 2-in. diameter split-barrel sampler (ASTM D-1557) and blow counts were recorded for each 6-in. penetration of the sampler. Two to three samples were selected from each boring for physical soils testing which included sieve analysis (ASTM D-422), hydrometer analysis (ASTM D-422), Atterburg limits (ASTM 4318), natural moisture content (ASTM D 2216), specific gravity (ASTM D2216) and USCS Classification (ASTM D2488). All other samples usually were classified in accordance with the Unified Soil Classification System (USCS) nomenclature.

Other geotechnical testing conducted to better characterize the St. Mary's clay included collecting 2-in. diameter Shelby tube samples from within the clay layer. A total of 20 samples was collected and tested for unconfined compression. Of these samples, three were also subjected to triaxial shear testing. The results of these soil characterization tests were used to design the steel sheet pile sections. It was calculated that a "Z" section comparable to the Bethlehem Steel PZ35 would be required (maximum design stress = 25,350 psi).

Compatibility Testing

Corrosion testing in accordance with U.S. EPA Method 1110 was conducted to examine potential impacts of contaminated groundwater on the barrier wall. Steel coupons, obtained from the sheet pile manufacturer, were immersed in contaminated groundwater collected from on-site monitoring wells. Two separate groundwater samples were used for compatibility testing. Test results indicated that the steel corrosion rate when immersed in contaminated groundwater was less than 7 mil per year (0.007 in./yr). This rate is considered to be an acceptable corrosion rate in accordance with U.S. EPA Method 1110.

Tie Backs

The wall alignment and depth of pile embedment were designed to minimize the need for tie-backs during OU2 excavation activities. In general, the wall was designed as a cantilevered retaining wall with a depth of embedment of approximately 11.5 ft Greater depth of embedment was avoided to prevent puncture of the St. Mary's clay. Structural calculations indicated a maximum allowable freestanding cantilever section length of 13.4 ft for most of the site; this design will not impact excavation activities. However, along the western section of the wall,

where depth to clay is up to 40 ft and excavation will be conducted right up to the wall, it will be necessary to provide tie-backs. A preliminary design was performed to locate tie-backs. Detailed design was delayed until OU2 when the limits and procedures for excavation are more clearly defined.

Disposal

The final issue considered is ultimate disposition of the barrier wall. According to the ROD, the barrier wall is intended to be a temporary, not permanent, remedy. As such, it will need to be removed at the conclusion of OU2 to allow reestablishment of local groundwater flow patterns. By using a sheet pile barrier wall, it will be relatively easy to remove the barrier wall after it is no longer needed. The steel "Z" sections could then be decontaminated and reused. Other types of low permeability barrier walls, such as sheet pile walls, would need to be excavated and disposed of as contaminated soil with no potential for subsequent reuse.

IMPLEMENTATION

The implementation of the OU1 remedial action at this site involved the construction of the sheet pile barrier wall and a permanent decontamination facility. The bid price for the installation of this wall was $1,383,113. With site preparation, decontamination facility, contaminant containment, site maintenance and miscellaneous costs the total bid price for the project was $2,599,852.

For the most part, the construction proceeded as planned starting with the construction Contractor developing the work plans required for construction at an NPL site. These plans include a Site Health and Safety Plan, Chemical Quality Control Plan, Site Construction Quality Control Plan and other documents. Upon Corps of Engineers approval of these documents in December 1989, the contractor began work. By August 1990, the vast majority of the piles had been installed and the decontamination facility and appurtenant facilities were in place. The expected construction time for this project was 6 months.

Successes

The primary objective of the OU1 barrier wall was to contain the contaminated soil and groundwater south of the process buildings at the SMWT site until OU2 excavation and removal actions are initiated. The barrier wall was designed to minimize infiltration both into and out of the contaminated area, thus minimizing potential contaminant transport. Predesign studies indicated that a sealed sheet pile barrier wall would effectively satisfy these objectives. Post-action inspection of the construction indicates that the sealed sheet pile is effectively providing a barrier to subsurface flow through the watertable aquifer and is effectively containing the contaminated material at the SMWT site.

A major success in the project implementation was the relative ease with which the design was translated into construction. The decontamination facility was constructed without change, and most of the sheet pile wall was installed using the minimum driving force. Above all, the measure of success on this project can be characterized best by the cooperative effort on this project between the federal and state government, the architect-engineer and the construction contractor to provide an innovative, cost-effective and timely remedial action. The remedial action met regulatory and statutory requirements, met the SARA mandate requirement and was highly cost-effective.

Lessons Learned

Many lessons can be drawn from this project. Various operational difficulties with driving sheet piles on a fixed-price contract became apparent. However, none of these difficulties was insurmountable. The major problem involved approximately 80 piles that could not be driven, with either a vibratory hammer or a large impact hammer. Apparently, a combination of high soil density and subsurface anomalies contributed to this problem. The problem was resolved by drilling an 8-in. auger boring at each sheet pile joint at an angle allowing the boring to reach underneath the undriven pile. This process reduces soil density and allows for complete driving of the piles. This increased the cost of the

overall installation by approximately $500,000. The lesson learned here is that contingencies need to be built into fund allocations for these types of projects to make adjustments when site conditions merit.

Adequate time should be allowed to perform geotechnical borings along the expected perimeter of the wall prior to design so that pile size, driving force and type of driver can be appropriately evaluated.

Prior to on-site work under the construction contract, a local business had to be moved outside the property so as not to interfere with the remedial action. Also, a temporary construction easement to allow use of a small strip of property on the south and west side of the site had to be acquired to facilitate construction. The lesson learned is that it is very important that real estate concerns be addressed early in predesign or design so that site access is not affected.

Finally, sufficient time must be provided for design. Reasonable time schedules facilitate better design and greater cost-effectiveness.

CONCLUSIONS

The use of an interlocking "Z" section steel sheet pile barrier wall was found to be an effective approach to containment of contaminated soil and groundwater at the Southern Maryland Wood Treatment Superfund site. The sheet pile barrier wall was implemented to overcome constructability, cost and compatibility concerns identified with use of a soil-bentonite-concrete slurry wall at the site. Factors that may influence selection of a sealed sheet pile barrier wall over a slurry wall include structural integrity, chemical compatibility, constructability, property access constraints, cost and compatibility with the final remedy. Based upon experience at the SMWT Superfund site, the sheet pile barrier wall offers a constructible, cost-effective and technically sound option to the traditional slurry wall for temporary containment at hazardous waste sites.

Site Safety Equipment: Moving Towards Improved Protection

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ABSTRACT

The Final Rule of OSHA's Hazardous Waste Operations and Emergency Response regulation became effective in March 1990. The Interim Rule of that regulation had been in effect since 1986. Although this regulation has been in effect for four years and Superfund for ten years (since December 1980), only minor advancements have been made in site safety equipment for hazardous waste site workers. This paper discusses advancements and refinements in air quality monitoring techniques and personal protective equipment that would enhance the safety of workers in the hazardous waste industry. Limitations of available site safety equipment also are highlighted.

INTRODUCTION

Employees working with hazardous waste may be exposed to hazardous materials primarily through two routes: skin contact and inhalation. Skin contact is prevented or minimized by requiring employees to wear chemical protective clothing. Inhalation of hazardous materials is prevented or minimized by testing the ambient air for the presence of air contaminants and by requiring employees to wear respirators.

Unfortunately, these protective measures are not fail-safe. Chemicals can permeate gloves and other chemical protective clothing. Air purifying respirators may leak around the face seal: moreover, they do not completely filter all air contaminants. Gas detection devices are not ideally designed for use at sites where the air contaminants and concentrations are unknown.

In late 1980, the Surgeon General of the United States reported to the U.S. Senate Committee on Environment and the Public Works Committee on exposure to toxic chemicals. The Surgeon General's report emphasized: (1) the lack of scientific methods for evaluating the health effects of chemical waste dumps on human health, including the lack of adequate tests to evaluate the effects of chemicals in human populations; (2)the lack of data and experience in testing mixtures of chemicals for potential health effects; (3) the lack of information identifying complex mixtures of chemicals; and (4) the lack of ways for dealing with the time lag between chemical exposure and the manifestation of health effects.[1] Although advancements have been made since the Surgeon General's report, there is still much room for improvement. This paper briefly discusses improvements in air quality monitoring techniques and personal protective equipment that would provide increased protection for hazardous waste site employees.

AIR QUALITY MONITORING

Industrial hygiene monitoring for air quality employs two basic techniques. The first is the use of direct-reading instruments. These instruments must be calibrated to respond accurately to a limited number of chemicals. Direct-reading instruments respond quantitatively, are generally used for acute-acting toxic substances and generally have both a visual and an audible alarm system for predetermined concentration(s) of the chemical substance(s).

The second technique requires laboratory analysis of samples which are obtained with collection devices. The collection device may be a Tedlar or similarly constructed bag, a filter, a solid sorbent, or a liquid sorbent. Both techniques require accurate identification of the air contaminants in order to be most useful.[2] For example, when using a direct-reading instrument that measures only carbon monoxide, other chemicals will not be analyzed. Also, a laboratory will analyze only the chemicals for which tests were requested. Therefore, unknown chemicals on a site may remain undetected, creating a potentially hazardous situation for the workers who may be exposed to those chemicals.

Instruments most commonly used to screen atmospheres containing both known and unknown organic contaminants are the flame ionization detector (FID) and the photoionization detector (PID). A combined O_2/LEL meter, otherwise known as an oxygen/combustible gas indicator, is used in confined spaces.

The PID is relatively simple to use but has a limited application, since it yields total concentration of many organic and some inorganic compounds present in the atmosphere. Because only the total concentration of vapors present is provided, it is difficult to determine the concentration of a particular substance. In practical terms, this means that if two substances are present in the atmosphere, one with an exposure limit of 50 ppm, the other with an exposure limit of 1,000 ppm, a PID reading of 200 ppm is inconclusive with respect to the need for personal protective equipment. The use of air-purifying respirators would be required in that situation, since an overexposure is likely.

In the above situation, detector tubes help to determine the approximate concentrations of the two substances. The results of a detector tube test would show whether respirators were required in that situation. But it is a rare site that has only two air contaminants.

Another potential problem with the PID is that the instrument uses lamps of certain energies to detect air contaminants. Often, only one lamp is brought onto a site. The lamp that is used to detect petroleum hydrocarbons such as gasoline (10.2eV) will not accurately detect the presence of chlorinated hydrocarbons.

The FID operated in the survey mode also provides a total organic vapor reading. Unlike the PID, the FID can also be operated in the gas chromatography (GC) mode. In the GC mode, the instrument is capable of identifying and measuring the concentrations of specific organic gases and vapors. However, the GC mode requires a higher level of expertise than many users have. As a result, the FID is usually operated in the survey mode, which provides nearly the same information as the PID.[2]

The following case example discusses the monitoring of hazardous

waste workers at a dumpsite. The industrial hygienist on this site has records of 113 hazardous materials that were disposed at the site. Many of those 113 materials have most likely decomposed to other substances. Other chemicals were probably disposed at the site, but how many and which ones are unknown since the records are incomplete.[3]

The industrial hygienist is able to determine with the records that 32 chemicals plus 21 decomposition products are the most likely substances to be present in significant concentrations. Of those 53 chemicals, 38 can be tested with grab sample detector tubes at a cost of $6.00 per test. Eight of the 15 remaining chemicals can be analyzed in one week using standard methods at a cost of $30.00 per substance. The remaining seven chemicals require special analytical work that will take three weeks to complete at a cost of $100.00 per substance. The other chemicals, present in insignificant concentrations, must be analyzed with a general adsorbent grab sample tube at a cost of $200.00. The total analytical cost is $1,368; the total elapsed time is four weeks.[3]

On-site safety would be significantly improved if air monitoring techniques were developed to provide on-site results for all substances. By making grab sampler detector tubes available for more substances and increasing their accuracy, many of the analyses currently done in a laboratory could be done on-site, reducing costs and lag time.[3]

NIOSH successfully used the SDRITS (the Simultaneous Direct Reading Indicator Tube System) to monitor for acutely toxic concentrations of chemical substances when performing Health Hazard Evaluations. The SDRITS uses battery-operated pumps to draw air through ten indicator tubes simultaneously. This system, or a similar one, used in conjunction with other direct-reading instruments may provide the needed on-site air quality information.[4]

Screening techniques currently used on the gas chromatograph/mass spectrophotometer to analyze unknown organic chemicals need to be improved. This procedure is very expensive ($400 - 800 per test), must be done off-site and typically cannot positively identify many of the substances that are present. Wide spectrum, on-site screening techniques for unspecified substances would protect workers from potential exposures to hazardous chemicals of which the industrial hygienist is unaware. Also, low-cost direct-reading monitors for more substances would provide hazardous waste workers with improved protection. Currently, direct-reading monitors are available for approximately fifteen substances.[3]

PERSONAL PROTECTIVE EQUIPMENT

Employees working with and around hazardous materials wear personal protective equipment (PPE) to prevent or minimize exposure to those hazardous materials. Often, too much reliance is placed on the PPE: air purifying respirators do not effectively filter out all air contaminants; air purifying respirator cartridges have breakthrough times; chemicals can permeate the materials that comprise the PPE; and wearing PPE creates other potential health hazards, most commonly heat stress.

Respirators

A potential route of exposure that is often difficult to control is linked to the life span of the cartridges used in air purifying respirators. The lifespan of a cartridge is dependent on two main factors:

- Contaminants in the ambient atmosphere
- Humidity and temperature of the ambient atmosphere

It is often incorrectly assumed that a cartridge to be used in atmospheres containing organic vapors will effectively filter out all organic vapors. Unfortunately, this is not the case. Many chlorinated hydrocarbons will break through the cartridge in less than one hour of use. Methylene chloride, a common industrial solvent, will break through in one to two minutes.[5] The term "breakthrough" means that the chemical is not adsorbed on the filter; instead, it passes through and is inhaled by the wearer of the respirator. Respirator breakthrough may inadvertently expose hazardous waste site workers to methylene chloride and other common chlorinated solvents in this way.

The current NIOSH/MSHA respirator approval methods are also misleading to the average respirator user. An organic vapor cartridge which is stamped "NIOSH/MSHA APPROVED" has only been proven to provide protection for 50 minutes against 1000 ppm carbon tetrachloride in 50 +/- 5% relative humidity air at 25 °C and at a test air flow rate of 64 liters/minute for the "as received" cartridges. Since the cartridges are used in atmospheres with wide ranges of temperature and humidity and usually with several air contaminants present in the ambient atmosphere, relatively little is known of the actual effectiveness of air purifying respirators.[6]

The cartridge's life span is affected not only by the contaminants in the ambient atmosphere, but also by the temperature and humidity. Any outdoor worker frequently works in atmospheres of high humidity. The atmospheric concentrations of the contaminants and water vapor have a significant effect on the saturation capacity of the charcoal bed in the respirator cartridge.[7]

Another factor which affects the saturation capacity of the cartridge is the relative humidity of the conditioning environment. (Respirator cartridges are conditioned prior to use.) It has been determined that a high humidity (20 to 90%) in the conditioning environment has little effect if the humidity in the use environment is low. However, if the humidity in the use environment is over 20%, the breakthrough time may be significantly decreased. One study determined that a three-fold decrease in breakthrough time resulted under such conditions when the atmosphere contained 50% carbon tetrachloride.[7]

Respiratory protection for hazardous waste site workers would be improved by increasing the effectiveness and lifespan of air purifying cartridges and refining the current test approval procedures for air purifying cartridges.

Air purifying respirators are virtually ineffective if the user has not been fit-tested with the respirator to be worn. Fit-testing determines if an adequate seal exists between the user's face and the respirator. Fit-testing is currently performed using either quantitative or qualitative techniques. Qualitative techniques are generally used because they are less time-consuming, less costly and are performed with the actual respirator that the worker will wear. However, OSHA prefers that quantitative fit-testing be performed. The quantitative method currently used is awkward and very expensive. In addition, the actual respirator is not worn by the test subject. Since a surrogate mask is used, differences in shapes and pliability between masks are not taken into account.[8]

A quantitative fit test is performed by measuring the concentration of an aerosol inside the test respirator while it is worn on the test subject. The fit test is performed inside a chamber containing a certain known concentration of the aerosol. A probe is inserted in the respirator to measure the concentration of the aerosol. The accuracy of this method is compromised in two ways. The probe is invasive, meaning that the probe itself may affect the fit of the respirator. Also, if the aerosol enters the respirator through a seal leak, it may not equalize quickly in the space between the wearer's face and the respirator. Therefore, the results are dependent on the location of the probe in relation to the leak.[8]

An improved fit-testing method has been developed by two scientists at the University of Cincinnati. An invention by one of these scientists, K. Willeke, uses a dynamic pressure sensor which is directly connected to the respirator cavity. The fit test is performed by attaching the pressure transducer to a modified filter cartridge and placing it on the respirator. After making some other minor modifications and determining the volume inside the respirator, pressure measurements can be easily taken and recorded. Since pressure changes instantaneously, any leaks occurring as a result of the wearer's movement will be instantly recorded.[8]

This method offers several advantages over other quantitative fit-test methods:[8]

- The measurements are a unique and sensitive function of air leakage into the respirator and therefore of respirator fit
- The method is less expensive and requires less equipment than the currently used quantitative method
- The test is fast, requiring only a few seconds
- The test is non-invasive

- The respirator that the subject will use is worn for the test
- The method can be performed anywhere

Chemical Protective Clothing

Chemical protective clothing is worn by people working around hazardous materials to prevent skin contact with those hazardous materials. However, wearing chemical protective clothing (CPC) presents other problems. When the entire body must be protected by a chemical-resistant suit, heat stress becomes a potential health hazard even in moderate temperatures. Tiny pinholes in gloves may cause skin contact with chemicals without the wearer being aware of it. Chemicals may permeate the materials the CPC is made of, particularly gloves because hands are the most likely to contact hazardous materials.

The same materials that resist chemicals also prevent the evaporation of sweat, creating a potential heat stress problem. The immediate, and for the time being the simplest, solution to heat stress is finding a means to cool the body so that it can comfortably work longer. Long-term solutions to heat stress should emphasize finding a means to allow the evaporation of sweat while still providing chemical resistance.[9]

The most popular cooling device is the ice vest. The basic ice vest consists of frozen packets of phase change solution, sewn into a vest lined with Nomex or a similar material. The advantages of wearing an ice vest are that the worker is mobile and can work in intense heat for up to ninety minutes without resting. Working in intense heat without an ice vest may require rest periods after fifteen to forty-five minutes. The disadvantage of the ice vest is that it weighs approximately ten to fifteen pounds. If a worker is performing heavy physical labor, the added weight can negate any cooling effects provided by the vest.[9]

Another cooling method uses forced air. The air is pumped inside the suit at key points. This cooling method generally is impractical for hazmat teams since the worker must be tethered to the air supply.[9]

A new cooling device uses pressurized tanks of a coolant such as Freon. The tanks are worn on the person's back and weigh approximately three to six pounds. This system is ideal for a hazmat worker since the tanks are lightweight and the worker is still mobile. However, this system is very expensive. The expense is due to the cost of the coolant canisters rather than the cost of the vest, which is approximately $1,300. The canisters last only thirty minutes and cost approximately $25.00 each.

Since heat stress is probably a more widespread potential health hazard among hazmat workers than chemical exposure, advances in cooling systems would greatly benefit these workers. An inexpensive system that also provides the worker with mobility is needed.[9]

As stated earlier, CPC may not necessarily provide the worker with full protection from chemical contact. Chemicals can permeate gloves and other CPC. Also, some solvents can extract chemical additives in gloves or can break down glove material. These reactions alter the glove, increasing the potential for permeation, in addition to exposing the wearer to the reaction products.[10]

Effective decontamination of the CPC will minimize the amount of chemical permeation and maximize the safe usefulness of the CPC. CPC must be decontaminated before field personnel leave the site, even if the CPC is disposable. Most decontamination procedures use a basic rinsing of the garment followed by a detergent wash and another rinse. Sometimes the contaminated clothing is aerated for several days.[10]

The most practical decontamination method for hazmat workers is the detergent wash and rinse method. This method allows decontamination to take place quickly and easily in the decontamination zone. However, a study performed using the ASTM permeation test method determined that for several chemical and CPC material combinations, this decontamination method was not effective. This determination was made by comparing the breakthrough times for new and decontaminated materials. The breakthrough times for decontaminated materials were less than for new materials in most cases, indicating that permeation was gradually occurring, even after decontamination.[10]

The same study determined that thermal decontamination was effective. CPC materials were heated for sixteen hours at 100 °C. The breakthrough times for new and thermally decontaminated materials were nearly equal, indicating that heating the materials stopped chemical permeation.[10]

Thermal decontamination, although more effective than wash-rinse decontamination methods, is not easily performed in the field. Gloves and boot covers, the items most likely to contact chemicals, can be fairly easily decontaminated in this manner. Other items, such as butyl rubber suits and respirators, may have to be washed and rinsed. Further testing should be done to study the effects of heat on the CPC materials and the effectiveness of other decontamination methods.

CONCLUSIONS

The safety of hazardous waste site workers would be significantly improved with these refinements in site safety equipment:

- Improved on-site air monitoring techniques to accurately analyze a wide range of air contaminants
- More effective air purifying respirators and refined fit-testing methods
- Improved systems for alleviating heat stress
- More effective decontamination methods that can be easily performed on-site

Increased awareness of the limitations of site safety equipment and the potential for heat stress when wearing protective clothing would also enhance the health and safety of the hazardous waste site worker.

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Contaminant Stratification at a Deeply Penetrating, Multiple Component DNAPL Site

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ABSTRACT

An estimated 150,000 liters of solvent, including at least 13 halogenated and six aromatic hydrocarbon compounds as well as three ketones and one alcohol, were released over a 20- to 30-year period at a solvent reclamation facility in the midwestern United States. These chemicals contaminated the groundwater and produced dense nonaqueous phase liquids (DNAPLs) to a depth of at least 55 meters. To date, seven major investigations of groundwater and soil impacts at the site have been completed.

The seventh investigation was performed during 1989 to more precisely define the nature and extent of groundwater impacts within the bedrock. The investigative procedures consisted of a carefully packaged combination of methodologies, including rock coring, packer installation, in situ hydraulic conductivity testing and groundwater sampling in three boreholes ranging in depth from 69 to 85 meters. These procedures provided a nearly continuous profile of bedrock stratigraphy and structure, hydraulic conductivity, and groundwater chemistry.

One significant result of the investigation was recognition of at least two types of stratification of contaminants beneath the site. The first type of stratification is the occurrence in downgradient areas within the bedrock of three physically distinct plumes separated by low or nonimpacted zones and apparently coinciding at least partially with zones in which extensive accumulation and lateral spreading of DNAPLs has also occurred.

A second type of stratification is in the types and physical properties of the VOCs found at different horizons. Within the unconsolidated deposits, the predominant compounds are ketones and isopropyl alcohol, which have very high solubilities and low specific gravities. Within the bedrock, the predominant compounds are chlorinated hydrocarbon compounds, which have very low solubilities and high specific gravities. As a result of differences in the solubilities of the predominant compounds, total VOC concentrations in the unconsolidated deposits are as great as 17,000 mg/l, whereas the maximum concentration measured within the bedrock, even for wells from which DNAPLs have been recovered, is 1619 mg/l.

Recognition of these types of contaminant stratification may be essential to development of effective remediation programs at sites where multiple-component DNAPLs occur.

INTRODUCTION

The mechanisms which control the subsurface migration of soluble organic and inorganic compounds and to some extent "light nonaqueous phase" compounds are relatively well understood. The migration or potential migration of these compounds are predictable to the extent that earth scientists with an insight into the nature of the compounds can execute field programs using conventional investigatory techniques to evaluate the nature and extent of subsurface impacts.

The hydrogeological understanding of the mechanisms that influence the migration of dense nonaqueous phase liquids (DNAPLs) in the subsurface is, however, less well understood by the hydrogeological community. The state of our understanding of DNAPL migration in 1990 is perhaps most clearly summarized by Schwille[1] who states that the forces dominating the migration of DNAPLs are gravitational in nature rather than hydraulic. Simply put, DNAPLs will sink through a water saturated medium until the body no longer holds together as a single related continuous phase, but rather lies in isolated residual globules in the so-called condition of residual saturation.

As is apparent from Schwille's experiments,[1] the migration pathways of the DNAPLs are dominated by gravitational forces and modified by what may appear to be subtle changes in the magnitude and nature of the hydraulic conductivity. The result is a migration pathway that may appear both tortuous and difficult to rationalize.

In complex and hydrogeologic settings, conducting a hydrogeological investigation can be extremely expensive to implement with the inherent safety and QA/QC protocols. Nonetheless, in order to develop an effective remedial program, the nature and extent of the potential impacts must be evaluated in sufficient detail to allow for the design of the remedial measures.

INVESTIGATIONAL PROCEDURE

The methodology discussed in this paper was developed and applied at a RCRA-permitted solvent reclaiming facility in the United States Midwest where up to 150,000 liters of organic solvents may have been released from leaking drums over a period of several years. The contaminants released include at least 13 high density halogenated hydrocarbon VOCs and 10 low density VOCs including aromatic hydrocarbons, alcohols and ketones. Five phases of investigation using conventional investigation techniques were performed at the site between 1982 and January, 1988 to define soil and groundwater impacts. Based on these investigations, it was believed that vertical and horizontal migration of the DNAPL was limited. Vertical migration of the DNAPL beneath the facility was believed to be restricted at the bedrock surface at a depth of approximately 25 m. Although soluble organic impacts were measurable several hundred meters downgradient from the site, these soluble impacts were viewed as being manageable. The sixth phase of investigation, performed in July 1988, resulted in the discovery of DNAPLs in monitor well P-38 (Figure 1) at a depth of 55 m below ground level at a distance of 100 meters from the facility boundary.

With the discovery of the DNAPLs in the P-38 monitor well, it became apparent that the distribution of the DNAPLs had not been adequately determined and that significant additional investigatory work was necessary before final remedial measures could be selected, designed and installed.
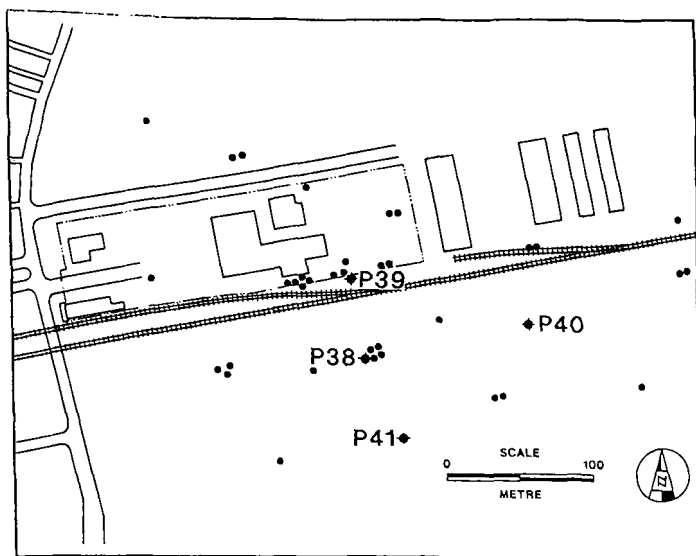
Figure 1
Site Location

In order to produce a maximum understanding of the impacts and hydrogeological setting of the deeper bedrock units, a method was developed that provides a nearly continuous profile of rock core, hydraulic conductivity and groundwater chemistry.

The scope of the Phase VII investigation consisted of packer testing of three deep boreholes (P39, P40 and P41) ranging in depth from 69 m to 85 m. One borehole was located on-site in the area of highest contaminant concentrations in the unconsolidated deposits. A second borehole was located 100 meters southeast of the site in the apparent migration direction for impacted groundwater. The third borehole was located approximately 122 m south of the site, in alignment with previous locations in which DNAPLs had been found. The work performed at each borehole location included collection of continuous bedrock core samples and, at selected intervals, purging and collection of groundwater/DNAPL samples, and performance of hydraulic tests.

Coring

A total of 158 meters of bedrock was cored as part of this investigation. Bedrock coring was performed using a Mobil B-57 drill rig equipped with a Longyear HQ wire-line system with a 3.3-m core barrel. The diamond coring bit produced a 96-mm diameter borehole and 63.5-mm diameter core samples.

During coring, the approximate volumes of drilling fluid lost to the borehole were estimated and recorded. PID measurements of rock core were also recorded.

Temporary and/or permanent 254, 152 and 102-mm diameter steel casings were installed in the boreholes during drilling to seal off multiple impacted, highly transmissive or incompetent zones present in each borehole (Figure 2). Permanent 254-mm diameter steel casings were installed in all three boreholes prior to the start of packer testing to seal off the incompetent sand and gravel surficial deposits and upper 1.5 to 3.0 meters of bedrock.

The permanent casings were cemented in place by pumping a 15:1 cement (Portland Type I)/bentonite (Aquagel Goldseal) grout through a tremie pipe into the annular space between the casing and the borehole wall.

The temporary 102-mm diameter casing was fitted with a reaming shoe, which allowed it to be advanced by rotating the 102-mm casing and reaming out a thin rim of rock at the edge of the 96.5-mm diameter core hole.

Packer String

After removal of the core sample from a test interval, the drilling rod was raised to expose the borehole walls within the test interval. An inflatable packer was attached by a stainless steel nipple to 3-m sections of stainless steel pipe which were inserted and lowered through the center of the drill rod to the precise top of the planned test interval. The pipe was 50.8-mm inner diameter, 314 stainless steel with flush threaded joints and the packer was a Tigre Tierra Model 34B-60-1.0 with stainless steel heads and center tube. The packer had a maximum inflated diameter of 127 mm and an uninflated diameter of 54.1 mm. The center tube had a 25.4-mm inner diameter.

After lowering the packer to the desired depth, the packer inflation line was attached to a pressure regulator on a nitrogen tank and the packer was inflated to a pressure of between 1,380 to 1,517 kPa.

CORING
CONFIGURATION
(Typical)

PACKER TESTING
CONFIGURATION
(Typical)
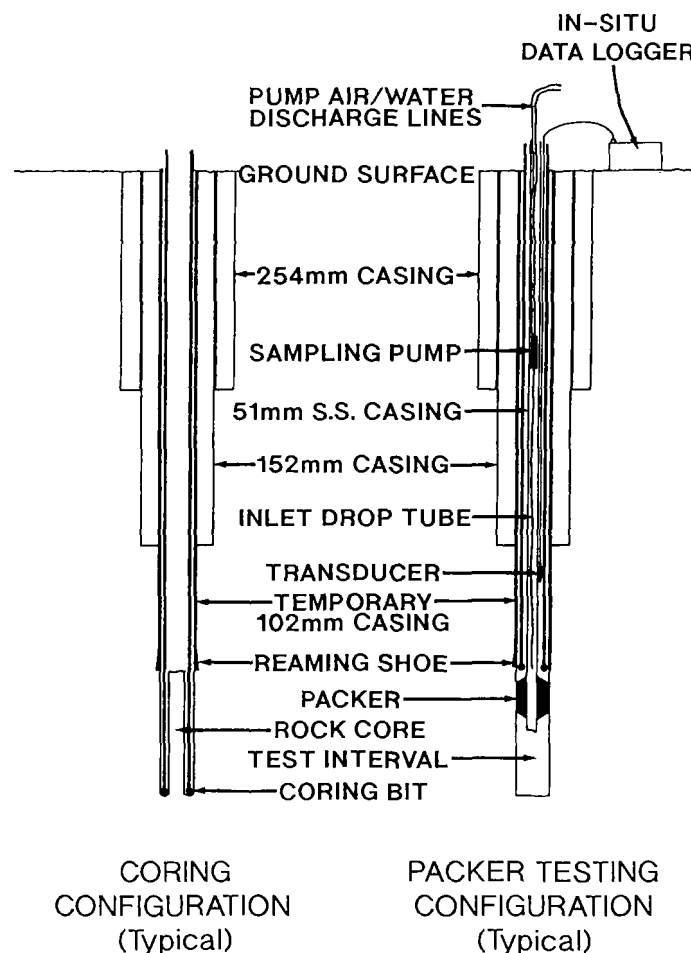
Figure 2
Testing Configuration

Hydraulic Testing

For hydraulic testing and sampling, a QED Well Wizard Model HR-4200 gas displacement pump made of stainless steel and Teflon and equipped with a drop tube inlet was connected to bonded 19-mm and 12.7-mm outside diameter polyethylene tubing and inserted into the packer string to a depth of 17 meters. A drop tube of 12.7-mm outside diameter Teflon lined polyethylene tubing, attached to a one-meter long 12.7-mm diameter stainless steel pipe was attached to the bottom of the purge pump. The use of the inlet drop tubing allowed progressively deeper intervals to be tested by adding sections to the drop tubing, while maintaining the pump at a relatively shallow, optimal pumping depth. The Model HR-4200 purge pump was used throughout the investigation.

A 345-kPa pressure transducer was inserted into the stainless steel riser pipe at a depth of approximately 0.5 meters above the top of the purge pump. The transducer was connected to an In Situ SE 1000B data logger. The data logger was used to record water level changes in the test interval during the purging interval and during the recovery

period following purging. The recovery data were used to calculate the hydraulic conductivity of the test intervals using two methods: (1) the Jacob method[2] and (2) the Cooper method.[3]

Groundwater and DNAPL Sampling

As the well was being purged, field measurements, including pH, specific conductance, temperature and photoionizable constituent concentrations, were conducted on the purged water. Photoionizable constituents were measured using an HNu Model PI-101 PID equipped with an 11.7-eV probe.

Groundwater samples collected during testing were initially analyzed for VOCs immediately after collection by the site laboratory.

Duplicate groundwater samples were analyzed by a contract laboratory for VOCs using U.S. EPA's SW846 Manual, Method 5030 for sample preparation and extraction and SW846 Methods 8010, 8015, 8020 and 8030 for determination of the compound concentrations.

Packer test equipment, including the packer, packer inflation tubing, stainless steel riser pipe, purge pump and pump tubing, were decontaminated by pressure washing and selected steam cleaning. This procedure was adequate until DNAPLs were exposed to the system during the 20th and 21st tests performed. Pump blanks were collected prior to subsequent tests, to evaluate the adequacy of decontamination procedures. These samples were immediately submitted to the site laboratory for VOC analysis.

Installation of Monitor Well

After completion of the final packer test in each borehole, the temporary 102-mm casing was removed and the borehole was reamed using a 149-mm diameter tricone bit.

Monitor wells were constructed according to Wisconsin state protocol using 50.8-mm I.D. schedule 80 PVC riser pipe with flush-threaded joints and three-meter long 0.010-mil slotted PVC screens.

IMPACT ASSESSMENT

Groundwater Impacts

Impacted groundwater at the site has a complex chemistry due to the large number of contaminant compounds released. A total of 23 compounds was detected, including 13 halogenated hydrocarbon compounds, six aromatic hydrocarbon compounds, three ketones and one alcohol. Table 1 summarizes the major physical and chemical properties of the VOCs detected in the groundwater samples. The halogenated hydrocarbons all have high specific gravities (1.17 to 1.68 g/cm³) and extremely low to moderately low solubilities in water (79 to 20,000 mg/L). The aromatic hydrocarbons have low specific gravities (0.861 to 0.880 g/cm³) and very low solubilities in water (130 to 1,750 mg/L). The ketones have even lower specific gravities (0.79 to 0.806 g/cm³) and variable solubilities ranging from 19,100 mg/L for methyl isobutyl ketone to complete miscibility within water for acetone. In addition

Table 1
Physical and Chemical Property Data for Volatile Compounds Detected

Chemical Group	Parameter Name (Common)	Parameter Name (Synonym)	Abbreviation (2)	Chemical Abstracts Service Registry Number (1)	Specify Gravity (g/cm³) (2)	Solubility in Water (mg/L) (1)	Molecular Weight (g/mole) (1)	Organic Carbon Partition Coefficient (ml/g) (1)	Log (Octanol-Water Partition Coefficient) (1)	Vapor Pressure (mm Hg) (1)	Henry's Law Constant atm-m³/mole (1)	Liquid Water Interfacial Tension (dynes/cm) (2)
Halogenated Hydrocarbons	Bromomethane	Methyl bromide	MTB	74-83-9	1.68	17800[3]	94.95[3]	--	--	1420[3]	--	--
	Chloroform	Trichloromethane	CRF	67-66-3	1.490	8200	119.39	31	1.97	151	2.87E-3	32.8
	1,3-Dichlorobenzene	M-Dichlorobenzene	DBM	25321-22-6[2]	1.288	123	147.01	1700	3.60	2.28	3.59E-3	--
	1,4-Dichlorobenzene	P-Dichlorobenzene	DBP	106-46-7	1.458	79	147.01	1700	3.60	1.18	2.89E-3	--
	1,1-Dichloroethane	Ethylidene chloride	DCH	75-34-3	1.174	5500	98.97	30	1.79	182	4.31E-3	--
	1,2-Dichloroethane	Ethylene dichloride	EDC	107-06-2	1.253	8520	98.96	14	1.48	64	9.78E-4	30
	1,1-Dichloroethene	Vinylidene chloride	VCL	75-35-4	1.21	2250	96.95	65	1.84	600	3.40E-2	37
	trans-1,2-dichloroethene	--	DEL	540-59-0	1.27	6300	96.95	59	0.48	324	6.56E-3	30
	Methylene chloride	Dichloromethane	DCM	75-09-2	1.322	20000	84.93	8.8	1.30	362	2.03E-3	--
	Tetrachloroethene	Perchloroethylene	TTE	127-18-4	1.63	150	165.83	364	2.60	17.8	2.59E-2	44.4
	1,1,1-Trichloroethane	--	TCE	71-55-6	1.31	1500	133.41	152	2.50	123	1.44E-2	45
	Trichloroethene	--	TCL	79-01-6	1.46	1100	131.39	126	2.38	57.9	9.10E-3	34.5
	Trichlorofluoromethane	Freon 11	TCF	75-69-4	1.494[3]	1100	137.38[3]	159	2.53	667	1.10E-1[4]	--
Aromatic Hydrocarbons	Benzene	--	BNZ	71-43-2	0.879	1750	78.11	83	2.12	95.2	5.59E-3	35.0
	Ethylbenzene	Phenylethane	ETB	100-41-4	0.867	152	106.17	1100	3.15	7.00	6.43E-3	35.5
	Toluene	Methylbenzene	TOL	108-88-3	0.867	535	92.14	300	2.73	28.1	6.37E-3	36.1
	O - Xylene	1,2-Dimethylbenzene	XLO	95-47-6	0.880	175	106.16	--	2.95	10	--	36.1
	M - Xylene	1,3-Dimethylbenzene	XLM	108-38-3	0.864	130	106.16	--	3.26	10	--	36.4
	P - Xylene	1,4-Dimethylbenzene	XLP	106-42-3	0.861	198	106.16	--	3.15	10	--	37.8
Ketones	Acetone	2-Propanone	ACT	67-64-1	0.791	1000000	58.08	2.2	-0.24	270	2.06E-5	--
	Methyl ethyl ketone	2-Butanone	MEK	78-93-3	0.806	268000	72.11	4.5	0.26	77.5	2.74E-5	--
	Methyl isobutyl ketone	4-Methyl-2-Pentanone	MIK	108-10-1	0.802	19100[3]	100.16	--	--	--	--	15.7
Alcohols	Isopropyl alcohol	2-Propanol	IPA	67-63-0[2]	0.785	1000000[3]	60.10[2]	--	--	--	--	17.1

References (principal noted at top of each column; exceptions noted adjacent to data)
1. U. S. EPA (1986)
2. Weiss (1986)
3. Vindholtz, et al. (1983)
4. Schwille (1988)
"--" indicates data not available

to the complex chemistry, the geometry of the impacted groundwater is complex due to the occurrence of numerous high permeability zones within the bedrock and multiple zones of DNAPLs potentially acting as individual sources for groundwater impacts.

Previous investigations at the site defined the magnitude and extent of impacts within the unconsolidated deposits, but not within the bedrock. Figure 3 is a conceptual isoconcentration profile of total VOCs in the groundwater at the site.
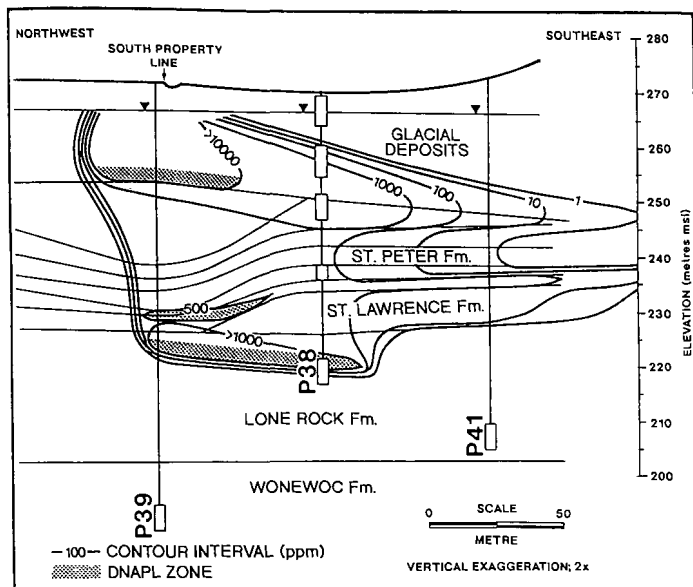
Figure 3
Extent of Impacts

Directly beneath the site, the groundwater impacts appear to be present in all zones from the water table surface in the unconsolidated deposits to the upper portion of the Lone Rock Formation within the bedrock. In downgradient areas, the impacted groundwater appears to form three distinct plumes which occur mainly within the upper and lower sandstone units of the Readstown Member of the St. Peter Formation and the upper portion of the Lone Rock Formation.

The upper and middle bedrock plumes occur within the permeable sandstone beds situated at the top and base of the formation and are separated by a low permeability siltstone, mudstone and shale unit. The plumes were differentiated based on relative contaminant concentrations and stratigraphic position. In boreholes P39 and P41, the position of the packer test intervals did not allow precise differentiation of the plumes; however, in the other borehole (P40), the plumes were clearly demonstrated to be separate by the occurrence of an intervening zone with a total VOC concentration of only 0.001 mg/L.

The deep bedrock plume occurs within the upper 6 to 10 meters of the Lone Rock Formation. Groundwater impacts in the upper Lone Rock were present in two of the boreholes. In P40, the groundwater sample from the upper Lone Rock Formation contained a total VOC concentration of 75,125 mg/L, the highest concentration present in tests performed at the borehole. In P39, the groundwater sample from the upper Lone Rock Formation had a total VOC concentration of 1,619.10 mg/L and contained up to 20^4 by volume of DNAPLs. In both of the P39 and P40 boreholes, groundwater samples from the subsequent deep packer test intervals contained total VOC concentrations approximately 150 to 300 times lower than those in the upper Lone Rock Formation. These low level concentrations were attributable to contamination of the deeper zones as a result of drilling, sampling and decontamination procedures. However, even with contamination from the procedures, the packer test methodology still was able to demonstrate the existence of an extremely sharp concentration gradient between the upper and middle portions of the Lone Rock Formation.

At least two major trends are apparent from the present data. First, there are major differences in the maximum total VOC concentrations that have been observed at different horizons beneath the site. Within the bedrock, the maximum total VOC concentration found in any groundwater sample collected from any well or packer test interval, including the three impacted by DNAPLs, is 1,619 mg/L. Within the unconsolidated deposits, particularly within wells intercepting the water table, total VOC concentrations greater than 17,000 mg/L have been measured in the groundwater in three wells. The differences in total VOC concentrations are due primarily to the presence of very high concentrations of high solubility compounds (ketones and isopropyl alcohol) within the unconsolidated deposits and their near absence within the bedrock.

The predominance of ketones and isopropyl alcohol as groundwater contaminants within the unconsolidated deposits, and halogenated and aromatic hydrocarbon compounds as groundwater contaminants within the bedrock, is the second major trend apparent in the groundwater chemistry data.

The differences in contaminant chemistry are evidence that the bedrock groundwater contamination probably is a secondary result of initial contamination by sinking DNAPLs composed of halogenated hydrocarbon and aromatic hydrocarbon compounds. In contrast, within the unconsolidated deposits, highly soluble contaminants, including the ketones and isopropyl alcohol, dissolved rapidly upon entry into the groundwater and have migrated downward only to a limited extent.

Extent of DNAPLs

Prior to this investigation, the extent of DNAPLs at the site was inadequately defined. It was known that DNAPL was present in at least three site wells; two were completed within the base of unconsolidated deposits, and the other within the upper portion of the Lone Rock Formation. The occurrences indicated only that DNAPL was present in some form at one or more horizons that intersected with the well completion interval. The exact elevation at which the DNAPLs entered the well and the nature of the DNAPLs' occurrence (i.e., isolated ganglia versus continuous bodies of DNAPL in pools) were unknown.

Insights into the nature of the DNAPL occurrences were gained through careful observation and monitoring of the DNAPLs as they were recovered during the packer tests. The DNAPLs recovered during test P39-4 occurred in the form of extremely small dispersed droplets which initially were invisible, but which coalesced after five to ten minutes to form a thin layer of large droplets on the bottom of the sample jar, representing approximately 1 to 2% of the total sample volume. This finding suggests that the DNAPLs in the P39-4 test interval may have occurred in the bedrock in the form of small droplets dispersed in intergranular pore spaces.

In contrast, the DNAPLs recovered during test P39-5 occurred as large globules of DNAPLs which were readily visible and settled immediately to the bottom of the sample jar. The DNAPLs initially represented as much as 20% of the total sample volume. An extended pump test was performed at P39-5 to determine the rate at which the proportion of DNAPL (as a percent of total fluid pumped) would decrease over time. The test was performed for 5 hours, during which the volume of DNAPL decreased steadily from 20% to 1.2% of the total fluid volume. An estimated total volume of 83 liters of DNAPLs was recovered.

The volume of DNAPLs recovered and their occurrence in the form of large globules, suggests that the DNAPLs in the P39-5 test interval may occur as a continuous body of DNAPLs concentrated within open fractures. A likely location for such a fracture would be at an elevation of 221 meters msl., where a 100% loss of drilling fluid occurred during coring of the P39-5 test interval. It is very significant that a 100% drilling fluid loss occurred at the same elevation in a second site borehole (P41). This finding suggests the existence of a continuous high permeability layer in the upper portion of the Lone Rock Formation with a lateral extent of at least 122 m. This same elevation also coincides with the test interval in which the greatest impacts were present in the third borehole (P40).

The maximum lateral and vertical extent of DNAPLs within the upper Lone Rock Formation at the site is unknown. Based on the known occurrence within the Lone Rock Formation of interbedded high and low permeability rock units that are nearly horizontal and laterally continuous over wide areas, it is possible that DNAPLs have spread outward in several directions within one or more high permeability layers in the upper Lone Rock Formation. The maximum vertical extent of DNAPLs within the Lone Rock Formation is unknown.

Two DNAPL samples (both from the upper Lone Rock Formation) have been analyzed for VOCs by an outside laboratory. By weight, halogenated hydrocarbons as a group account for 83.3% and 90.1% of the total organic concentrations in the two DNAPL samples, versus 16.7% and 9.9% for the aromatic hydrocarbons. The concentrations of individual DNAPLs compounds, as a percentage by weight of total detects, vary greatly. The DNAPL is composed, in order from greatest to least percentage by weight of total detects, of the following compounds:

- 1,1,1-trichloroethane (40.8% and 47.0%)
- trichloroethene (22.2% and 23.9%)
- tetrachloroethene (11.8% and 13.9%)
- toluene (5.2% and 7.4%)
- 1,2-dichloroethane (5.3% and 6.1%)
- xylenes (3.6% and 7.6%)
- ethylbenzene (1.1% and 1.7%)
- methylene chloride (0.8% and 0.9%)

Several new insights into the migration and dissolution dynamics of DNAPLs at the site were gained from evaluation of the DNAPL and groundwater chemistry data. For each compound, the concentrations measured in the DNAPL samples (in units of mg/liter) were converted to units of moles/liter, based on the molecular weight of each compound. The mole concentration of each compound was divided by the total molar concentration of all the compounds in each sample to

calculate the mole fraction of each compound of the total organics in each DNAPL sample. The mole fractions were then multiplied by the solubility in water for each compound to derive the estimated concentration for each compound for groundwater saturated with respect to the DNAPLs. These predicted values can be compared with the measured values in groundwater samples collected from each DNAPL zone (Table 2).

The validity of this analytical method can be demonstrated in DNAPL and groundwater samples by the relatively close correlation between the predicted and observed concentrations of various compounds, in particular for the aromatic compounds. The only anomalous values are for 1,2-dichloroethane, for which the observed concentrations are approximately 30 times lower than the predicted concentrations.

The application of this procedure provides several significant insights. First, the relative concentrations of individual compounds present in the groundwater may vary greatly from their proportion in the DNAPL. Methylene chloride comprises approximately 1% of the DNAPL, but 10% to 25% of the total organic concentrations in the groundwater. In contrast, ethylbenzene, which also comprises 1 to 2% of the DNAPL, comprises only 0.3% of the measured concentrations in the groundwater.

One implication of this relationship is that removal of methylene chloride will occur far more rapidly than removal of ethylbenzene or other lower solubility compounds. A second implication is that as the DNAPL is depleted over time, the ratio of the concentrations of high and low solubility compounds should change, as the high solubility compounds are depleted at a higher rate. These changes potentially could be monitored and used to estimate the rate of DNAPL removal over time during remediation.

The evaluation of the distribution of organic compounds in groundwater samples also potentially could be used to provide insights into the location and nature of DNAPL sources based on concentrations measured in downgradient monitor wells. For example, the mole fractions of the compounds in the P40-4 sample are virtually identical to

Table 2
Measured and predicted VOC Concentrations in
Groundwater Samples from DNAPL Zones

| Chemical Group | Parameter Name | Specific Gravity[1] (g/cm³) | Solubility in Water[2] (mg/l) | Molecular Weight[2] (g/mole) | Reported Concentrations in DNAPL Samples | | | | | | Predicted Concentrations at Saturation in Ground Water[6] mg/liter | | Reported Concentrations in Ground-Water Samples[7] mg/liter | |
| | | | | | mg/liter[3] | | moles/liter[4] | | mole%of total[5] | | | | | |
					P38	P39-5	P38	P39-5	P38	P39-5	P38	P39-5	P38	P39-5
	Chlorobenzene	1.11	488	112.6	2,570	0	0.0228	0.0	0.26	0.0	1.3	0.0	0.0	0.0
	1,1-Dichloroethane	1.174	5,500	98.97	0	326	0.0	0.00329	0.0	0.029	0.0	1.6	0.0	1.95
	1,2-Dichloroethane	1.253	8,520	98.96	69,860	74,109	0.706	0.749	7.90	6.69	673.0	570.0	16.9	21.70
Halogenated Hydrocarbons	1,1-Dichloroethene	1.21	2,250	96.95	2,850	2,131	0.0294	0.022	0.33	0.20	7.43	4.50	1.6	2.67
	trans-1,2-dichloroethene	1.27	6,300	96.95	380	484	0.00392	0.00499	0.044	0.045	2.77	2.80	1.6	7.75
	Methylene Chloride	1.322	20,000	84.93	8,640	12,825	0.102	0.151	1.14	1.35	228.0	270.0	109.8	401.79
	Tetrachloroethene	1.63	150	165.83	134,500	195,813	0.811	1.181	9.08	10.55	13.6	15.83	29.3	31.01
	1,1,1-Trichloroethane	1.31	1,500	133.41	536,300	575,779	4.020	4.316	44.99	38.56	674.9	578.4	460.9	619.24
	Trichloroethene	1.46	1,100	131.39	272,700	313,448	2.076	2.386	23.23	21.32	255.5	234.5	232.4	344.79
	Benzene	0.879	1,750	78.11	380	752	0.00486	0.00963	0.054	0.086	0.94	1.51	0.6	1.11
Aromatic Hydrocarbons	Ethylbenzene	0.867	152	106.17	12,590	24,540	0.119	0.231	1.33	2.06	2.02	3.13	3.1	3.14
	Toluene	0.867	535	92.14	59,770	104,051	0.649	1.129	7.26	10.09	38.8	53.98	35.9	57.86
	Xylenes	0.868[8]	168[8]	106.16[8]	41,541	107,090	0.391	1.009	4.38	9.02	7.36	15.15	10.9	14.40
	Totals				1,142,081	1,411,348	8.935	11.192	100	100	1906	1751	903.0	1507.41

Notes
1. Data from Weiss (1986)
2. Data from U.S. EPA (1986)
3. Concentrations in units of mg/liter for parameters found in DNAPL, as reported on Svanson Environmental, Inc. Laboratory analytical reports.
4. Concentrations converted to units of moles/liter for parameters found in DNAPL.
5. Concentrations expressed as percent of total organic concentrations calculated in units of moles/liter for parameters found in DNAPL.
6. Predicted parameter concentrations in ground water are calculated by multiplying the mole % of total for each parameter by the parameter's solubility in water, and dividing by 100.
7. Concentrations reported for ground water samples collected from the same well or test interval as DNAPL samples and analyzed by Svanson Environmental, Inc.
8. Average of reported values for m-xylene, o-xylene, and p-xylene.

the fractions in the P38 groundwater sample, and the concentrations are approximately 10% of those observed in the P38 groundwater sample. This finding suggests that the source of the contaminated groundwater plume at P40-4 is DNAPL with a composition identical to the P38 DNAPL sample, and a relatively near source.

CONCLUSIONS

The detailed investigation conducted at the facility confirmed extensive migration of DNAPLs in the subsurface. The physical and chemical dynamics of the migration are not well understood; however, it is apparent that chemical stratification of groundwater impacts does occur. This stratification is strongly influenced by the solubility of the individual components within the DNAPLs. Predictions of the relative combinations of compounds that will dissolve into the groundwater using the Bannergee[4] method compared well with results of analysis groundwater samples collected from the site. Additional detailed groundwater chemical analysis is necessary at this site prior to selection and design of remedial technologies.

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Use of MINTEQA2 and MULTIMED Models to Evaluate Soil Cleanup Levels at a Lead Battery Superfund Site

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ABSTRACT

Two computer models, MINTEQA2,[1] a state-of-the-art equilibrium metal speciation model, and the U.S. Environmental Protection Agency's Multimedia Model (MULTIMED),[2] a contaminant fate and transport model, were coupled and applied to the C&R Battery Site, a CERCLA site characterized by extensive lead contamination in the soil (0 to 15 ft deep). Downgradient groundwater lead concentrations were predicted for a no action and two remedial action scenarios. Development of a soil cleanup level for lead based on compliance with the Maximum Contaminant Level (MCL) for drinking water also was investigated. The results of the study were used to supplement the comparison of remedial alternatives included in the Feasibility Study (FS) for the site.

INTRODUCTION

To date, CERCLA has not adopted a standard methodology for determining soil cleanup levels for metals based on the potential for inorganic contaminants to migrate and contaminate groundwater. Lack of such an approach is a result of the complex behavior of metals in the soil-water system, in which the various reactions among solution species, gases, solids and sorbed phases are not easily described. Characterization of the behavior of metals in the soil-water equilibrium system requires quantification of their distribution between solid and liquid phases as well as the speciation of the resultant soluble components. Due to their complexity, the reactions of metals in the soil-water system are most easily quantified through the use of geochemical computer models.

In this study, the MINTEQA2[1] and MULTIMED[2] models were applied in series to the C&R Battery Site to achieve the following objectives: (1) predict downgradient groundwater lead concentrations for a no action and two remedial action scenarios (10,000 mg/kg and 1,000 mg/kg cleanup levels); and (2) develop a soil cleanup level for lead based on compliance with the Maximum Contaminant Level (MCL) for drinking water. The 1,000 mg/kg cleanup level is a risk-based level applicable to the "non residential" or industrial environment of the C & R Battery Site.[3] The 10,000 mg/kg cleanup level corresponds to remediation of only the highly contaminated "hot spots" at the site and is designed to optimize the amount of lead remediated with respect to soil volume and cost.[3] Information about MINTEQA2 and MULTIMED is available from the Center For Exposure Assessment Modeling, U.S. Environmental Protection Agency, Athens, Georgia.

SITE BACKGROUND

The C&R Battery Site was a battery-sawing and shredding facility which operated from the early 1970s until 1985. The facility was located on a 4.5-acre tract of land approximately 650 feet south of the James River in Chesterfield County, Virginia. A Remedial Investigation (RI)[4] and FS[5] were completed by NUS Corporation in January 1990. Lead was detected in both the surface and subsurface soils throughout most of the site in concentrations ranging from 16 to 122,000 mg/kg and 15 to 41,400 mg/kg, respectively. Because no inorganic contaminants were detected in the dissolved metals fraction in groundwater at concentrations above the National Primary Drinking Water Standards, groundwater remediation was not included in the FS.

The lithology beneath the site consists of a surficial layer of clay and silt with minor amounts of sand, ranging from 20 to 60 feet in thickness. Below this clay layer is an extensive fine to coarse sand and gravel deposit whose thickness is unknown.

GENERAL APPROACH

Development of Test Cases

MINTEQA2 was used to predict the equilibrium lead concentration in the leachate leaving the area of contamination, or source volume, whereas MULTIMED was used to simulate lead transport downgradient from the source. MINTEQA2 simulations were also conducted to calculate the distribution coefficients, or retardation factors, required by the MULTIMED unsaturated and saturated zone transport modules.

Based on the results of a sensitivity analysis,[5] pH and total inorganic carbon were determined to have the greatest influence on the amount of dissolved lead in the soil-water system. To bracket the uncertainties associated with these two parameters, average and worst case scenarios were formulated for the three cleanup levels developed in the FS; no action, 10,000 mg/kg and 1,000 mg/kg.

For the average case simulations, the mean pH values for the saturated and unsaturated zones were used (4.82 and 6.17, respectively). For total inorganic carbon, the median of observed CO_2 partial pressures in soil from the literature (3.5×10^{-3} atm) was used. For the worst case simulations, the 10 percentile soil pH value for the site (4.08) was used for the unsaturated zone, and the lowest measured groundwater pH value (approximately 4.08) was used for the saturated zone. For total inorganic carbon, atmospheric CO_2 partial pressure (3.5×10^{-4} atm) was used.

Maximum lead concentrations were predicted for two downgradient receptor wells located at distances of 10 and 100 meters, respectively, from the source volume. The 10-meter well location was chosen to represent a worst case scenario in which a drinking water well is installed directly downgradient from the source, near the site boundary. The 100-meter well location enabled the rate of contaminant migration to be estimated as well as the amount of attenuation and dilution offered by the aquifer. As a conservative approach, the receptor wells were placed along the centerline of the plume, and the well screens were assumed to be located at the water table.

A series of MULTIMED simulations was performed to predict whether or not the maximum lead concentration at each receptor would

ever exceed the current or proposed[6] MCL values for lead (50 ug/L and 5 ug/L, respectively) and, if so, the time required to surpass these values.

Back-calculation of a Soil Cleanup Level

Back-calculation of a soil cleanup level from a groundwater concentration requires estimation of the dilution-attenuation factor (DAF), which quantifies the amount of dilution and attenuation provided by the unsaturated and saturated zones. Source and downgradient lead concentrations are related to one another by the DAF as follows:

$$C_L = DAF*C_{RfD} \qquad (1)$$

where

C_L = leachate concentration (mg/L)
C_{RfD} = concentration limit at the well (i.e., MCL) (mg/L)

Equations 2 to 5 below show how the soil cleanup level, C_s, is related to the concentration limit at the well (C_{RfD}) through the DAF:

$$CS = A*d*D_{cs} \qquad (2)$$

where

CS = mass of contaminated soil (kg)
A = area of contaminated soil (m²)
d = depth of contaminated soil (m)
D_{cs} = density of contaminated soil (kg/m³)

$$CSc = C_s*CS*10^{-6}D \qquad (3)$$

$$CSc = q*A*C_L*T_p*10^{-3}D \qquad (4)$$

where

CSc = mass of chemical contaminant (kg)
C_s = soil contaminant (cleanup) level (mg/kg)
q = net infiltration rate (m/yr)
T_p = source duration time (yr)

Combining equations 1 to 4 and rearranging yields:

$$C_s s = [q*DAF*C_{RfD}*T_p*10^{-3}]/[d*D_{cs}] \qquad (5)$$

MINTEQA2 ANALYSIS

Characterization of the soil-water system using MINTEQA2 requires specification of basis species or components which represent reactants in all reactions considered by the model. The free metal ion, Pb^{+2}, was used as the component for lead. Only ions expected to have a major influence on the complexation and solubility of lead, either directly or indirectly, were chosen as components. Components were estimated from dissolved groundwater concentrations and are presented elsewhere.[5] Because of the uncertainties associated with measured Eh values,[7] redox reactions were ignored in the MINTEQA2 simulations.

Source Specification

The contaminated soil at the C&R Battery Site was depicted as a homogeneous, rectangular source volume with a depth of 15 feet. To simplify calculations, the volume of contaminated soil was held constant for all test cases, while the average lead concentration in the source volume was varied according to the amount of lead remaining in the soil following remediation. The source volume lead concentrations (soil

Table 1
**Average Initial Source Volume Lead Concentrations
for Three Cleanup Levels and Corresponding Initial
Pore Water Lead Concentrations**

Cleanup Level	Average Initial Soil Lead Concentration (mg/kg)	Initial Pore Water Lead Concentration (mg/l)
No Action	4,146	18,533
10,000 mg/kg	699	3,125
1,000 mg/kg	127	565

and pore water) for the three cleanup levels (Table 1) were calculated by dividing the total amount of residual (untreated) lead in the soil by the source volume. The residual lead quantities were estimated from measured site data using lead isoconcentration contours developed in the FS.[3]

Solids Selection Procedure

The solid phase lead speciation at the C&R Battery Site is not well-defined. X-ray diffraction analysis indicates that the lead is distributed among several minerals including lead sulfate ($PbSO_4$), lead carbonate ($PbCO_3$), lead oxide (PbO_2) and metallic lead (Pb^{-8}). The relative amounts of these lead minerals in the soil were not quantified during the mineralogical analysis. For this reason, finite solids were not input into MINTEQA2, but rather the total system concentration for lead was specified by the Pb^{+2} component and entered into the model as a pore water concentration (Table 1). MINTEQA2 was then allowed to determine which solids control the solubility of lead in the soil at the C&R Battery Site. Based on MINTEQA2 analysis, these solids include Anglesite ($PbSO_4$), Cerrusite ($PbCO_3$), Lanarkite ($PbSO_4 \bullet PbO$) and Diaspore ($AlO(OH)$).

Adsorption Modeling Approach

The diffuse layer algorithm of MINTEQA2 has been experimentally verified in the laboratory for the adsorption of lead (and other metals) onto a pure-phase amorphous iron oxide (FeO) surface.[9] Loux et al.[10] have demonstrated that the diffuse layer model, as incorporated into MINTEQA2 with the surface species given by Dzombak,[9] performs well in predicting the adsorption of lead onto amorphous FeO contained

Figure 1
Average Case Adsorption Isotherm for Saturated Zone

in a natural aquifer material. Hence, the diffuse layer algorithm of MINTEQA2 was used in this study to model adsorption of ions onto an FeO surface. The amount of amorphous FeO in the soil at the site was estimated to be approximately 1700 mg/kg.[5] Other input data required to run the diffuse layer algorithm were derived from Dzombak.[9]

MULTIMED requires specification of the distribution coefficient, K_d (ml/g), for both the unsaturated and saturated zones. A number of other input parameters, such as longitudinal, transverse and vertical dispersivities, are required by MULTIMED and are presented elsewhere.[5]

To determine K_d values for the unsaturated and saturated zones, a series of MINTEQA2 simulations was performed and adsorption isotherms were plotted under average and worst case conditions. The average case adsorption isotherm for the saturated zone is shown in Figure 1. The shapes of all four isotherms were best described by a Freundlich or Langmuir equation. MULTIMED, however, can only accommodate a linear adsorption isotherm, or constant K_d value, for both the unsaturated and saturated zones. Therefore, to determine K_d values for both zones for the three cleanup levels, linear approximations were made over the predicted equilibrium lead concentration range for each scenario using a simple linear regression program.

MINTEQA2 RESULTS

Using the calculated initial source volume lead concentrations (Table 1), the total dissolved equilibrium lead concentrations were determined by MINTEQA2 for the three cleanup levels under the average and worst conditions as shown in Table 2. The values shown in Table 2 represent the total concentrations of all dissolved lead species in the source volume leachate for each cleanup scenario. The influence of pH and total inorganic carbon on the solubilization and adsorption of lead species are illustrated by the differences in the equilibrium leachate lead concentrations between the average and worst case conditions.

The unsaturated and saturated zone K_d values for the three cleanup levels are shown in Table 3. The differences in K_d values between the unsaturated and saturated zones under average case conditions are a result of the different pH values used for the two zones (4.82 and 6.17, respectively). The unsaturated and saturated zone K_d values for the worst case scenarios are identical because the same pH value was used for each zone (4.08). A very high saturated zone K_d value (45,091 mL/g) was calculated for the 1,000 mg/kg cleanup level under average pH and inorganic carbon conditions. The high K_d value, which is outside of the range of observed K_d values,[11] is a result of the very low equilibrium lead concentrations used in the regression calculation. A value of 1000 mL/g was substituted for the 45,091 mL/g value because

it was considered a more realistic estimate of K_d when compared with the K_d values calculated for the other test cases.

MULTIMED ANALYSIS

To accommodate the constraints of the MULTIMED framework, the unsaturated zone beneath the source volume was represented by a homogeneous, isotropic layer having a thickness of 22 feet. The saturated zone was represented by a single layer with a uniform thickness of 100 feet. The boundary condition for the saturated zone transport module was specified as a Gaussian distribution in the lateral direction and uniform over the vertical mixing zone or source penetration depth (100 feet).

MULTIMED was run under a transient state condition in which leachate leaving the source was represented by a step function. Using the Hydrologic Evaluation of Landfill Performance (HELP) Model,[12] the net amount of annual infiltration into the soil was estimated to be 0.24 in./yr. The small amount of annual infiltration is a result of the low hydraulic conductivity of the soil (8.87 x 10^{-6} cm/sec on average). The duration of the source step function was determined for each test case by dividing the total mass of lead in the source volume by the leachate flux rate (annual infiltration volume times leachate concentration). Source duration times for the three cleanup levels are shown in Table 4.

Table 4
Source Duration Times for Three Cleanup Scenarios
Under Average and Worst Case Conditions

Cleanup Level	Source Duration Time (years)	
	"Average" Case	"Worst" Case
No Action	2,580	611
10,000 mg/kg	4,500	1,121
1,000 mg/kg	1,622	439

MULTIMED RESULTS

The times required to exceed the current and proposed[11] MCL values for lead for the three cleanup levels are presented in Tables 5 and 6 for the 10-meter and 100-meter receptor wells, respectively. The DAFs for the three cleanup levels ranged from 19 to 3,900 for the average case conditions and from 19 to 33 under worst case conditions.

Table 2
Equilibrium Source Volume Total Dissolved Lead
Concentrations Determined by MINTEQA2 for Three Cleanup
Levels Under Average and Worst Case Conditions

Cleanup Level	Equilibrium Total Dissolved Lead Concentrations (mg/l)	
	"Average" Case	"Worst" Case
No Action	2,057	8,684
10,000 mg/kg	199	789
1,000 mg/kg	100	369

Table 3
Unsaturated Zone and Saturated Zone K_d Values for Three
Cleanup Levels Under Average and Worst Case Conditions

Cleanup Level	Unsaturated K_d (ml/g)/Saturated K_d (ml/g)	
	"Average" Case	"Worst" Case
No Action	0.5/104	0.034/0.034
10,000 mg/kg	3.2/752	0.097/0.097
1,000 mg/kg	176/1,000*	0.214/0.214

*Substituted for actual calculated value of 45,091 ml/g

Table 5
Predicted Times Required to Reach Current and Proposed
MCLs for Lead at 10-m Well for Three Cleanup Levels Under
Average and Worst Case Conditions

Cleanup Level	Time to Reach MCL 50 µg/l (years)		Time to Reach Proposed MCL - 5 µg/l (years)	
	"Average" Case	"Worst" Case	"Average" Case	"Worst" Case
No Action	1,300	203	1,230	202
10,000 mg/kg	7,290	263	6,330	261
1,000 mg/kg	Never	265	190,000	261

Table 6
Predicted Times Required to Reach Current and proposed
MCLs for Lead at 100-m Well for Three Cleanup Levels Under
Average and Worst Case Conditions

Cleanup Level	Time to Reach MCL 50 µg/l (years)		Time to Reach Proposed MCL - 5 µg/l (years)	
	"Average" Case	"Worst" Case	"Average" Case	"Worst" Case
No Action	3,860	217	3,310	213
10,000 mg/kg	29,600	287	23,900	279
1,000 mg/kg	Never	411	275,000	396

DISCUSSION

For a given soil cleanup level, the time required for the groundwater lead concentration to reach the current and proposed MCL values at each receptor well (Tables 5 and 6) is dependent on the equilibrium leachate lead concentration (Table 2) as well as on the estimated unsaturated and saturation zone K_d values (Table 3). For both receptor wells, the variation in times to reach the current and proposed MCL concentrations among the three cleanup levels is much greater under average pH and inorganic carbon conditions than under worst case conditions. This difference is a direct result of the large variation in K_d values between the three cleanup levels calculated under average conditions compared with the much narrower K_d range obtained under the worst case scenario. Consequently, under average case conditions, removal of lead from the source volume produces the desired result of retarding contaminant migration, whereas under low pH and inorganic carbon conditions, the effectiveness of source remediation is severely impaired.

A comparison of the times required to reach the MCL value at the 10-meter and 100-meter receptors (Tables 5 and 6) reveals that the time differences between these two locations are much greater under the average case scenario than under worst case conditions. This variation is another manifestation of the different K_d values calculated under average and worst case pH and inorganic carbon conditions. Under average conditions, lead concentrations are significantly attenuated both with depth and laterally, decreasing lead concentrations in the contaminant plume while slowing its rate. Under the worst case scenario, once the contaminant front has reached the water table, little time is needed for the plume to travel from the 10-meter to the 100-meter well.

The strong influence of the adsorption process on predicted groundwater lead concentrations in the downgradient receptor wells is also reflected in the wide variation in the calculated DAF values between the average and worst case conditions.

Adsorption Analysis

Many of the K_d values calculated using MINTEQA2 fall below the range of values typically estimated in the laboratory (4.5 to 7640 mL/g).[11] The low K_d values used in this study (Table 3) are a result of using only amorphous FeO as the adsorbent in the MINTEQA2 simulations and using a linear approximation to estimate K_d. Other types of adsorbing surfaces present in the soil at the C&R Battery Site, such as the natural clay, organic and other metal oxide surfaces, provide the soil with additional adsorptive capacity than that offered by amorphous FeO alone. Because of the nonlinearity of the adsorption isotherms, the estimation of K_d values using a linear approximation introduced additional uncertainty into the adsorption analysis.

Source Specification

Although a step function was used to characterize the leaching of lead from the source volume over time, the use of an exponentially decaying function is expected to be a more physically representative approach. Because no data were available to estimate the source concentration decay rate, however, the step function approach was used. Conceptually, the source duration time should be directly proportional to the amount of lead contained in the source volume. As shown in Table 4, however, the calculated source duration times for the 10,000 mg/kg cleanup level are longer than those estimated for the no action test cases. This inconsistency is a result of all of the adsorption sites being full (i.e., breakthrough) under the no action cleanup level, which yields much higher equilibrium lead concentrations in the source volume for this scenario than those calculated for the 10,000 mg/kg and 1,000 mg/kg cleanup levels (Table 2). As evidenced by the MULTIMED results (Tables 5 and 6), the shorter pulse duration used for the no action cleanup level is balanced to some extent by the high equilibrium lead concentration used (Table 2).

Back-calculation of a Soil Cleanup Level

Under both average and worst case conditions, the DAF values vary according to the cleanup level used. This variation is due to the fact that the DAF is a non-linear function of various source-specific parameters, such as lead concentration and source duration time. Consequently, Equation 5 could not be solved directly for the soil cleanup level, C_L. Instead, derivation of a soil cleanup level from a groundwater concentration, in this case the MCL value, would require the following trial-and-error approach:

- Choose (estimate) soil cleanup level
- Determine source-specific parameters required by MINTEQA2
- Run MINTEQA2 to determine equilibrium lead concentration in leachate, K_d values and source duration time (using HELP)
- Run MULTIMED to determine lead concentration at receptor well
- Compare lead concentration at receptor well to MCL value and refine soil cleanup level estimate accordingly
- Repeat steps 1 through 5 until receptor lead concentration = MCL value

As shown in Tables 5 and 6, under the average case scenario, a soil cleanup level based on the current MCL value for lead (50 ug/L) would fall between the 1,000 mg/kg and 10,000 mg/kg cleanup levels. To support comparison of alternatives in the FS,[3] further refinement of a soil cleanup level using the above trial-and-error approach was not required.

CONCLUSION

The MINTEQA2 and MULTIMED simulations indicate that the adsorption process plays a key role in determining the long-term effectiveness of a remedial action at the C&R Battery Site.

The wide variation in modeling results suggests that accurate contaminant fate and transport predictions for metals are dependent on a well-defined set of physical/chemical parameters since uncertainties in model inputs, particularly K_d, may lead to false conclusions. Nevertheless, the application of the MINTEQA2 and MULTIMED models to the C&R Battery Site exemplifies their potential to serve as valuable engineering and management tools in the development and evaluation of soil cleanup levels.

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Regimen and Practical Considerations for Cross-Training of Industrial Hygiene and Health Physics Technicians

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ABSTRACT

Historically, the characterization and remediation of radioactive waste sites have been treated as if the only hazards present were due to radiation and radioactive materials. However, it has become apparent that work on many of these sites poses a number of industrial hygiene and safety concerns as well. Hazards created by heat stress, heavy equipment, excavation, silica dust and noise may pose much more significant health hazards than the radiation. In addition, most of the radioactive waste sites that are being remediated have an inventory of process chemicals or hazardous wastes that must be reckoned with. For these reasons, companies that traditionally have been in the health physics field services industry are finding it advantageous to employ individuals who are cross-trained in both health physics and industrial hygiene technologies. This paper:

- Summarizes those changes in the regulatory environment that have accelerated this trend
- Summarizes the minimum requirements set by regulatory agencies
- Describes a training sequence that TMA/Eberline has used to producing cross-trained technicians

INTRODUCTION

Health physics and industrial hygiene are very similar in their stated purpose, but for the most part have progressed through parallel evolutions. Health physics is often thought of as being the younger of the two disciplines although it became organized and regulated earlier than industrial hygiene in the United States. Formation of the U.S. Advisory Committee on X-Ray and Radium Protection (forerunner of the National Council on Radiation Protection) in 1929[1] was a milestone in the organization of health physics. Authority to regulate radioactive materials and radiation protection practices was provided by the Atomic Energy Act of 1954. Meanwhile, the American Conference of Governmental Industrial Hygienists was established in 1938. Authority to regulate occupational safety and health did not occur until passage of the Occupational Safety and Health Act of 1970.[2] The authority to regulate chemicals and chemical wastes was established during the 1970s and 1980s with the passage of a number of environmental laws.

The twenty five year lapse between the passage of the Atomic Energy Act of 1954 and the OSHA of 1970 resulted in rapid growth in the field of health physics. More recently, the passage of the OSHA, the enactment of environmental protection legislation, and the publication of OSHA's hazardous waste operations standards in 1986 has meant increased attention to chemical pollutants and the occupational safety and health of mixed-waste site workers.

Much of our nation's inventory of mixed hazardous and radioactive waste was generated under contracts with the U.S. Atomic Energy Commission and its progeny. During the 1980s, an upswing in environmental restoration activities at the U.S. Department of Energy's nuclear weapons plants stimulated the demand for field technicians who are cross-trained in industrial hygiene and health physics sampling and monitoring methods.

MINIMUM REQUIREMENTS

At this time, the minimum legal training requirements for working on a mixed-waste site are provided by a combination of OSHA regulations and one of the following: DOE Orders or Nuclear Regulatory Commission regulations or state radiation protection regulations.

The OSHA training requirements are primarily found in 29 CFR 1910, Section 120 (Hazardous Waste Operations and Emergency Response), Section 134 (Respiratory Protection) and Subpart Z (Toxic and Hazardous Substances). Depending on the job description, 24 to 40 hours of training can satisfy the OSHA requirement. A detailed discussion of which subjects should be included in hazardous waste operations training may be found elsewhere.[3]

In the case of work done under contract to the DOE, the radiation protection training requirements are specified in DOE Order 5480.11, "Radiation Protection for Occupational Workers." The minimum radiation protection training program specified by the DOE includes indoctrination in the following topics:

- The risk of low-level occupational radiation exposure, including cancer and genetic effects
- The risk of pre-natal radiation exposure
- Basic radiation protection concepts
- DOE and company radiation protection policies and procedures
- Employee and management responsibilities for radiation safety
- Emergency procedures

Where work is done for a Nuclear Regulatory Commission licensee in a restricted area, the minimum radiation protection training requirements for workers are specified in 10 CFR 19. The following information must be provided to workers:

- Locations and levels of radiation
- Health protection problems associated with exposure to radiation
- Precautions and procedures to minimize radiation exposure
- Purposes and functions of protective devices
- Applicable regulations
- Responsibility to inform licensee of violations of Commission regulations and unusual occurrences

Radiation protection training can be included as an integral part of the 40 hours of hazardous waste training required by OSHA standards. This level of training generally is adequate for drillers, surveyors and other individuals with limited responsibilities on a mixed-waste site. Unfortunately, this level of training is insufficient to qualify individuals

as entry level radiation protection or industrial hygiene technician.

INDUSTRIAL HYGIENE TECHNICIAN TRAINING

The goals of our industrial hygiene training program are to acquaint the hazardous waste site worker with using direct reading instruments, air sampling hardware, and noise monitoring equipment. In order to use the equipment properly, a worker needs to understand the basic operational principles, calibration procedures, simple trouble-shooting techniques, limitations of the device and interpretation of instrument readings.

The amount of training required will depend on how sophisticated the individual must become in industrial hygiene measurement techniques. Approximately 40 hours of training are required to make employees comfortable with the following training topics:

- Concentrations: ppm, mg/m3, volume percent, percent of LEL
- Use of bubble tube meters and mass flow meters to measure the flow rates of air sampling pumps; correcting air sample data to reference conditions
- Air sampling procedures requiring the use of particulate filters, sorbent tubes, impingers and dust cyclones
- Use and interpretation of colorimetric detector tubes
- Combustible gas indicators (CGI): how they work, how to calibrate them, and how to use them
- Portable flame-ionization detectors (FID): how they work how to calibrate them, how to use them
- Portable UV photo-ionization detectors (PID): how they work, how to calibrate them, how to use them
- Type II sound level meters: how to calibrate and use them o perform noise surveys

The employees who receive industrial hygiene measurement training are often health physics technicians who have training or experience which satisfies the requirements of 29 CFR 1910.120. Their response to the training is remarkably positive. The typical student is very concerned about missing even a few minutes of training! Most of the students are anxious to get their hands on the equipment and learn how to operate and calibrate it. Hands-on practice serves to clarify and reinforce what the mind has learned; so it is helpful to have students go through each operation several times.

During the course of the industrial hygiene measurements training, students realize that the procedures of operating CGI, PID and FID detectors are rather simple. They also learn that calibration procedures for many direct reading instruments are rather similar even though there are differences in detail.

RADIATION PROTECTION TECHNICIAN TRAINING

The goals of a radiation protection training program are to acquaint the hazardous waste site worker with health physics concepts, procedures and instrumentation. The training sequence is a two-step process. First, the individual is given an 8-hour overview of basic radiation pro-

tection concepts, computations and procedures. The trainee then must pass a lengthy take-home examination. On an as-needed basis, the employee is provided with site-specific supplemental training in procedures and instrumentation. On the average, workers receive approximately one week per year of site-specific supplemental radiation training.

Upon satisfactory completion of the basic radiation training, the employee is certified as having radiation protection technician training which satisfies the requirements of DOE Order 5480.11. It is a DOE requirement that refresher training be provided once every two years.

The following topics are presented during the 8-hour overview of radiation protection:

- Basic atomic structure
- Characteristics of ionizing radiation
- Radioactivity and radioactive decay
- Radiation units and measures
- Biological effects of ionizing radiation
- Radiation detection instruments
- Radiation survey techniques
- Radiation exposure and contamination control
- Federal radiation protection regulations

CONCLUSIONS

Hazardous waste operations training which satisfies the requirements of 29 CFR 1910.120 can provide the essential information which all mixed waste site workers must know. This level of training often is sufficient for surveyors, craftsmen and utility technicians who are not involved with taking occupational health or radiation measurements. In addition to hazardous waste training, approximately one week of radiation protection training may be provided to entry level workers who need to become proficient in health physics instrumentation and procedures. Approximately one week of industrial hygiene measurements training is enough to provide basic proficiency in chemical air sampling procedures, noise monitoring hardware and direct reading chemical detection equipment.

The training regimen outlined in this paper has worked well for TMA/Eberline. Training programs that are adequate for one type of mixed waste site, type of work or type of management philosophy may prove inadequate when used in different circumstances. Training programs always should be carefully reviewed by qualified safety and health professionals before being accepted.

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Remediation of a Lead Contaminated Site in a Central Business District

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ABSTRACT

The City of Omaha/Douglas County Central Park Mall project is part of a multiyear riverfront redevelopment plan. The plan involves several commercial developments including a $275 million corporate headquarters campus, research and development center and 30 acres of public green-belt park space.

A major hazardous waste site was identified within the urban redevelopment during the early planning stages. The result was a fast-track, multimillion dollar site investigation, remedial design and remedial action conducted to make way for the now-completed public park, lake/marina complex and corporate headquarters.

The RI/FS was completed while the final design and early construction packages for other project phases were underway. The investigation concluded that the soil on the proposed park site was contaminated primarily with heavy metals.

The remedial design provided for multiple technologies to reach the project's overall objectives. This paper focuses on two technologies:

* Resource recovery through off-site smelting of the lead contaminated soil
* On-site stabilization of lead contamination with subsurface placement

This paper discusses how the hazardous waste site was remediated in only 18 months from remedial investigation to completion of remedial action allowing for successful public and corporate projects on the site. Fast-tracked site characterization, off-site and on-site contaminant treatment alternatives are reviewed and the lessons learned during the remediation are presented.

INTRODUCTION

The Central Business District of Omaha, Nebraska, lies immediately west of the Missouri River. Through the years, the land adjacent to the river, which was principally industrial and warehousing in nature, had fallen into disuse with many abandoned buildings. In late 1987, the City of Omaha and Douglas County reached an agreement with several corporations for a major urban redevelopment project in this area. ConAgra, a major food processing corporation, would relocate its corporate headquarters as the anchor of the redevelopment. The project would include six multistory buildings in a campus setting adjacent to a 30 acre park. The principal feature of the park would be a 15 acre lake and fountain. Development of the park was undertaken by Douglas County. Other major elements of the redevelopment included renovation of the historic Union Pacific Railroad freight house for use as a system-wide-dispatch center and construction of a major office building/computer center by U.S. West Communications. Also planned is construction of a hotel complex and parking garage.

Due to the former land use, Douglas County elected to conduct an environmental investigation of the park site in 1988. Former industrial facilities included a battery breaking and secondary smelting facility that operated from 1963 to 1982, a metal salvage operation, a railroad freight handling facility (which had been destroyed by fire), a World War II alcohol production plant and numerous railroad tracks serving the area. The project area is shown in Figure 1.
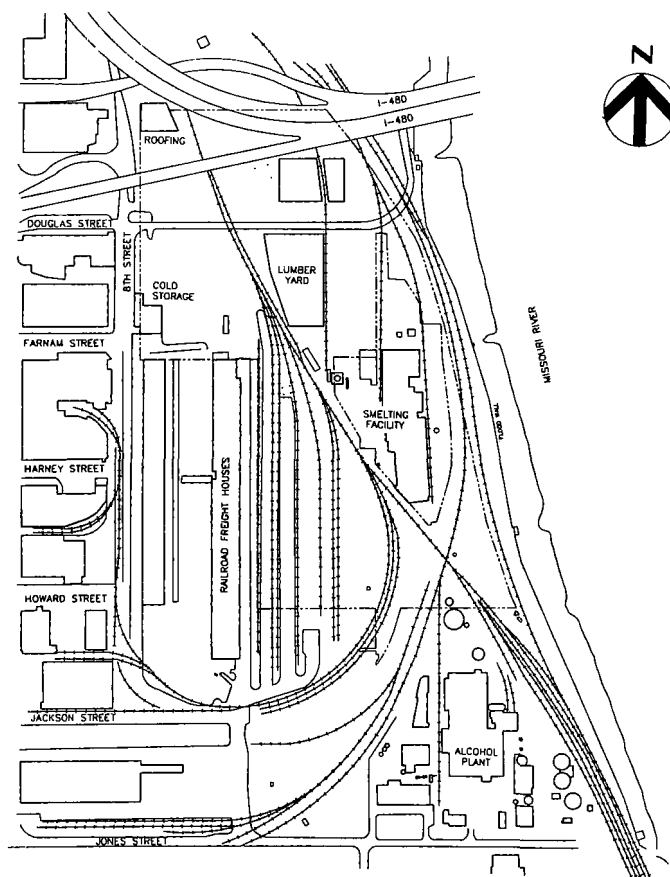
Figure 1
Project Area

SITE DESCRIPTION

The site lies west of the Missouri River on a floodplain that is approximately 1200 feet wide. The western portion of the site occupies

a higher mantled alluvial terrace and the ground surface slopes gently to the east. Ground elevations range from approximately 1,010 feet msl on the western edge to 975 feet msl near the eastern edge.

The soil in the floodplain consists of a clayey sand overlying limestone bedrock at a depth of 27-35 feet below the ground surface. The water table of the area is greatly influenced by the water level of the river and is generally 15 feet below ground surface. The site is bounded on the east by the Missouri River, on the north by the I-480 bridge, on the south by Jones Street and on the west by 8th Street.

DISCOVERY OF ENVIRONMENTAL PROBLEMS

Several environmental investigations were initiated during 1987 and 1988. Results from those investigations indicated that the soil on the proposed park site was contaminated with heavy metals with lead being the most prominent. These findings had an immediate impact on conventional park construction activities in the area. The contaminated areas were fenced and more detailed site investigations began. With the limited information available, the opinion was that before construction of the park could proceed, the site would require remediation.

SITE INVESTIGATIONS

In late 1987, random environmental samples from soil borings and monitoring wells were collected. Analysis of these samples revealed metal contamination in the upper few feet of soil. Groundwater samples indicated that metal contamination was confined to the soil overlying the aquifer. Petroleum hydrocarbon contamination was discovered in one of the monitoring wells. Elevated concentrations of VOCs and pesticides/PCBs were not detected in any of the soil and water analyses.

As the limits of contamination became better defined, subsequent investigations focused on approximately five acres of land encompassing the former secondary lead smelting facility. A detailed remedial investigation of this area was conducted in 1988. The assessment indicated that the area contained high levels of total arsenic, antimony, cadmium and lead. Twenty-five percent of the soil samples revealed cadmium in concentrations which exceeded the EP Toxicity standard, and 70% revealed lead in concentrations exceeding the EP Toxicity standard. Monitoring well samples did not indicate an exceedance of the U.S. EPA Maximum Contaminant Levels (MCLs) for drinking water metals. In addition to the metals, the investigation revealed the presence of petroleum hydrocarbons in the soil.

A subsequent investigation of petroleum hydrocarbons was conducted at the site to determine the magnitude and extent of contamination. Results of that investigation indicated that the contamination was primarily confined to the soils and no measurable thickness of floating product was detected on the groundwater.

In summary, the site investigations detected soil metal contamination with concentrations highest near the ground surface and decreasing with depth and distance from the smelting facility property boundary. Findings of the remedial investigation indicated the presence of the following soil contaminants:

Contaminant, Total Metal	Maximum Concentration, (mg/kg)
Lead	152,400
Arsenic	1,700
Cadmium	1,900
Antimony	3,400

REMEDIAL ACTION PLAN AND IMPLEMENTATION

In January 1989, a draft feasibility study which evaluated remedial action alternatives for the site was completed. Remedial action objectives contained in the feasibility study were based on contaminant specific applicable or relevant and appropriate requirements (ARARs), input from public meetings, health assessment information and a corrective action agreement between the State of Nebraska, Department of Environmental Control (NDEC) and Douglas County. The principal regulatory guidelines for the site contaminants include federal criteria

documents, epidemiologic studies, state regulations and health advisories.

Several technologies were made a part of the initial feasibility study screening process, including immobilization, landfilling, soil washing, resource recovery, vitrification and storage/capping. From that list, five technologies were selected for a detailed evaluation of alternatives. Rankings for each remedial alternative are presented in Table 1.

Table 1
Evaluation of Remedial Alternatives

Alternative	Effectiveness	Implementability	Cost	Compliance
No Action	Low	High	Low	No
Resource Recovery	High	Medium	Medium	Yes
Resource Recovery/ Immobilize on-site	High	Medium	Medium	Yes
Hazardous Waste Landfill off-site	High	High	High	Yes
Immobilization on-site	High	High	Medium	Yes

The feasibility study concluded that EP Toxic soils could be remediated through a combination of resource recovery or stabilization and that non-EP Toxic soils, generally containing total lead concentrations between 1,000-10,000 mg/kg, should be excavated and covered. It was determined that placing all soils left on-site under a cover of native fill would greatly reduce both potential airborne and direct contact exposure pathways and allow for future management of the material from the standpoint of maintenance and deed restrictions. Highlights of the corrective agreement with the NDEC are as follows:

- Douglas County would submit a Remedial Action Workplan, including a schedule to NDEC for review and approval.
- Douglas County would treat soils contaminated at or above 1000 mg/kg total lead or exhibiting EP Toxicity for metals using the treatment method approved by NDEC before covering the site with native fill.
- Douglas County would propose procedures for preventing fugitive dust emissions from the site.
- Once excavation, treatment and consolidation of soils was completed, the site would be regraded and covered with 3 feet of uncontaminated soil.
- Douglas County agreed to maintain the park throughout its ownership of the site or until it receives approval from NDEC for a change of use. Douglas County would place a notice in the deed to the property restricting any change of use without prior notification and approval of NDEC to ensure that the integrity of the cover is preserved and maintained.
- Douglas County would submit a worker Health and Safety plan to NDEC for review and comment.
- In the Remedial Action Workplan, Douglas County would propose, for NDEC review and approval, treatment of contaminated soils. Prior to NDEC approval, Douglas County shall provide documentation which demonstrates their effectiveness.
- Douglas County would submit to NDEC written monthly progress reports of remedial action activities.
- NDEC would provide oversight and review of documents and site operations on a frequent basis to ensure that the requirements of law and the goals of the Agreement are diligently met.

REMEDIAL DESIGN

The remedial design called for conventional construction activities to be initiated under a separate contract which would begin after site remediation had been completed. Additionally, all soil which was identified as recyclable following trial tests, that could be recycled within the scheduled remediation period, would be shipped to a primary smelting facility.

In March 1989, Douglas County advertised for sealed bids to secure a contract for the Central Park East - Site Remediation Project. The contract documents, including drawings and specifications, detailed the character and scope of work to be performed and standards applicable to the work.

The site remediation project was divided into nine bid items. Each bid item set forth a request for the price of the work and services to be performed under the contract. These items included:

- Mobilization/Demobilization
- Earthwork (EP Toxic Soil)
- Earthwork (Non-EP Toxic Soil)
- Earthwork (Landscape Fill)
- Soil Stabilization Treatment
- Structural Demolition
- Pipeline Removal
- Miscellaneous Removal
- Rubble Disposal

REMEDIAL ACTION

Soil stabilization and resource recovery were selected as the remediation processes. For remediation purposes, contaminated soils were grouped into three categories based on lead content and remediation method:

- Soil that contained greater than 20,000 mg/kg lead and was of proper gradation was considered a lead ore and could be used as feedstock for a primary smelting facility.
- Soil that exhibited EP Toxicity characteristics for metals required stabilization if not recycled in the smelter.
- Soil that did not exhibit EP Toxicity characteristics for metals, but had total lead concentrations greater than 1000 mg/kg, required excavation, placement and covering.

By using resource recovery, the lead was reclaimed as a substitute for raw material and the process qualified as recycling. Initially, 300 tons of soil were shipped by gondola railcar to a Missouri smelting facility for processing. Test results from that shipment indicated that the soil was compatible with their operations although somewhat lower in quality than initial bench tests indicated. As a result, a second shipment of approximately 500 tons of soil from the site took place in early summer 1989.

The stabilization process was used for the on-site remediation of the remaining EP toxic soils. Stabilization is a chemical fixation and solidification process designed to produce a nontoxic, environmentally safe material that can be used as fill. The process utilized a two-part inorganic chemical system which reacts with polyvalent metal ions and with certain other waste components. It also reacts within itself to form a chemically and mechanically stable solid. This system is based on the reaction between silicates and silicate-setting agents which react in a controlled manner to produce a solid matrix.

The chemical stabilization process used for this project involved three classes of soil/chemical interactions. First are the very rapid reactions between silicates and polyvalent metal ions, producing very insoluble metal silicates. A second set of reactions occurs between the silicate and reactive components of the setting agent. The third class of reactions occurs between the setting agent and the waste and/or water as it undergoes a series of hydrolysis, hydration and neutralization reactions.

The soil was excavated using scrapers and back-hoes and was screened to remove debris. Pockets of slag discovered on the site had to be crushed in order to make the material compatible with the stabilization process. Following excavation and crushing, the soil was stockpiled for screening. Front-end loaders were used to sift material through a two inch shaker screen with soil falling onto a conveyor belt for transfer to the chemical feed system. Following chemical addition, the soil was dropped into a pug mill for thorough mixing. Following mixing, the treated soil was dropped onto a conveyor belt and moved to its designated fill area where the material was shaped and compacted. The stabilization process flow diagram is presented in Figure 2.
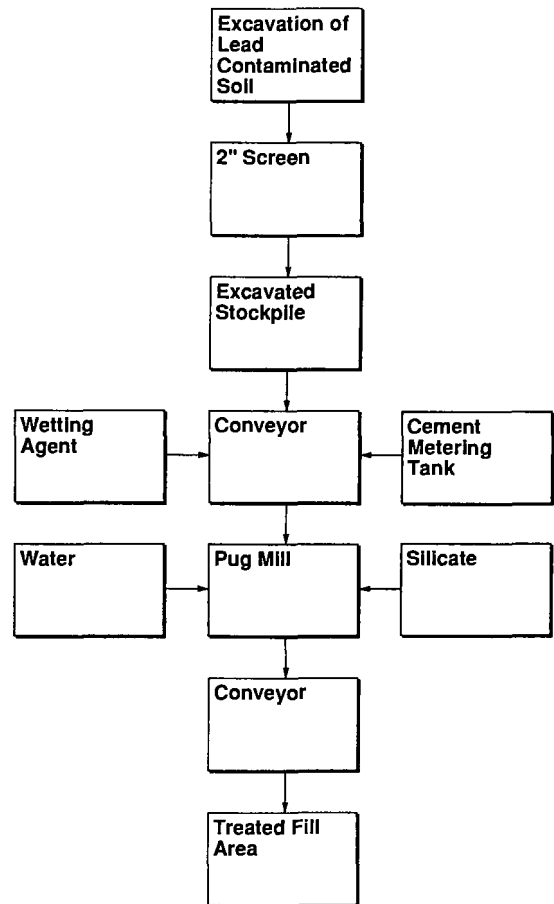
Figure 2
Stabilization Process

SUPPORT ACTIVITIES

Samples of treated EP Toxic soil were collected to confirm that the soil treatment process had stabilized the metals to remedial action levels. A sampling frequency of one sample per 1000 yd^3 of stabilized soil was used for quality control. If a sample failed to meet the remedial action level, the batch representing the failed run was returned to the stockpile of untreated material for reprocessing. These soils were retreated until testing confirmed acceptable treatment levels had been achieved.

Excavation areas established during the remedial design were subdivided into sample areas of approximately equal size with defined boundary coordinates. Within these sample areas, coordinate point references were established to aid in developing a sample grid. Twenty aliquots were gathered using an Oakfield manual sampler from each area and composited to represent the level of remediation for that area.

After the general contractor had excavated the contaminated soil to planned depths, the exposed ground surface was sampled by the field team. These analyses were used to confirm that site excavation activities had removed the contaminated soil to the remedial action levels.

If the remaining soil was determined to have a metal concentration greater than the remedial action levels, the area was excavated an additional one foot. After the additional one foot of soil was removed, the newly exposed ground surface was retested. These same procedures were followed throughout the project until the remaining soil exhibited a metal concentration which met the remedial action levels.

Air monitoring was performed using four high volume air samplers to determine if dust suppression activities were minimizing fugitive dust emissions during remediation. Background samples were collected at the site prior to remediation activities to serve as a baseline for measuring the effectiveness of dust mitigation. A goal of the site

remediation team was to reduce off-site releases of dust through tasks such as frequent application of water for dust control and modification of excavation and treatment practices contributing to off-site releases.

FINDINGS

Many problems were experienced throughout the project. Some initially were thought to be minor obstacles, while others went undiscovered until the site remediation was well underway. All impacted the project from a cost and schedule standpoint.

Underground Storage Tanks

The discovery of five underground storage tanks (USTs) occurred during various stages of excavation throughout the project site. Three of these tanks had suffered gross failures making it necessary to deal with the petroleum hydrocarbon-contaminated soil underlying the UST to clear the area for conventional construction.

Excavation and removal of 20,000 yd³ of petroleum-contaminated soil was accomplished in three weeks using a back-hoe and several bottom dump trucks to haul the material to a local site where landfarming of the soil took place over a period of two months.

Pipeline

It was determined that a four inch diameter abandoned pipeline ran parallel to the project site for a distance of 1600 feet. The pipe was removed and capped at both ends of the project site. Petroleum hydrocarbons, discovered in the soil near the pipeline, were suspected to have leaked at some time during its 40 years of operation. The pipeline contained several hundred gallons of product which were removed and hauled away by an oil recycling company.

Slag

It was determined during the site investigations that slag was a component of the contaminated fill material which required remediation. During construction, it was determined to be a major component of remediation requiring a change order. This change over resulted from the discovery of burial pits containing chunks of slag, measuring four to ten inches in diameter. In total, 2000 yd³ of slag were excavated from the site. Due to the large particle sizes, it was necessary to crush the slag in order to stabilize it with the soil for placement on-site. The large volume of material requiring crushing caused significant delays in the scheduled completion of the project.

Rubble

Although some rubble was expected to be encountered, the actual amount was greatly in excess of expectations. This was the result of long abandoned storm sewers and building foundations not shown on any existing plans. This unanticipated material resulted in additional project cost for removal as well as schedule impacts.

Ingots

Three ingots of nearly pure lead, approximately eight feet in diameter and one foot thick, were discovered. These ingots were transported to a local smelter for recycling. Considerable extra cost was incurred in procuring a crane of sufficient capacity to lift the ingots to a flatbed truck.

Smelting

Problems were encountered during the transportation and recycling of the lead-contaminated soil at the smelting facility in Missouri. The smelting facility is a primary smelter designed to handle homogeneous crushed lead ore from a mine and not material of various sizes. The smelter's feed specifications resulted in a one inch screening size requirement being placed on the soil shipments. Screening the soil to this size was time-consuming and in some instances required several screenings of a single load. When the soil became damp, it was nearly impossible to sift soil through a one inch screen. This problem was unfortunate because metal assays indicated that a large percentage of the soil on the site would have been suitable for smelting from the standpoint of the lead content, but it could not be processed in a timely manner.

The other problem encountered during smelting was coordination of the shipments by railcar and storage capacity at the smelter. Storage bins at the smelting facility had a limited capacity and restrictions were put on the number of railcars that could be sent at one time. Scheduling the relatively small number of railcars, by railroad standards, was difficult to coordinate because the length of time to screen the material was variable. Several days of time were lost due to screening and late arrival and departure of railcars.

Resource recovery ended up being a cost rather than a benefit. The smelting fee of $150 per ton, the transportation costs of $25 per ton and screening costs exceeded the lead ore value. When all factors were considered, a unit price of approximately $100 per ton was the resulting cost for soil disposal.

Remediation Volume

Initially, based on soil borings, it was estimated that 30,000 yd³ of soil would fail the EP Toxicity test and require remediation by chemical fixation and stabilization. An additional 20,000 yd³ were estimated to have total lead concentrations between 1,000 and 10,000 mg/kg. However, this material generally would pass the EP Toxicity test. Thus, remediation could consist of excavation, placement and covering. In the end, the EP Toxic soil volume increased to approximately 49,800 yd³ while the non-EP Toxic soil volume decreased to approximately 13,400 yd³. Thus, the total volume requiring remediation increased by 13,200 yd³ or 26% of the total. Of greater significance is the fact that the increase in EP toxic soil resulted in considerable extra cost since this soil had to be processed through the treatment process, the most costly phase of the remediation on a unit price basis. Soil borings, being discreet in nature, resulted in an underestimation of remediation quantities.
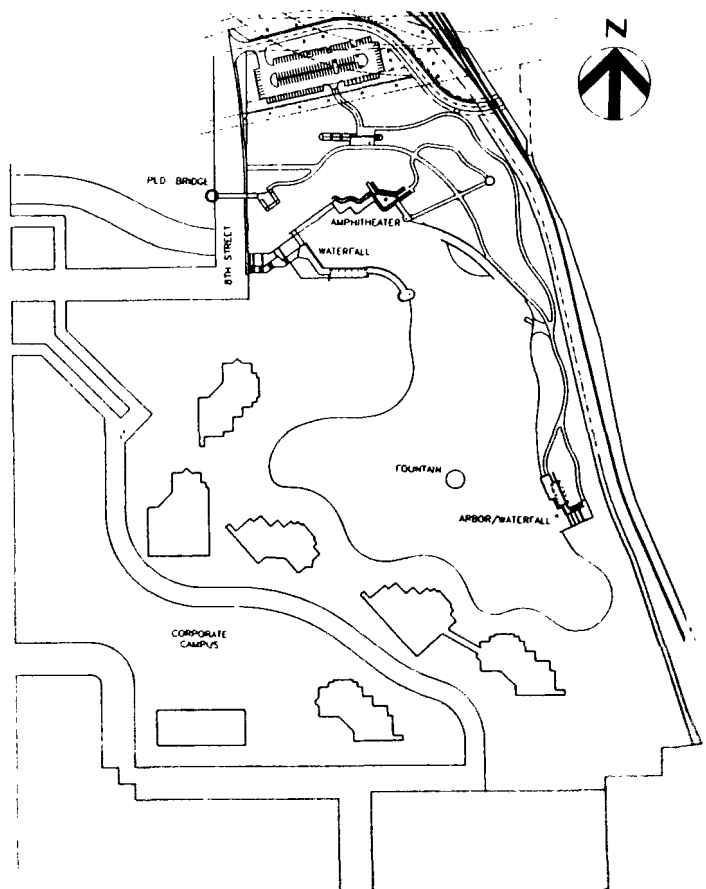
Figure 3
Corporate Campus and Public Park

POST REMEDIATION

A total of 63,200 yd^3 of contaminated soil was excavated and managed in some fashion either by stabilization, recycling, or excavation and covering. Of that volume, 48,000 yd^3 of soil were stabilized on-site. The remainder was either managed on-site or sent to the smelter.

The project which began with a remedial investigation in May 1988 was completed in December 1989 at a cost of $7,100,000. Of this total, $1,200,000 was reimbursed to the County by the previous owner of the site.

The willingness of Douglas County to address the hazardous waste issue in a technically sound, yet rapid manner, resulted in remediation of the site at much lower cost and in much less time than typically would have been required. The detailed cooperation of the state regulatory agency, which has delegated authority for RCRA from the U.S. EPA, also contributed to project success.

Today the site is nearly complete with six office buildings and a 15 acre lake containing two water fountains as shown on Figure 3. The development has become an integral element of redevelopment of Omaha's Central Business District.

Status of Developing Land Disposal Restrictions for Superfund Soils

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ABSTRACT

RCRA Land Disposal Restrictions (LDRs) for contaminated soil and debris at Superfund sites are currently being developed. This paper discusses the steps the U.S. EPA is taking to gather data for the development of LDR treatment standards for contaminated soil and debris (CS&D) and discusses the challenges of treating contaminated soils, sludges and debris wastes.

The unique physical and chemical characteristics of Superfund soil and debris make these wastes more difficult to treat than more homogeneous industrial process wastes. In response to this, the U.S. EPA is in the process of developing separate LDR standards for soil and debris. LDRs for CS&D are being developed under section 3004 of the Hazardous and Solid Waste Amendments of 1984 to RCRA. Until the final CS&D standards are in place, the National Contingency Plan specifies that Best Demonstrated Available Technology (BDAT) standards are generally inappropriate for Superfund soils and that treatability variance levels, based on the actual treatment of soil, will be used. This paper discusses the U.S. EPA's accomplishments in the collection of existing soil treatment data, the development of variance procedures and variance levels for remedial/removal actions (Superfund LDR guidelines 6A and 6B) and the issues involved in treating soil and debris. In addition, the paper discusses some preliminary findings on the treatment of debris and the analytical methods used for determining the BDAT for CS&D. The schedule for rulemaking also is discussed.

INTRODUCTION

The U.S. EPA's Office of Solid Waste and Emergency Response (OSWER) recognized that contaminated soil is more difficult to treat than RCRA industrial process (hazardous) wastes and that it is not likely to meet the LDRs developed for RCRA hazardous wastes. In response, OSWER began a program to develop Contaminated Soil and Debris (CS&D) Treatability Variances, which are alternate treatment levels, based on actual treatment of Superfund and RCRA soil and debris. Data were collected, and in 1989, Treatability Variance Levels were established for soils (Superfund LDR guides 6A and 6B).[1,2]

OSWER, the Office of Solid Waste (OSW) and the Office of Emergency and Remedial Response (OERR) determined that the existing soil treatment data base is not comprehensive enough to support a formal set of LDRs for CS&D. Sixty-seven data sets were suitable for calculating treatability variance levels; however, several technologies had little or no data so they were not included in the data

base. OSWER implemented a research program to obtain all of the necessary data to support LDRs for CS&D.

In 1988, OSWER including the new Technology Innovation Office (TIO), and the Office of Research and Development (ORD), Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio, established a work group to develop BDAT standards for CS&D. The work group objectives include a review of the current data base, recommendations for additional studies on treatment performance, implementation of treatability studies, identification of newly available data and development of BDAT regulations based upon new and available data. There has been significant progress with these efforts.

DATA COLLECTION

OERR, in its initial data collection effort, examined more than 500 studies conducted by the U.S. EPA, federal agencies, industries and universities. Of these studies, 67 met the criteria established for the development of variance levels for contaminated soils. The criteria require that: (1) the soil originates from contaminated sites (soils are not spiked with contaminants); (2) data are of sufficient quality; and (3) the untreated and treated soil contamination is measured. The criteria for setting final LDR treatment standards are more rigorous than the criteria for variance levels, requiring more documentation of QA/QC procedures and bench, pilot- and full-scale data. Of the 67 studies used for variance levels, only 13 were adequate for consideration in the development of LDR treatment standards.

Lack of soil treatment data prompted a more aggressive data collection effort by OERR, OSW, TIO and ORD. Figure 1 shows the basic approach for data collection in the CS&D program. Additional data will be collected from recent remedial/removal actions, including DOD and DOE actions, SITE program demonstrations and treatability tests conducted by the CS&D program. Twenty-seven additional data sets already have been obtained. Currently the CS&D data base contains not only the original data base, but also studies that have been collected since the variance levels were published.

OERR developed a strategy for calculating variance levels from a quantity-limited data base. OERR grouped the data by "contaminant groups" which are groups of contaminants having similar chemical and physical characteristics. Contaminants are categorized into 13 groups; examples of contaminant groups include nonpolar halogenated aromatics and PCBs/dioxins/furans including their precursors. The variance levels that were developed quantified the effectiveness of various available technologies on the contaminant groups (Table 1).
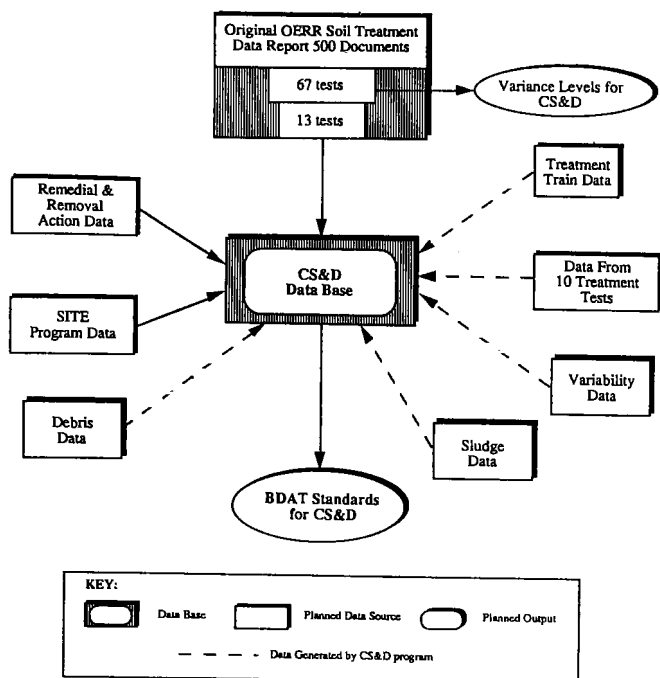
Figure 1
Development of LDRs for CS&D
Data Collection Approach

SOIL TREATMENT TESTS

The CS&D Program, after reviewing available data sets, identified technologies that lacked treatment performance data, but would be available technologies for treating CS&D (Table 1). Ten treatment tests are planned; the technologies that will be tested include bioremediation, low temperature thermal desorption, chemical extraction, soil washing, stabilization and high temperature distillation (Table 2). The technologies are applied to different types of soils and wastes. For example, the biotreatment tests will be conducted on three soil types. The soil classifications range from sandy to clay. In addition, different types of wastes, including wastes high in PNAs, PCBs and metals, will be tested. The stabilization technology will be tested as both a primary technology and as a residual treatment.

The treatability tests will be conducted according to the OSW Quality Assurance Project Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris Program[3] and site-specific Sampling and Analysis Plans. The individual sampling plans specify holding times, analytical methods, chain-of-custody and quality control measures, such as blanks and spikes. The tests will include measurements of contaminant concentrations before and after treatment, and measurements of the waste characteristics that affect the performance of soil treatment technologies. Examples of waste characteristics that affect treatment performance are moisture content, oxidation/reduction potential and particle size distribution and are listed in the QA Project Plan.

Table 1
BDAT Soil Treatment Data

TECHNOLOGY / TREATABILITY GROUP	BIOREMEDIATION	IMMOBILIZATION	DECHLORINATION	CHEMICAL EXTRACTION	THERMAL DESTRUCTION	LOW TEMPERATURE THERMAL DESORPTION	SOIL WASHING	MISCELLANEOUS TECHNOLOGIES
NON-POLAR HALOGENATED AROMATICS (W01)	CS&D			CS&D		CS&D		
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	CS&D		CS&D			CS&D	CS&D	
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	CS&D			CS&D		CS&D		
HALOGENATED ALIPHATIC COMPOUNDS (W04)	CS&D	X	CS&D			CS&D		
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	CS&D			CS&D		CS&D		
NITRATED COMPOUNDS (W06)		X	X	CS&D		CS&D		
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	CS&D	X	X	CS&D		CS&D		CS&D
POLYNUCLEAR AROMATICS (W08)	CS&D	X	X	CS&D		CS&D		CS&D
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	CS&D		X	CS&D		CS&D		
NON-VOLATILE METALS (W10)	X	CS&D	X	CS&D		X	CS&D	CS&D
VOLATILE METALS (W11)	X	CS&D	X	CS&D		X	CS&D	CS&D
ARSENIC (W11)						CS&D	CS&D	CS&D
CYANIDE (W12)						CS&D	CS&D	CS&D

| | Existing Data Expected | | CS&D Test Data | | INDICATES TECHNOLOGY IS NOT EXPECTED TO BE EFFECTIVE |

Table 2
Planned CS&D Treatability Tests

SITE	TECHNOLOGY	SOIL TYPES	MAJOR CONTAMINANTS
MOTCO, TX	Low Temp Thermal Desorption Bioremediation Chemical Extraction	Clay Sludge	Halogenated and non-halogenated aromatics PNAs, metals
MIDCO IN	Soil Washing, Low Temp Thermal Desorption	Sandy	PCBs PNAs other non-halogenated and halogenated organics
Bayou Bonfuca, LA	High Temp Thermal Distillation	Silty clay	PNAs, metals
Ninth Avenue IN	Bioremediation	Sandy	PCBs PNAs metals
Burlington No MN	Low Temp Thermal Desorption Bioremediation	Sandy Silty Sludge	PNAs, other non-halogenated organics and aromatics
Brown Battery, PA	Stabilization	Silty loam	Lead

DEBRIS

OSWER has collected and continues to collect existing data on debris treatment programs. This collection and assessment project determined that debris could constitute as much as 50% of the contaminated media at a wood preserving site. The assessment also found that the sampling procedures were not well documented. Recognizing the importance of debris, the CS&D Program has implemented a comprehensive review of debris sampling, analysis and treatment. The treatment technologies that require treatment performance data will be tested by the CS&D Program. The characteristics of debris that have been determined to affect treatment include permeability and destructibility. The potential treatment technologies for debris are destruction, chemical extraction, physical removal and sealing/solidification (Table 3).

Table 3
Potential Management Practices for Debris Decontamination

DEBRIS MATRICES \ CONTAMINANT GROUPS	ORGANICS * (EXCEPT NITRATED ORGANICS)	NITRATED COMPOUNDS	METALS	CYANIDE
PERMEABLE DESTRUCTABLE	Destruction	Destruction	Chemical Extraction Physical Removal Sealing/Solidification	Destruction
PERMEABLE NON-DESTRUCTIBLE	Chemical Extraction Physical Removal Sealing/Solidification	Chemical Extraction, Physical Removal	Chemical Extraction Physical Removal Sealing/Solidification	Chemical Extraction Physical Removal Sealing/Solidification
NON-PERMEABLE DESTRUCTABLE	Chemical Extraction, Physical Removal Destruction Sealing/Solidification	Chemical Extraction, Physical Removal Destruction	Chemical Extraction, Physical Removal Sealing/Solidification	Chemical Extraction Physical Removal Destruction Sealing/Solidification
NON-PERMEABLE NON-DESTRUCTIBLE	Chemical Extraction, Physical Removal, Sealing/Solidification	Chemical Extraction, Physical Removal	Chemical Extraction, Physical Removal Sealing/Solidification	Chemical Extraction Physical Removal Sealing/Solidification

* Organics include volatile, acid extractable, and base neutral organics, pesticides, dioxins and PCBs

SLUDGE

An OSWER survey of Superfund sludge data found that sludges are not consistently defined in the studies by the authors. Further-more, sludges, when identified, had higher concentrations of contaminants than soils and, as a result, did not meet variance level standards as frequently as soil. Of the OSWER survey data, 55% of the sludge treatment met variance levels, while 78% of the soil treatments met variance levels. These results indicate that sludge may require its own treatment standards and that additional data on the definition and treatability of sludges should be obtained. If required, treatability tests will be conducted.

VARIABILITY

The OSWER study of Superfund soil treatability has found an order of magnitude difference in treatability between remedy selection testing and full-scale treatment. The factors that affect treatment effectiveness include mixing effectiveness, homogeneity of the soil matrix, feed specifications and contaminant concentrations. Variability of the treatment results for the relatively homogeneous RCRA waste streams have been accounted for using classical statistics which assume a less variable data set than Superfund soils.

A study has begun to identify the historical approaches to quantifying variability of treatment results for Superfund soils. Once completed, a testing program will be developed and implemented. This program will be designed to quantify the effects of soil classification, contaminant concentration heterogeneity, diverse technology feed specification, mixing requirements and scale-up factors on the full-scale treatment results.

CONCLUSIONS

The current schedule provides for completion of data collection and data analysis in the summer of 1991. We are soliciting existing treatment data and new tests which may meet these needs. We welcome comments on this program to advance this study effort on soils, sludges, debris and variability. If you have data, comments or questions regarding the LDRs for contaminated Superfund soils and debris, please contact:

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Helen Kramer Landfill Superfund Site Remediation

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ABSTRACT

The 80-acre Helen Kramer Landfill Superfund site in Mantua Township, New Jersey is currently undergoing remedial action by IT-Davy, a joint venture of International Technology Corporation (IT) and Davy McKee Corporation (Davy). The $55.7 million, two-year construction effort represents the second largest single remediation contract awarded to date under the Superfund Program. The Army Corp of Kansas City District, as the U.S. EPA's project manager, awarded IT-Davy a contract to carry out remedial action in October 1989. On-site construction has commenced with a planned completion date of January 1992.

The Helen Kramer site received municipal solid wastes, hazardous chemical wastes and hospital wastes from 1963 to 1981. Contaminated leachate has been detected in both surface and groundwaters near the site. The site is physically and chemically hazardous, with wastes, surface rifts and sharp objects (including hypodermic needles) exposed at the surface. Landfill gas and particulates are being discharged into the atmosphere, and several large fires have occurred at the site

The remedial action for this site includes isolation of the contamination through the installation of a multilayer cap over the site and a slurry wall around the site to isolate the contamination from the surrounding environment. Leachate and run-off liquids will be collected and treated utilizing airstripping and carbon absorption. Landfill gas also will be collected, treated and flared. IT-Davy has total site remediation responsibility including construction and implementation of site security, health and safety programs, personnel training programs, chemical and geotechnical testing and facility operation for one year.

This paper presents an overview of this large superfund site remediation project and the status as of September 1990.

INTRODUCTION

The Helen Kramer Landfill Superfund Site is currently undergoing remedial action to isolate toxic contaminants from the local community and environment. The Army Corps of Engineers (COE), Philadelphia District is acting as project manager for the U.S. EPA. IT-Davy, a joint venture of International Technology Corporation (IT) and Davy McKee Corporation (Davy), is the remedial action contractor (RAC) for this site. IT-Davy has total site remediation responsibility including construction and implementation of site security, health and safety programs, personnel training programs, chemical and geotechnical testing and operation of the site treatment systems for one year.

At the time of award, October 1989, the remedial action contract value, $55.7 million, represented the largest single site remediation contract awarded to date under the Superfund program. The size of the project and its proximity to residential and farming communities have generated substantial public interest in the progress of the remedial action and the process leading up to the actual construction activities.

This paper presents a description of the site and reviews its progress through the Superfund process. The remediation project is described, and the current status as of September 1990 is discussed. Problem areas encountered in the remediation effort are identified.

SITE DESCRIPTION

The Helen Kramer Landfill is located in Mantua Township, Gloucester County, New Jersey, approximately 20 miles south/southeast of Philadelphia, Pennsylvania. The site encompasses an 80-acre refuse area and an 33-acre stressed area. The site is bounded on the north by Jessups Mill Road, the south by Boody Mill Road, the west by Leave Road and the east by Edwards Run. The stressed area lies between the refuse area and Edwards Run. Centre City, the nearest residential area, is 1200 feet east of the site. Active farms are located just west of Leave Road and south of Boody Mill Road.

A north-south ridge, approximately 1500 feet long, divides the site. The western slope is moderate, whereas the eastern slope is long, steep and extends into Edwards Run. Edwards Run flows into Mantua Creek which is a tributary of the Delaware River.

Table 1
Leachate and Groundwater Contaminants

ORGANICS	INORGANICS
Bromomethane	Arsenic
Dichloroethenes	Chrome
Trichloroethanes	Cobalt
Benzene	Iron
Toluene	Lead
Xylenes	Magnesium
Ketones	Nickel
Phenols	Sodium
	Calcium

A 2- to 3-acre pond, containing approximately 5000 gallons of water is located in the northeast corner of the site. Two smaller leachate

collection ponds are located along the eastern slope. One of these ponds is lined with a Hypalon membrane, that has many visible tears, whereas the other is unlined. Leachate discharges from these ponds to Edwards Run.

The site surface is characterized by surface rifts and loose, uncompacted exposed refuse. Numerous cracks are apparent where methane, steam and leachate are vented. Sharp objects, including hypodermic needles, are exposed. These conditions represent physical hazards for personnel entering the site.

Groundwater and leachate leave the site via Edwards Runs and are heavily contaminated with organic and inorganic compounds. The Mount Laurel aquifer which underlies the landfill is also heavily contaminated. Groundwater from this aquifer flows into Edwards Run. Bioassay and Ames testing indicate the waters in Edwards Run are both toxic to the test species (bioassay) and mutagenic according to the Ames test. Table 1 Lists major contaminants which have been found in the water in Edwards Run.

Methane and other landfill gases discharge into the atmosphere through natural vents or cracks in the landfill surface. Methane concentrations above the lower explosion limits have been detected at the landfill surface. VOCs were measured in the ambient air on and near the site; however, concentrations did not indicate an imminent threat to nearby residents.

SITE HISTORY

The Helen Kramer site was originally used as a sand and gravel pit. Sometime in 1963, the site began receiving refuse while the excavation of sand and gravel continued. When New Jersey enacted a Solid Waste Management Act in 1970, the site operator was given a temporary registration valid until July 1, 1971. By that time, the operator was required to have submitted a sanitary landfill design for permanent registration.

Beginning with this first submittal date, all deadlines for submitting documentation were missed and the Helen Kramer Landfill became the subject of numerous inspections and characterizations. The following chronology highlights the site history from this initial regulatory action up until the issuance of a Notice To Proceed with the remedial action.

- July 1973 — Landfill design submitted to New Jersey Department of Environmental Protection (NJDEP) and rejected as incomplete.
- October 1973 — Site inspection by NJDEP noted disposal of chemical and sanitary wastes on-site.
- January 1974 — NJDEP inspections noted presence of chemicals and drums on-site, as well as chemical waste disposal in at least seven lagoons.
- January/ March 1974 — Revised landfill designs submitted and again rejected as incomplete.
- April 1974 — NJDEP noted leachate discharging into Edwards Run. NJDEP issued a Department Order, a Notice of Prosecution and a Notice of Intent to Deny Renewal of Approved Registration. NJDEP issued a stipulation restricting dumping to municipal household wastes, commercial wastes, sewage sludge, septic tank wastes, leaves, tree stumps and branches.
- November 1974 — Revised engineering design submitted and rejected as incomplete.
- September 1976 — Second Notice of Prosecution issued requiring submittal of an acceptable engineering design within 30 days. Revised engineering design resubmitted.
- April 1977 — Engineering design rejected Notice of Registration Revocation issued informing the owner to cease operation of the landfill. Hearings on the revocation continued until early 1981.
- March 1981 — Gloucester County court ordered the landfill to cease operations effective March 7, 1981.

- June 1981 — U.S. EPA sent out "Information Request" letters to 11 PRPs.
- July/ August 1981 — Several fires broke out in the landfill and were not extinguished until November 1981.
- 1981-1983 — Preliminary site assessments carried out.
- January 1982 — U.S. EPA sent out additional Information Request letters.
- July 1982 — Helen Kramer Landfill proposed for inclusion on the NPL.
- March 1983 — Notice letters to conduct the RI/FS sent to eight PRPs. No response.
- July 1985 — "Draft Remedial Investigation Report and Feasibility Study of Alternatives, Helen Kramer Landfill" was issued by R.E. Wright and Associates. Inc.
- September 1985 — Helen Kramer landfill placed on NPL with a ranking of 4. Final ROD issued by the U.S. EPA. Notice letters offering the opportunity to conduct the remedial design and implementation sent to PRP's.
- 1987-1989 — Remedial Design and construction bid package prepared by URS, Company, Inc.
- May 1989 — Invitation to bid Remedial Action issued by Kansas City District, Army Corps of Engineers.
- Sept. 19, 1989 — Bid Opening.
- Oct. 6, 1989 — Army Corps of Engineers awards Remedial Action contract to IT-Davy. Execution of the contract transferred to the Philadelphia District of the Corps of Engineers.
- Nov. 13, 1989 — Notice To Proceed issued to IT-Davy

REMEDIAL ACTION

The goal of the Helen Kramer remedial action plan is: "The prevention or mitigation of migration of hazardous substances from the site." During the RI/FS phase of the project, a number of different remedial actions were investigated. These actions were then considered as components of different remedial action alternatives. The components investigated include:

- *Security Fence* - This fence would completely encircle the site allowing for controlled access to the site, thus substantially reduce the hazard of direct contact with waste material.
- *Groundwater/Leachate-Collection Trough* - This trench, located along the entire eastern border of the site, would be used to collect groundwater prior to it entering the Edwards Run.
- *Upgradient Soil - Bentonites Slurry Wall* - This component consists of installing the slurry wall along the north, west and south sides of the site. This wall would substantially reduce the flow of groundwater flowing under the landfill, thus reducing the quantities of leachate requiring treatment.
- *Surface Grading and Capping* - This component would consist of filling areas of the site with local borrow, grading the soil to a maximum 20% slope and placing a cap over the site. The cap would serve to prevent direct contact with the exposed waste, assist in landfill gas control and reduce the amount of leachate generated. Both a soil and a multilayer clay cap were considered.
- *Leachate Treatment* - This component consists of three unit operations in series; flow equalization, metals precipitation and air stripping. This component is considered feasible for producing water with a quality acceptable for discharge to a sewer system.
- *Gas Generation/Migration And Treatment* - This component includes a gravel layer under the cap and piping under the cap to collect the landfill gas and transport it to an on-site facility. Treatment would consist of carbon adsorption followed by methane flaring. Both active and passive gas collection systems are considered.
- *Excavation* - This component would remove the source of contamination resulting in an improvement in leachate quality. However, this option would expose the workers and general community to a greater

safety hazard and probably is not feasible due to cost and unavailability of landfill capacity.

* *Construction of On-site RCRA Facility* - This component assumes that a hazardous waste landfill conforming to RCRA requirements would be constructed adjacent to the Helen Kramer site. Waste from this site would be excavated and disposed of in the new landfill.
* *Lagoon Dewatering and Excavation* - The approximately 1.52 million gallons of leachate and 2,400 yd³ of highly contaminated soil would be removed from the existing lagoon and two leachate collection ponds. The leachate would be treated or reinjected into the fill. The soil would be placed beneath the landfill cap.
* *Surface Water Controls* - This component consists of storm water run-off controls to protect the landfill cap from erosion.
* *Alternative Water Supplies* - This component would eliminate the low potential for residential wells to become contaminated by supplying an alternative source of uncontaminated water.
* *Monitoring* - This component would include quarterly monitoring of groundwater, surface waters and ambient air samples at the site to document the effectiveness of the remedial action.

Five categories (and eight cases) of Remedial Action Alternatives were developed for evaluation against U.S. EPA guidance criteria, incorporating various combinations of these remedial action components. Table 2 summarizes the alternatives evaluated in the feasibility study.

Table 2
Remedial Action Alternatives

CASE 1: security fence; site monitoring (No action Alternative).

CASE 2: RCRA landfill; excavation; groundwater/leachate collection trough and treatment; dewater, excavate and fill lagoons; security fence; and monitoring.

CASE 3: clay cap; groundwater/leachate collection trough and treatment; passive gas ventilation; dewater, excavate and fill lagoons, surface water controls; security fence; and monitoring.

CASE 4: clay cap; groundwater/leachate collection trough and treatment; active gas ventilation; upgradient slurry wall; dewater, excavate and fill lagoons; surface water controls; security fence and monitoring.

CASE 5A: clay cap; passive gas ventilation; upgradient slurry wall; dewater, excavate and fill lagoons; surface water controls; security fence and monitoring.

CASE 5B: soil cap; groundwater/leachate collection trough and treatment; upgradient slurry wall, passive gas ventilation; dewater, excavate and fill lagoons; surface water controls; security fence; and monitoring.

CASE 5C: clay cap; passive gas ventilation; dewater, excavate and fill lagoons; surface water controls; security fencing; and monitoring.

CASE 5D: soil cap; groundwater/leachate collection trough and treatment; passive gas ventilation; dewater, excavate and fill lagoons; surface water controls; security fence; and monitoring.

A detailed evaluation of each alternative was performed against the following criteria:
* Performance (effectiveness), reliability and implementability
* Institutional constraints/issues
* Any adverse environmental or health effects
* Cost

Using these criteria, Case 4 was selected as the remedial action of choice as it effectively mitigates all current and potential adverse environmental and health impacts. This case was modified during the remedial design phase with the addition of a roller compacted concrete retaining wall placed along a major portion of Edwards Run and the extension of the slurry wall to completely encircle the refuse area. The purpose of the retaining wall is to support the slurry wall and protect it from storm water run-off in Edwards Run. The extension of the slurry

wall replaced the groundwater/leachate collection trough. Key elements of the remedial action as it is being implemented are summarized below:

* *Clay Cap* - the entire refuse area will be graded and covered first with common fill material and then with a multilayer clay cap. This cap consists of a 12-inch rock gas collection layer, a filter fabric, a 24-inch clay layer, a 12-inch sand drainage layer, an 18 inch common borrow layer and 6-inches of top soil layer.
* *Soil-Bentonite Slurry Wall* - this three foot thick wall up to 75 foot deep will completely encircle the refuse area, thus minimizing migration of leachate into and out of the contaminated zone.
* *Roller Compacted Concrete (RCC)* - approximately 30,000 yd³ of roller compacted concrete will be placed to form a retaining wall along the side of a major portion of Edwards Run.
* *Pretreatment Facility* - a leachate and run-off water pretreatment facility will incorporate a metals precipitation and separation step followed by an air stripping process for organics removal. Treated water will be discharged to the local sewer system. Vapors from the air stripping process will be treated by activated carbon adsorption.
* *Gas Collection and Treatment Facility* - this facility will collect and treat landfill gas using activated carbon adsorption to remove VOCs followed by flaring of the methane.
* *Roads with Associated Grading and Drainage* - gravel roads will be installed connecting the pretreatment facility and other points on the site. Roads will be installed with the approximate grading and drainage features to minimize the amount of surface water percolating into the site.
* *Lagoon Dewatering and Cleanup* - the existing lagoons and leachate collection ponds will be dewatered, and the water will be sent to the pretreatment facility prior to discharge. Contaminated lagoon sediments will be excavated and placed under the multilayer cap. The lagoons will be filled with suitable clean materials from off-site.
* *Security Fence* - a temporary chain link fence with a limited number of locked gates will be installed around the site to protect humans and animals from potential site hazards during construction. A permanent fence will be installed at the completion of construction activities.
* *Monitoring* - a series of monitoring wells will be drilled on- and off-site, and a series of ambient air monitoring stations will be installed.
* *Startup, Testing and Operations* - upon completion of construction, activities of all systems will be started up and tested to ensure that they achieve design goals. The treatment facilities (water and gas) will be operated for one year prior to training and turnover to a permanent operating team.

PROGRESS TO DATE

Upon notice of award in October 1989, IT-Davy mobilized a task force off-site to begin preparation of site operations plans required for approval prior to the Corps of Engineers issuing the Notice To Proceed (NTP). These plans included:

* Contractor Quality Control Plan
* Chemical Quality Management/ Sampling Plan
* Site, Safety, Health and Emergency response Plan
* Fire Fighting Plan
* Materials Handling Plan
* Project Schedule
* Environmental Protection Plan
* Security Plan
* Air Monitoring Plan
* Emergency Leak Response (Spill Control) Plan
* Dust, Odor and Vapor Control Plan
* Lagoon Seawatering Plan/

The plans have been submitted, reviewed, revised as needed and approved by the COE. The NTP was on November 13, 1989. Site work was delayed until early April 1990 while IT-Davy awaited the issuance of a partial Gloucester county soil conservation and erosion control permit. Initial site work included installation of the temporary construction facilities, installation of the site security fence and implementation of the site security and health and safety plans. The IT-Davy task

force moved on-site in mid-May 1990.

Major construction milestones achieved as of September 1990 include:

- Completion of temporary facilities (offices, decontamination pad, personnel decontamination facilities and truck weigh scales)
- Negotiation of a site agreement with major unions
- Completion of site clearing and grubbing
- Commitment of all major purchases
- Commitment of all major subcontracts
- Initial site compaction completed
- Slurry wall platform completed (west side of site)
- Extensive air monitoring program in place (approximately 1000 samples collected and more than 350 analyzed with all giving nondetect values)
- Approximately 50% of the targeted common fill (270,000 yd³) has been delivered on-site.
- Pretreatment facility foundations essentially complete

The project task force is at full strength; however, progress has been limited by problem areas discussed below. Under the current schedule, the project will be completed and ready for operation in January 1992.

PROBLEM AREAS

Until recently, problem areas have not been substantial and have been satisfactorily resolved. These problems have included delays in mobilizing on-site because of difficulties in obtaining the county soil conservation permit and the extended review time required in arranging for local emergency response. The soil conservation permit was received after causing an approximately 45 day delay in starting work in the pretreatment area on-site. Schedule impacts due to this delay are being addressed.

As part of the Emergency Response plan, local fire departments and health care providers were contacted to supply emergency service as required. These agencies initially responded negatively because of concerns over entering a Superfund site. After many meetings and discussions, the following was agreed upon and is being implemented. IT-Davy constructed clean roads on-site so that emergency vehicles and personnel would have minimum contact with hazardous materials when responding to an emergency. IT-Davy also agreed and is proceeding with site-specific hazards training for local emergency response personnel as well as supplying protective clothing to responding personnel.

Two major problems have surfaced recently which may impact significantly the cost and schedule for the remedial action. These are a change in the pretreatment water quality requirements and identification of differing site conditions for the placement of the roller compacted concrete (RCC) retaining wall.

In July 1990, IT-Davy was notified by the COE that the water quality requirement for the pretreatment facility had been made more stringent.

This change in discharge requirements will require additional water treatment facilities in order to produce the required quality. The air stripper capacity must be increased and a polishing aqueous carbon adsorption column must be added to the treatment process. The COE, their engineer (URS) and IT-Davy are currently investigating the cost and schedule impacts of this change in scope. Delay of completion of the pretreatment facility impacts the overall project schedule significantly.

The second major problem area is the discovery of differing site conditions where the roller compacted concrete (RCC) retaining wall will be placed. Soil tests and borings conducted by IT-Davy indicate that the base area for the RCC is saturated and has very low soil-bearing capacity. The test borings indicate that these conditions extend as much as 18 feet below the surface. The soil, as it exists, does not have sufficient soil-bearing capacity for placement of the RCC retaining wall. Investigations of these soil conditions are continuing and alternative concepts are being developed. The solution to this problem may also have significant impact on the overall project schedule as completion of the slurry wall and the multilayer cap follow the installation of the RCC.

CONCLUSIONS

All major contracts are in place, all site plans are approved and IT-Davy is proceeding with remedial action at the Helen Kramer site. When completed, the site improvements will effectively isolate the contaminants from the surrounding environment. Surface water and leachate will be treated to local POTW pretreatment standards prior to discharge to the local sewer system. Landfill gases will be collected and treated prior to being flared. Access to the site will be limited, thus minimizing the potential for humans to be exposed to site hazards. Approximately ten years after first being proposed for inclusion on the NPL, the remediation phase of the Superfund process will be complete.

Recently two problems have surfaced which may substantially impact the overall project schedule. These are a change in the water pretreatment requirements and differing site conditions along the east side of the site where the RCC retaining wall is to be placed. IT-Davy is currently proceeding to identify the magnitude of these impacts and assist the Corps of Engineers in investigating alternatives to minimize these impacts.

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After Design, Installation and Start-up, Groundwater Remediation Really Begins

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ABSTRACT

Discovery of contaminated compounds in municipal groundwater supplies has become a frequent headline. Implementation of effective treatment systems is crucial in order to remediate these contaminated aquifers. It is after completion of the regulatory requirements, including design, installation and startup, that the remediation really begins.

The best available technology (BAT) and state-of-the-art systems are rendered useless without a detailed approach for startup and facility operation and maintenance. Selection of the proper operator becomes the critical link between a well designed system and deliverable results. Interaction between the contract operator and design engineer strengthens the link and plays a major role in the system's success. Compliance with effluent discharge permits and avoidance of civil and/or criminal penalties which can result from permit violations are evidence of successful system operation.

This presentation will focus on these issues and will describe to administrators and managers of groundwater remediation systems the critical need for a planned strategy to operate and monitor compliance with the requirements of the remediation program. Supporting and documenting information will be presented from the perspective of the design engineer and contract operator who provided engineering, staffing and management services to a Fortune 500 company. Two facilities at remote sites were involved, where operations issues were complicated by the sale of the facilities (though the original owner remained responsible for environmental remediation).

INTRODUCTION

With increasing frequency, contaminated sites are being discovered. Subsequently, the principally responsible party (or parties) are being required to conduct a cleanup and other necessary remedial action.

In the case study discussed in this paper, a Fortune 500 company was involved with two facilities at remote sites. At the first site in eastern Ohio, the owner notified the U.S. Environmental Protection Agency and the appropriate state agency that soil containing residual concentrations of polychlorinated biphenyls (PCBs) and volatile organic compounds (VOCs) had been discovered at an inactive industrial site. VOC contamination, which presented significant potential for degradation of the municipal water supply, was also reported at the site.

At the second site in western New York, a program was initiated to update and consolidate underground storage facilities. The program involved testing selected underground tanks in accordance with the State Environmental Agency Petroleum Bulk Storage Program and the excavation and removal of several tanks. As a result of this consolidation work, O'Brien & Gere Engineers, Inc. was retained to conduct a Phase I hydrogeologic investigation. The investigation's objectives were to determine the presence of groundwater contaminants resulting from previous manufacturing and storage operations. The state agency reviewed and approved the investigation work, which identified free floating petroleum product and an isolated area of VOCs in the groundwater.

Actual system components will be described focusing on the state-of-the-art technology employed to meet defined effluent limitations; 1,400-gallon per minute (gpm) and 360-gpm treatment systems utilizing recovery wells, pumps, collection vaults, packed column air strippers, blowers, pipelines and electrical controls. Key tasks of the operator will be presented and explained including routine inspections, leachate monitoring of the secure cell, preventative maintenance, emergency repairs, sample and data collection protocol, and record-keeping. Additionally, advantages of effective interface between the owner/client and engineer and system operator will be discussed, supported by actual project experience.

O'Brien & Gere Engineers, Inc., (Syracuse, New York) was retained by the owner to perform remedial investigations, feasibility studies and preliminary and final designs and to provide construction-phase services at both sites.

The program involved coordinated efforts of several companies:

- O'Brien & Gere Engineers, Inc. - study, design and construction phase services
- OBG Laboratories, Inc. - analytical services related to site investigation and construction activities
- OBG Technical Services, Inc. - construction management services including the operation of a mobile treatment system for supernatant removal from the holding pond
- OBG Operations, Inc. startup services and full operation and maintenances services for the groundwater remediation facilities. Services include grounds care, leachate monitoring of the secure cell and mechanical and electrical maintenance of the groundwater treatment system.

The coordination within the family of firms effected a smooth transition from one work function to the next and maximized critical communication links. The net effect resulted in a turn-key approach which created "one-stop shopping" for the owner.

PROGRAM OBJECTIVES

At the eastern Ohio site, the owner's goal was to identify and control the environmental and health impacts associated with the hazardous waste contaminated site. Responding directly to owner/client-identified needs, the remediation program had five objectives:

- Prevent potential degradation of municipal potable water supply
- Secure PCB contaminated materials
- Recover/treat ground water to surface water discharge standards

- Maintain positive community relations
- Keep costs within budget

At the western New York site, the owners objectives were:

- Minimize the migration of free floating petroleum product and VOCs toward the river
- Operate the system as efficiently as possible and to maximize free product recovery and VOC removals

The importance of a well-operated and maintained system at both locations was especially critical due to the nature of the groundwater contamination. Proper operating procedures were required to prevent violation of the National Pollutant Discharge Elimination System (NPDES) permit that was granted for each system: groundwater discharge is not to exceed the concentrations as defined in the discharge permit.

EASTERN OHIO FACILITY

Facility Components

The purpose of the individual system components is to function as a single unit to prevent future migration of contaminants by collecting, transporting and treating the contaminated groundwater. The major components of the remediation system include a secure cell for containment of on-site materials containing PCBs, secure cell leachate collection and monitoring equipment, recovery wells, pumps, vaults, collection vault, air stripper, blower, pipelines and electrical controls.

Secure Cell

An on-site secure cell was designed and constructed to contain the soil and waste containing PCBs. With a final design volume of 20,000 cubic feet, the secure cell employed a 3-foot thick impermeable base of compacted clay and high density polyethylene (HDPE) liner. A 2-foot thick layer of compacted clay and a HDPE liner were also employed for a top cap.

The secure cell design (Figure 1) also included a drainage system

for leachate collection and monitoring components. The design incorporated a system of collection layers and piping discharging to a holding tank. Components of the leachate system outside the cell included an underground tank with secondary containment and state-of-the-art monitors and alarms. The early warning nature of this detection system represents a unique application of vacuum lysimeters coupled with groundwater monitoring wells.

Groundwater Treatment Facilities

Based on groundwater modeling of the contamination plume, eight recovery wells were installed both on and off the plant site. Recovered groundwater is pumped to a central collection vault for treatment in a packed column air stripper. The recovery wells range in capacity from 50 to 200 gallons per minute, and the air stripper is capable of treating approximately 1,500 gpm (2 mgd) of recovered groundwater. The packed column stripper is furnished air through the use of two 6,000 cfm blowers. The system's goal is to discharge an effluent with a concentration of 12 ppb VOCs or less. Current operating data indicates that the stripper is effectively removing in excess of 95% of the VOCs identified as the principal groundwater contaminants. Figure 2 presents a schematic of the system components.

Recovery Wells, Pumps and Vaults

The groundwater recovery wells consist of a steel casing and slotted screen section installed at a predetermined depth in the aquifer. All recovery wells contain submersible pumps discharging the contaminated groundwater via pipelines to the treatment system. The submersible pumps in each recovery well were selected to deliver a flowrate greater than the required design flow.

By adjusting the butterfly valve located in the vault, the flow from each recovery well can be adjusted to fine tune the system. Flow sensors are located in the vaults to help regulate the flow from each recovery well. A sample tap has been provided in the vault to collect groundwater samples and evaluate the contaminants at each well location (Figure 3).
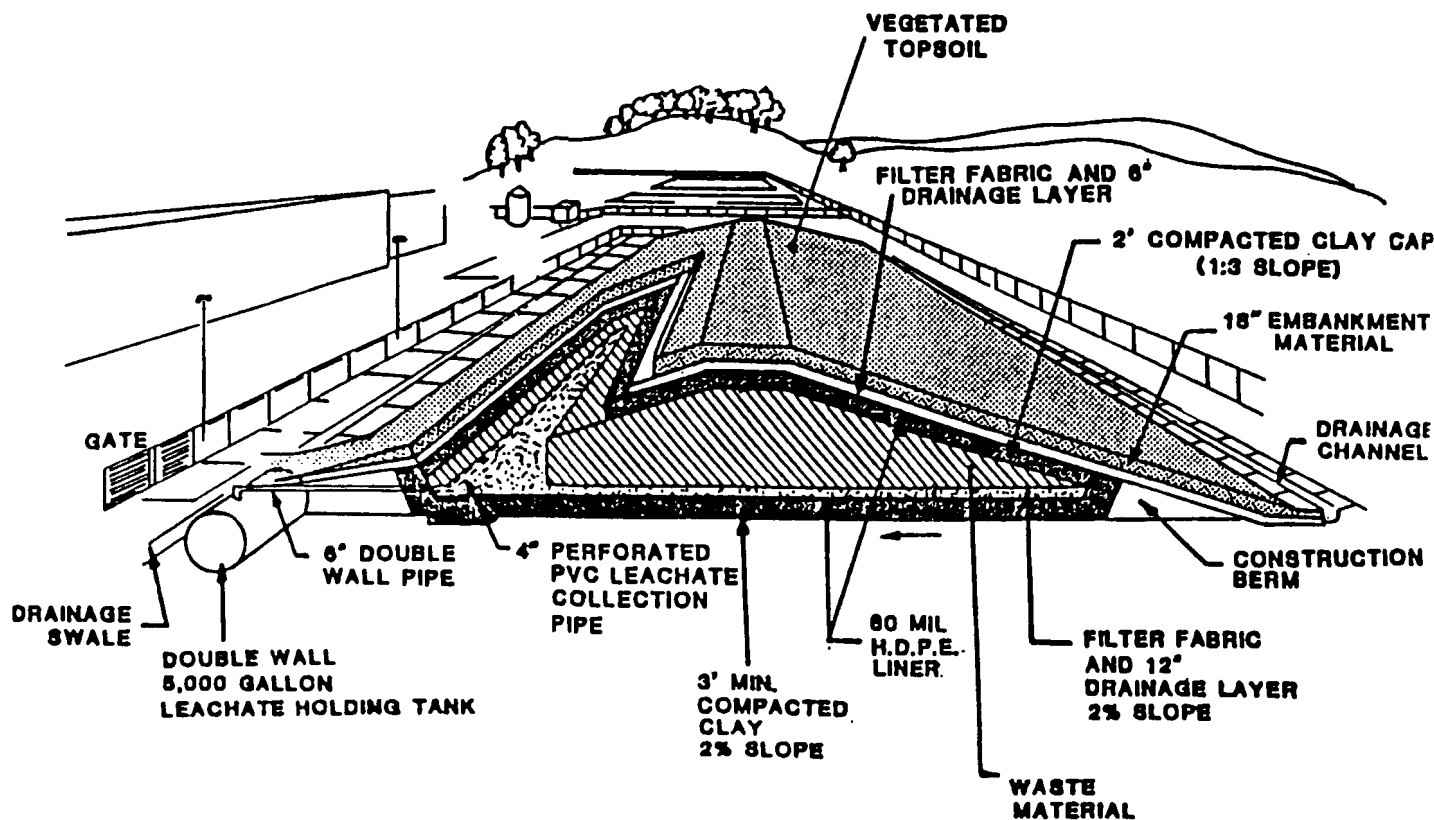
Figure 1
Typical Design of Secure Cell Liner System
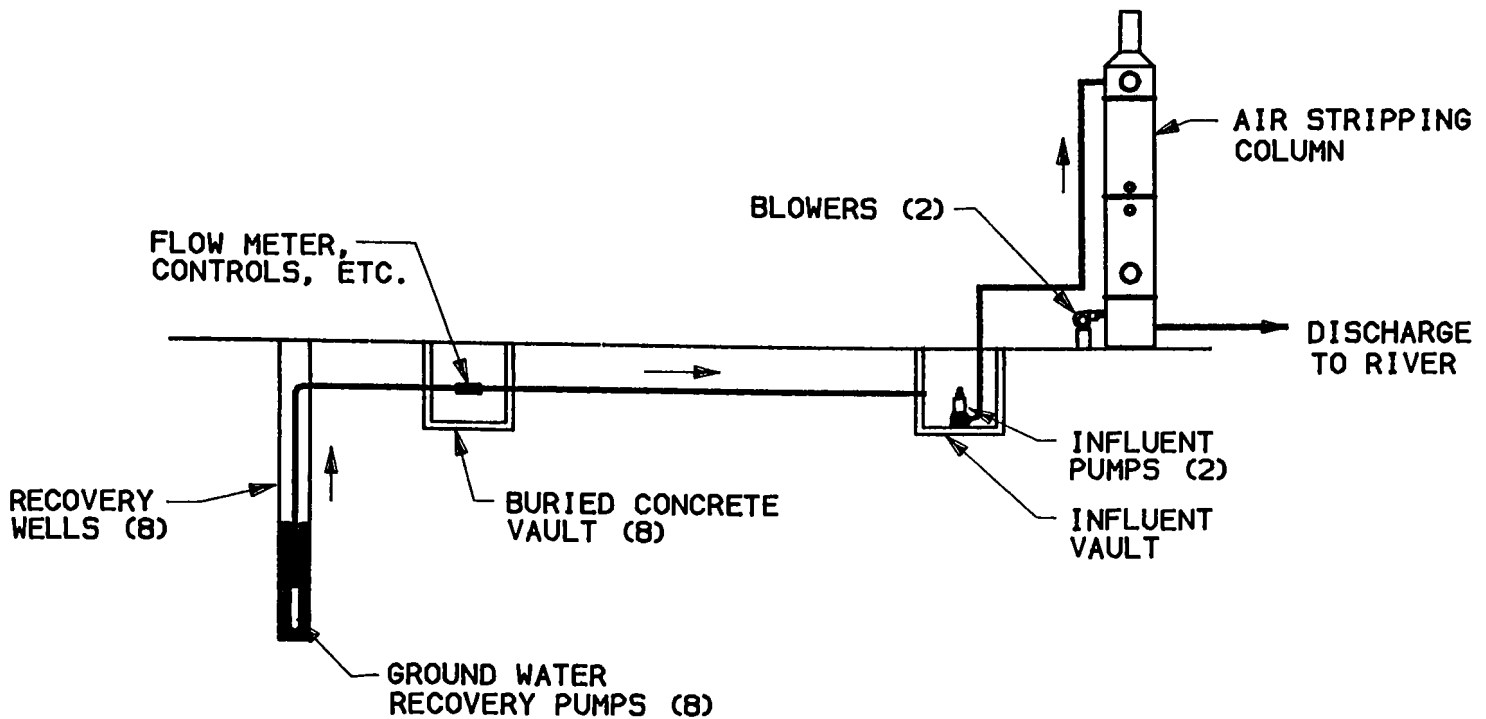
Figure 2
Eastern Ohio Facility
Treatment System Schematic
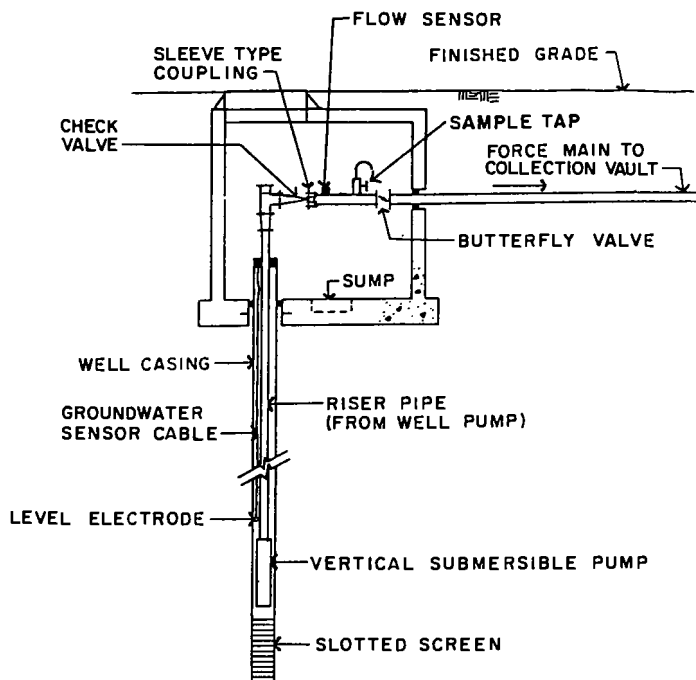
Figure 3
Typical Recovery Well, Pump and Vault

The collection vault receives contaminated groundwater from the various recovery wells and acts as an equalization basin for the air stripper. Equalization provides a steady flow of groundwater to the air stripper while minimizing the cycling of the submersible pumps. Two submersible pumps located in the collection vault have sufficient capacity to individually deliver the total system's flow in the event of one pump's failure.

Packed Column Air Stripper

The air stripper provides the mechanism for VOC removal from the contaminated groundwater. Pumps located within the collection vault discharge the contaminated groundwater to the top of the stripper. Contaminated groundwater travels downward over packing material, while countercurrent air from the blowers is forced upward through the packing material. This action strips VOCs from the contaminated groundwater.

A flowmeter and recorder on the influent line of the air stripper monitor and record the flow from the collection vault. Sample taps were installed on the influent and effluent line of the air stripper (Figure 4).

At the base of the air stripper, two blowers deliver air to the air stripper. Each blower has the capacity to deliver the total required air supply and, therefore, can act as a backup unit if one blower fails.

Pipelines and Electrical Controls

Pipelines, ranging in size from 4 to 12 inches, were installed to convey groundwater to and from system components. Recovery well locations required the installation of cased pipelines under city streets, streams and railroads.

Electrical controls play a major role in the startup and operation of the remediation system. Various controls provide automatic backup of certain equipment and shutdown the system in the event of equipment failure. High-level alarms in the collection vault and air stripper and air flow loss indicators automatically shut off all the recovery well pumps. An automatic dialer alerts the facility operator whenever there is a problem at the facility.

WESTERN NEW YORK FACILITY

Based upon the results of the field investigations, a semipassive groundwater recovery trench system was designed to intercept free floating product migrating radially towards the river. In addition to the recovery trench, a groundwater recovery well was designed to collect and treat an isolated area containing VOCs. A recovery trench, three pump stations, recovery well, oil/water separator and packed column air stripper were installed. Figure 5 presents a schematic of the system components.
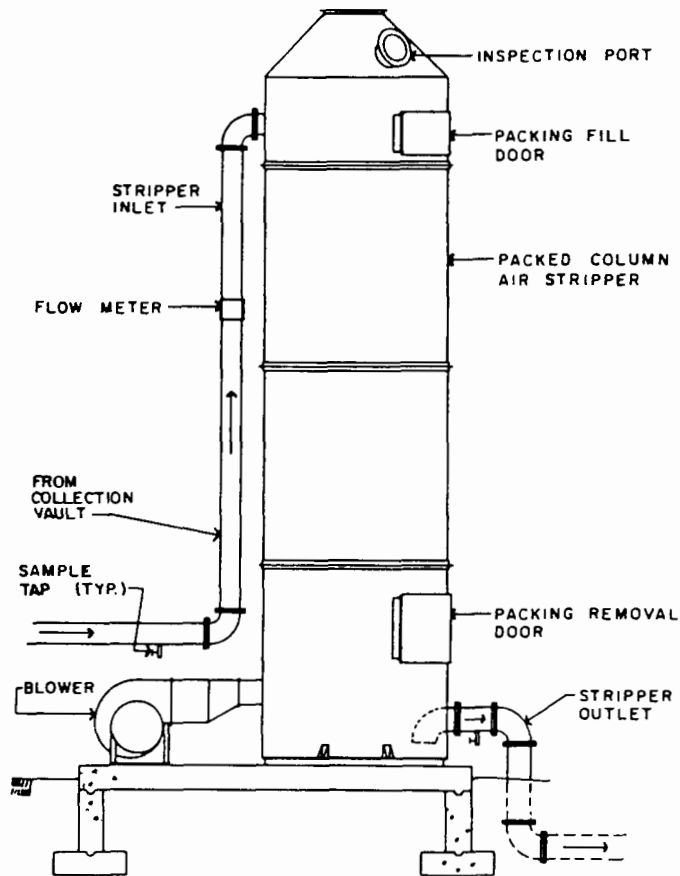
Figure 4
Typical Air Stripper and Blower

Recovery Trench

The recovery trench, located between the source and the river, intercepts groundwater contaminated with petroleum products and VOCs. The groundwater enters a perforated pipe within the trench and travels by gravity to the pump stations. Physical separation and accumulation of free floating product occur within the stations.

Level floats are located within the pump stations for on/off control of the pumps. Groundwater that accumulates in the pump stations is pumped through force mains to the oil/water separator for the removal of oil and grease residuals. Petroleum product is periodically removed from the three pump stations and oil/water separator by a local oil reclamation contractor via a vacuum tank. Once removed, the product is transported to a local plant for fuel blending/reclamation purposes.

Recovery Well Pump and Piping

Similar to the Eastern Ohio groundwater system, this facility has one recovery well for the removal of groundwater contaminated with VOCs. The recovery well has a submersible pump that discharges groundwater to the oil/water separator through force main piping. A level transducer within the well allows for the on/off control of the pump.

Oil/Water Separator

Groundwater from the three pump stations and recovery well enters a 4,000 gallon oil/water separator tank for the final removal of oil and grease constituents prior to being pumped to the packed column air stripper. The oil/water separator utilizes coalescer plates and polypropylene filter media to enhance the removal of the petroleum constituents from the groundwater. Groundwater travels by gravity through the separator to a pump-out compartment. A pump located within the pump-out compartment transfers the groundwater to the packed column air stripper for VOC removal.

Packed Column Air Stripper

Similar to the Eastern Ohio groundwater treatment system, this facility utilizes a packed column air stripper for the removal of VOCs from the groundwater. Upon entering the air stripper, groundwater travels
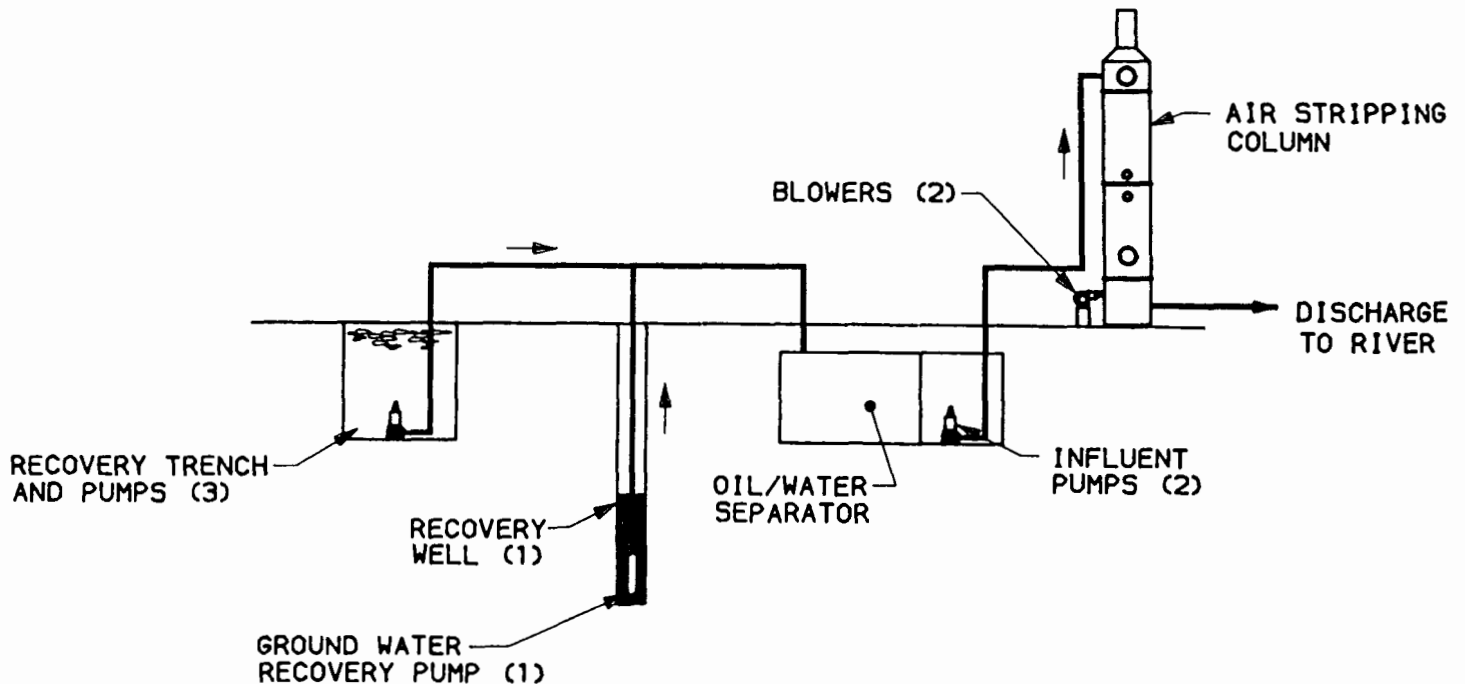
Figure 5
Western New York facility
Treatment System Schematic

by gravity over the packing material while countercurrent air from the blower travels upward through the packing, stripping VOCs. Treated water is discharged by gravity to the river.

OWNER CONSIDERATIONS

Numerous remediation sites across the country are now under design and construction with additional sites that have been identified for future study. Owners of these hazardous sites must be prepared to develop and implement efficient means of remedial operation in order to obtain efficient, reliable and long-term operational results. After design and installation is complete, the owner must proceed with long-term operation and maintenance of the facilities and must remain in compliance with effluent discharge permits. A possible result of inadequate facilities management may result in violations of effluent discharge permits which can lead to significant civil and/or criminal penalties. With the client facing prospects of long-term maintenance commitments (in many cases up to 30 years) a planned management strategy must be implemented. This approach should include routine inspection and maintenance of the facilities with periodic sample collection and analysis.

The owner is responsible for site security including fencing, security gates and signs, routine inspection, and maintenance, service and replacement of system components. Grounds maintenance includes the vegetation cover as well as weed and erosion controls. In the case of the secure cell, leachate collection, treatment and disposal are required in addition to groundwater monitoring conducted by a certified laboratory.

In the instance where groundwater is required to be treated to protect the environment and public health, the owner is required to operate and maintain the treatment system. This requirement may include stripping volatile compounds from the groundwater through the use of air or steam. Inorganic compounds are often precipitated from the groundwater matrix. For both organic and inorganic compounds, ion exchange, under certain conditions, is a workable treatment technique. Therefore, the owner must analyze the available alternatives and understand the potential complexity of each system as well as the effects of operation and maintenance.

The owner, now faced with a long-term maintenance program for the remediation system, must decide how to implement this program.

There are several considerations:

- How will the system be managed and operated; through corporate management or by private contract services?
- Does the system require full-time or part-time service?

Issues can be complicated by remote site locations and by transfer of facility ownership. In the cases described here, the original owner remained responsible for the environmental remediation. The owner of these facilities clearly had two choices:

- The owner can maintain management responsibility and provide operations for the facilities
- The owner can contract management and operations services.

In either case, the owner is clearly responsible for the financial obligations to remediate and to comply with the discharge permit.

The following information will present operator tasks as well as the necessary management tasks to implement a successful program.

OPERATOR RESPONSIBILITY

Required skills of the groundwater remediation system operator vary with the level of the system's complexity. However, the common requirement is to be mechanically-inclined, with an understanding of pumps and electrical control systems. Generally, operators must be self-motivated, capable of performing their job assignments without direct management on a day-to-day basis. Typically these facilities are not large enough to warrant direct supervision on a day-to-day basis; however, management is provided on a broad supervision level.

To properly operate the groundwater remediation systems, the operators at each location must be familiar with the following:

- Operation of all system components
- All maintenance requirements
- Local, state and federal laws which govern the operation of the system (including spill notification requirements)
- Safety precautions for system operation (including satisfactory completion of Health and Safety Hazardous Waste Operations course)
- Record-keeping, reporting and filing maintenance requirements

To execute the operation and maintenance services at the facility without direct supervision, management must provide additional means

DATE	TIME	ETM RUN TIME (HOURS)											TOTAL SYSTEM FLOW (GAL)	SYSTEM FLOW * RATE (GPM)	COMMENTS
		INFLUENT PUMP 1	INFLUENT PUMP 2	BLOWER NO. 1	BLOWER NO. 2	REC. WELL NO. 1	REC. WELL NO. 2	REC. WELL NO. 3	REC. WELL NO. 4	REC. WELL NO. 5	REC. WELL NO. 6	REC. WELL NO. 7			

* Measured at the Air Stripper Influent

Figure 6
Groundwater Remediation System
Daily Operating Log Sheet A

DATE	RECOVERY WELL 1				RECOVERY WELL 2				COMMENTS
	FLOW (GPM)	PRESSURE (PSIG) (1)	WATER LEVEL (FT) (2)	OILY PRODUCT (GALLONS)	FLOW (GPM)	PRESSURE (PSIG) (1)	WATER LEVEL (FT) (2)	OILY PRODUCT (GALLONS)	

(1) Recorded twice per month.
(2) Digital readout of water level above transducer.

Figure 7
Groundwater Remediation System
Daily Operating Log Sheet B

of project control. Record-keeping can take the form of bi-weekly or monthly reports of system operation. Routine inspection logs are created for management review and also serve as reinforcement for inspection of critical system components. Figures 6 and 7 are provided as typical log sheets used to develop the monitoring reports. These reports are also critical for effective presentation of data to regulatory agencies regarding the operations of the facilities.

Operation and maintenance activities related to the groundwater remediation systems include caring for the grounds; monitoring system components; coordinating activities with certified analytical firms; and special service activities such as leachate removal and disposal, oil reclamation, electrical and maintenance specialty services.

Routine inspection programs determine if the remediation system is operating at peak efficiency or is in need of maintenance. The major components of these programs are the log sheet forms which are com-

pleted by the facility operator addressing several tasks at the groundwater remediation facilities and secure cell (Tables 1 and 2).

At the facility located in eastern Ohio, a facility operator was provided on a full-time basis. The operator mans the facilities 8 hours per day, 5 days per week, with emergency calling capabilities during off hours and weekends. At this particular facility, the facility operator performs all electrical and mechanical maintenance activities; however, for reasons of safety and the need of additional manpower to perform certain tasks, the contract operator has arrangements with two individuals who are available to support the facilities operator and serve as the backup during vacation and other periods of absence. In addi-

Table 1
Groundwater Remediation Typical Operator tasks

1.	Inspect all indicator run-lights (daily).
2.	Record individual pump operating hours (daily).
3.	Record individual pump flow readings (daily).
4.	Check recovery well vaults for accumulation of water (daily).
5.	Check operation of all butterfly valves (weekly).
6.	Inspect blower belts (weekly).
7.	Inspect air-stripper nozzles and packing (weekly).
8.	Acid cleaning of stripper media (as required).
9	Lubricate equipment as recommended by the operation and maintenance manual (As required).

Table 2
Operator Duties at the Secure Cell

1.	Observe condition of cap and vegetative cover (no trees, shrubs, brush or deep rooting weeds should be allowed).
2.	Observe for signs of erosion, insect damage or thinning of vegetative cover.
3.	Maintain 3 to 4-inch grass height (taller grass can inhibit erosion and increase evapo-transpiration).
4.	Maintain access roads to support maintenance activities as required.
5.	Maintain fencing, gates and signs as a part of security.
6.	Inspect leachate collection system.
7.	Inspect floats and controls, operate periodically to insure their ability to function.
8.	Inspect and maintain protective casings and groundwater monitoring wells.
9.	Calibrate flow measurement devices.

tion to routine maintenance activities, the facility operator is often called on to make facility upgrades and/or modifications and perform corrective maintenance activities. In situations where activities are beyond the operator's capabilities and those of the support staff, the facility operator (through communication with the client/owner) is responsible for contacting and monitoring activities of outside subcontractors who are used to facilitate major repairs and/or capital improvements.

At the second site described herein, a part-time operator was provided for approximately 10 hours per week. The operator performs routine inspections, sample collections and determines system-wide groundwater levels. All electrical, mechanical and oil reclamation activities are coordinated by the contract operator with outside subcontractors on behalf of the owner.

OPERATING PROBLEMS

Groundwater treatment facilities have not been without difficulties during startup and initial phases of operation. The eastern Ohio facility has effectively met the discharge compliance standards; however, there was a period when permit limitations were exceeded.

Some of the problems were minor in nature and were corrected as described in Table 3. On the other hand, resolution of a major problem involved a very interesting step-by-step approach. The corrective measures demonstrate a capability to work with facility equipment, provide for necessary care and maintain compliance with the discharge permit.

Table 3
Difficulties Encountered and Measures Taken to Resolve Them

PROBLEM	RESOLUTIONS
Flow meter losing signal	Soldered bad connection of control board
Stripper channeling (i.e. water by passing air flow/media by short circuiting down side walls)	Installed deflector plates in top portion of stripper
Stripper cleaning pump corroded by HCl acid cleaning resolution	Replaced cast iron and stainless steel pump with PVC unit
Control panels of recovery wells #4,#5,#6 and #7 damaged due to flooding caused by excessive rainfall	Relocated control panels above grade on top of vault
LED level indicators in wells shorting out due to condensation	Placed LEDs in watertight NEMA 4X enclosures; installed dehumidifiers
Wells #5-#8 and blowers tripping out due to excessive temperatures	Air conditioner installed in control room
Controller automatically switches into manual mode	Reprogrammed controller and installed uninterruptable power supply on 110 volt system
Water leaking into wells #3 and #8	Raised well vault castings above grade
Overflow of collection vault when stripper pumps out of service	Installed automatic shutdown for all recovery wells
Motor to recovery well #4 burned out due to lighting and power surge	Installed surge protection and lighting arresters on all eight wells
Secure cell holding tank overflow alarm actuating with weather changes	Installed aluminum rain cap on top of casting
Level indicator probes in recovery wells shorting out	Replaced probes (damaged due to power surges)
Pump in well #6 clogging up and losing capacity (problematic well)	Pull and clean pump on a regularly scheduled basis
Safety hazards involving portable stripper climbing ladder and pulling of inspection window	Installed catwalk with permanent ladder and mansaver cage
Secure cell holding tank vacuum alarm actuating with weather changes	Reduced vacuum in holding tank walls
Chart recorder losing signal	Soldered function card diode
Manhole lids on recovery wells too heavy to remove manually	Installed sockets on each well and purchased portable crane to remove manhole lids

There was a period when the effluent standards were not being met on a consistent basis. Just prior to this period, a decrease in stripper effectiveness and efficiency was noticed. In efforts to remedy the situation, the stripper medium was cleaned using approximately 300 gallons of dilute hydrochloric acid. However, after experiencing an initial and brief recovery period, the stripper again started to discharge effluent in violation of the discharge permit allowable limit of 12 ppb of VOCs.

The facilities operator then initiated the removal and high-pressure washing of the medium after it had become evident that the acid cleaning was no longer completely effective in removing the iron and magnesium

buildup. Following reinstallation of the clean medium, the problems persisted and the stripper continued to exceed the permit limitations. The next course of action involved a three-phase process:

- Inspect spray nozzles; no adjustments were required.
- Inspect stripper for short circuiting of recovered groundwater down the stripper walls; this was not occurring.
- Evaluate the capacity of the blowers; both blowers tested in excess of name-plate capacity.

After these steps, the stripper manufacturer was contacted and all performance data were forwarded to the manufacturer. During their review process, two steps were taken to bring the facility into compliance:

- Both blowers were used in an effort to increase VOC removals.
- Flow from the well with the highest concentration of pollutants (by a factor of 10 or more) was cut back from 200 gpm to 100 gpm.

These measures proved to be temporarily effective; however, the system was not designed to operate without a backup blower or by decreasing the flow at the recovery well to reduce the concentration of contaminants in the groundwater. The manufacturer was committed to effecting the highest level of system treatment and, after analysis of the performance data, made two recommendations:

- Replace spray nozzles to effect a different spray pattern
- Replace the top seven feet of medium with a different type of medium

These recommendations were implemented but proved to be ineffective. It was finally decided, following a review meeting between the owner, engineer and manufacturer, that the height of the air stripper would have to be increased.

The stripper manufacturer installed an additional 10-foot section to the air stripper that effectively met permit compliance with all wells pumping at full capacity and one blower operating.

This effort demonstrates a methodical comprehensive approach to solving problems. By carefully analyzing and evaluating each operational unit, this step-by-step approach addressed and corrected difficulties. The same approach was used to correct the difficulties presented in Table 3.

PREVENTATIVE MAINTENANCE

The development of a preventative maintenance program is key to the success of the operation of the groundwater remediation system. Although redundancy has been designed into the system, the facility operator must take into consideration Murphy's Law. Therefore a systematic schedule has been developed at each facility which provides for a program of preventative maintenance on each component. The maintenance is conducted as recommended by the manufacturer's operation and maintenance manual for the equipment. A critical component of the program is an inventory at the facilities, keeping spare parts available such as floats, drive belts and recovery well pumps. For example, the replacement of the air-stripper blower drive belt is easily accomplished at 2:00 p.m. as opposed to having to replace the drive belt at 2:00 a.m. under adverse conditions.

EMERGENCY REPAIRS

It is axiomatic that emergencies will occur. However, the number and impact of these emergencies can be minimized with proper planning and with preventative maintenance. At the two sites discussed above, a plan has been developed evaluating critical components of systems. The contract operator has also recommended to the owner that critical spare parts be made available in the inventory at the facilities. In addition, emergency contractors, telephone lists and contact persons have been identified in the event that an emergency occurs. Emergency repairs are coordinated through communications between the owner and contract operator to facilitate repairs in the most practical fashion.

SAMPLE COLLECTION

In accordance with the NPDES permit, a sampling and analysis plan has been developed. This plan defines the sampling program from the groundwater remediation system to collect and analyze effluent discharge

in accordance with the discharge permit.

Monitoring data must be reported to the state regulatory agency on a monthly basis, and records must be maintained on file by the operator and owner. It is the responsibility of the operator to coordinate the collection and transmission of the samples from the remediation system effluent and also the complete chain-of-custody records to the laboratory. The certified laboratory performs the analysis and submits the data to the owner and to the contracted engineer. The engineering company monitors compliance of the sampling schedule and completes the necessary monthly reports on behalf of the owner.

Several sampling ports have been provided as part of the groundwater remediation system. These sampling ports are located at the discharge of the force main of the recovery wells and pump stations and at the influent and effluent of the air-stripper.

Sampling and analysis required by the NPDES permit are in accordance with the sampling and analysis plan established for each facility (Table 4). Samples are collected by a local certified laboratory at the eastern Ohio facility, and the data are distributed to the owner and to the contracted engineer for monitoring compliance schedules as well to complete the discharge monitoring reports. At the western New York facility, the operator has been trained to collect and transmit the necessary samples from the air stripper effluent to a certified laboratory. These samples are then analyzed for VOCs, oil and grease, ph and total iron.

Table 4
Sampling, Analytical and Water Level Data Collection

SITE 1 (Eastern Ohio)

TREATMENT SYSTEM EFFLUENT — FREQUENCY

Flow	Continuous
Volatile Organic Compounds (VOCs)	Monthly
pH	Monthly

MONITORING WELLS (9)

| VOCs | Every 3 Months |

WATER LEVEL ELEVATIONS

| Monitoring Wells (9) | Every 3 Months· |
| River Locations (3) | Every 3 Months |

SITE 2 (Western New York)

TREATMENT SYSTEM EFFLUENT — FREQUENCY

Flow	Continuous
Volatile Organic Compounds (VOCs)	Twice/Month
Iron	Twice/Month
Oil & Grease	Twice/Month
pH	Twice/Month

WATER LEVEL ELEVATIONS — FREQUENCY

| Monitoring Wells (16) | Monthly |

As mandated by the discharge permit, the facility operator, who plays a critical role in the monitoring and data collection functions, collects at least four unfiltered grab samples over the course of a 24-hour period. Samples are composited in the laboratory under control conditions to minimize volatilization of the sample prior to analysis. It is also the responsibility of the operator to obtain and transmit the samples in accordance with approved methods (including chain-of-custody).

It is management's responsibility to adequately train and to instill in the facility operator the significance and importance of this sampling process. To support this effort, a sampling and analysis plan was developed for the two sites, clearly indicating the locations of sampling, the parameters to be analyzed and the sample frequency. This plan has been issued to the facility operator and is posted at the facility.

REPORTS AND RECORD KEEPING

Depending on the size of the facility and complexity of the components used at the groundwater remediation facility, the operator will be required to complete operating log forms ranging from daily operating logs to monthly operating logs. Copies of the operating logs are retained at the facility to be utilized by the facility operator as well as to be accessible during regulatory agency inspections. In addition, copies are transmitted to the owner for the development of the monthly discharge monitoring reports.

It is the responsibility of the facility operator to collect the appropriate data throughout the month to allow the contracted engineer to prepare and submit, on behalf of the owner, the monthly discharge monitoring reports to the regulatory agencies. To accomplish this task, the facility operator must be familiar with the requirements of the discharge permit and record the information on the appropriate operating log.

Weekly, bi-weekly and monthly operating logs facilitate this function. These logs indicate such data as the date, total gallons discharged, the current flow rate through the system and the status of system components (such as recovery wells, pump stations and air strippers). Operating log forms (Figures 6 and 7) are developed specifically for each facility; however, there are several key items that are common to all systems:

- Identification of the facility
- The date of entry
- Totalizer reading in gallons
- Elapsed time meter readings for appropriate equipment (such as blowers and pumps)

This information is not only critical to the monthly monitoring reports, but also is equally important for the preventative maintenance program. For example, hours elapsed on operating equipment is utilized in the scheduling of preventative maintenance of critical components of the groundwater remediation facility.

In addition to the reports and record-keeping, an operating plan of procedures should be developed by the management team. This operating plan clearly develops an understanding of the interrelationship between the owner, the operator and the engineer, i.e., the management team. The plan also includes normal team operating procedures as well as emergency procedures. This communication link between the owner, engineers and system operator is vital to the success of the project, ultimately measured by the facility's ability to remain in compliance with the discharge permit.

CONCLUSION

Success of the remediation systems is a result of the operator's ability to operate and maintain the system. The facility must also be adequately designed and constructed. Another factor is selection of an engineer experienced in groundwater remediation investigations, feasibility studies, design and construction phase services.

The construction and installation capabilities of the contractor are vital to the ultimate reliability of the system. Therefore, careful consideration must also be taken into account during the selection process of a contractor to perform the construction services.

The true measurement of the system is its long-term operation. The owner must decide whether to provide the facility operator or select a facility operations contracting firm. In either case, the facility operator and the management necessary to overview the facility should possess skills and abilities proportionate to the complexity of the system.

The owner is also responsible for the adequate funding of the project to properly operate and maintain the facility. Funding encompasses items such as operation services including management and facility operators (either internal or external services); power; tools; supplies; spare parts; analytical services; and engineering services.

The owners, administrators and managers of remediation systems must be prepared to develop and implement sufficient means to obtain efficient, reliable and long-term system operation.

Remedial Design Considerations at the Sikes Superfund Site

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ABSTRACT

The Sikes Disposal Pits site was one of the first hazardous waste sites listed on the NPL. The Sikes site is located along the banks of the San Jacinto River, approximately 20 miles northeast of Houston, Texas. It was operated as an open dump in the 1960s and received drummed and bulk wastes from many of the area's petrochemical industries.

In 1982, the Texas Water Commission (formerly named the Texas Department of Water Resources) selected Lockwood Andrews & Newnam, Inc. as the prime contractor to conduct a Remedial Investigation at the site. Later contracts extended these services to include a Feasibility Study, Remedial Design and Construction Management.

The selected remedy on the Sikes site was for on-site incineration of approximately 300,000 tons of sludges, waste and contaminated soil. The shear magnitude of the site makes it the largest on-site incineration project attempted in the Superfund program. Remediation of the site is expected to take 5-6 years at a cost of approximately $90,000,000.

This paper will discuss the Remedial Design process used on the Sikes site, the major design issues that were identified and how they were addressed in the development of the plan and specifications.

The Remedial Design process involved conducting a major site sampling program designed to establish the specific physical and chemical characteristics of the wastes and soils required by the incineration contractors. This analytical phase was followed by developing a conceptual design and writing detailed specifications for cleanup.

Many difficult issues had to be addressed in the Remedial Design. These included:

- The entire site is 10-20 feet below the 100 year flood elevation
- Tree and stump removal is required in both contaminated and uncontaminated areas
- Trash and debris in contaminated pits ranges from toys to furniture to appliances
- Thousands of rusting drums and hundreds of tires will have to be incinerated
- Excavations will be up to 20 feet below the water table

INTRODUCTION

The Sikes Disposal Pits Superfund Site is a 185 acre tract of land approximately 20 miles northeast of Houston, Texas (Fig. 1). The site is within the flood plain of the San Jacinto River in an area that has many active and abandoned sandpits. In fact, the entire site is within the 10 year flood plain of the river with the highest portion of the site being 10 feet below the 100 year flood plain.

The Sikes site operated as an active waste dump from the early 1960s until it was closed in 1967. During this period, a variety of chemical wastes from area petrochemical industries were dumped in several abandoned sandpits. In addition, approximately 1500 drums of waste were stacked and scattered across the site.

A site map is shown in Figure 2. The site is bounded on the west by the San Jacinto River, the north by the Southern Pacific Railroad, the east by low swampy land and the south by US Highway 90. The primary features on-site are the Small Waste Pits, Tank Lake, the Main Waste Pit and the Overflow Area.
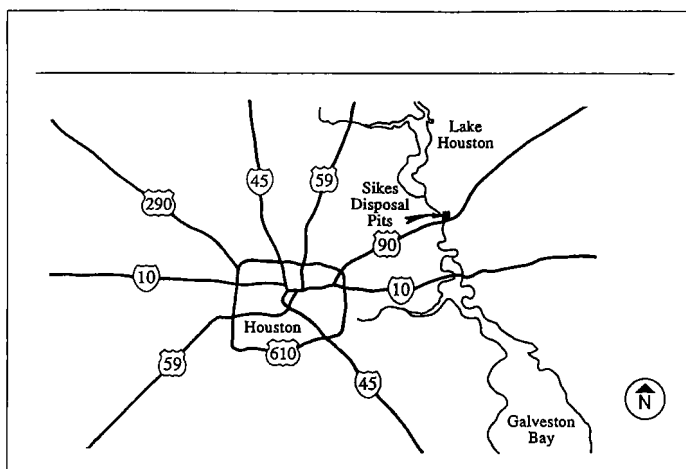
Figure 1
Site Location Map

PREVIOUS STUDIES

The Sikes site was placed on the NPL in 1982. In January 1983, the Texas Water Commission (TWC) contracted with Lockwood andrews & Newnam, Inc. (LAN) to perform a Remedial Investigation on the site. LAN has continued as the prime consultant on the site through the Remedial Investigation, Feasibility Study, Remedial Design and Remedial Action phases.

The RI found high concentrations of volatile and semivolatile organics in the sludges and underlying soils throughout the site. High concentrations of heavy metals also were found in selected areas. Several of the pits also contained contaminated surface waters.

Alluvial sand deposits underlie the entire site. The shallow aquifer (20-30 ft deep) is contaminated with the same volatile and semivolatile organic compounds found in the wastes on the site. A second aquifer lies below the first and is separated from it by approximately 65 feet of highly plastic clays. This deeper aquifer showed only trace concentrations of a few of the volatile organics.
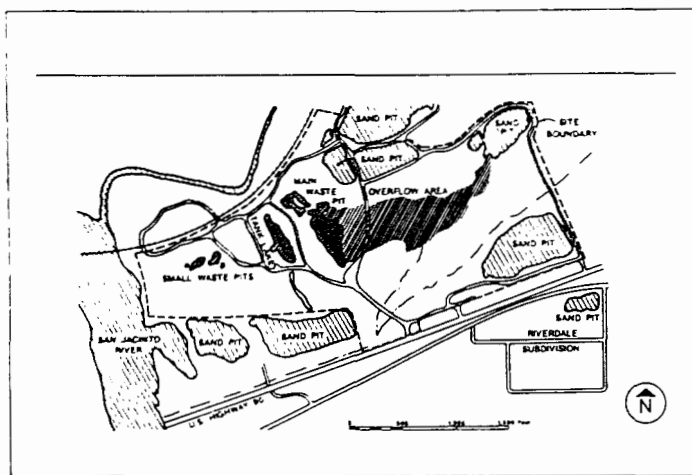
Figure 2
Site Map

Objectives and criteria were developed in the Feasibility Study in accordance with U.S. EPA criteria. Thirteen initial alternatives were developed, and this group was later screened to six for detailed evaluation and consideration in development of the ROD. The ROD, signed by U.S. EPA in September 1986, specified on-site incineration of the wastes and contaminated soils. A cleanup level of 10 mg/kg of any VOC and 100 mg/kg of total PAHs were established as the cleanup criteria. Groundwater modeling indicated that by removing the waste and contaminated soil to the 10 mg/kg level, the groundwater would naturally clean itself to the 10^{-4} Human Health Criterion within a 30 year period. Based on this determination, source control was judged to be the only remediation required.

Another important criterion is that no waste may leave the site and, equally important, no other waste may be brought onto the site.

DESIGN PROCESS

Once the remedy was selected, the TWC and LAN proceeded into the Remedial Design phase. The first task was to review the data collected during the RI/FS process to determine if sufficient data were available to design the on-site incineration remedy.

The RI process was designed to: (1) gather data to characterize the site and assess its risk to the population and environment; and (2) developed and evaluated alternatives in the Feasibility Study. It was not the intent of the RI, however, to develop detailed design data for each alternative that might be considered. Therefore, it was determined that more incineration) specific data would be required to adequately design the incinerators to be used during the remediation. The specific data needed included:

- Density
- Moisture
- BTU
- % Ash
- Viscosity
- Melting Point
- Flash Point
- Reactive Cyanide
- Reactive Sulfide
- Corrosivity
- pH
- TOX
- % Carbon
- % Hydrogen
- % Nitrogen
- % Sulfur
- % Phosphorus
- % Total Chlorine
- Sodium
- Potassium
- Grain Size Analysis

The original RI estimated that the site contained approximately 68,510 cubic yards of wastes and 81,300 cubic yards of contaminated soils for a total volume of 149,810 cubic yards of material to be incinerated. Experience with other remediation projects indicates that final remediation quantities are usually much higher than those identified in the RI. Since this is such a large site, with contamination spread over 33 acres, it was decided that a prime objective of the Remedial Design Sampling Program would be to better quantify the volume of material to be incinerated.

Two hundred twenty-seven locations across the site were investigated to quantify and/or characterize the wastes and underlying soils. The majority of the locations were investigated using a hollow stem auger with either a Shelby Tube or Split Spoon Sampler. A back-hoe was used in some locations, particularly when investigating areas suspected of containing buried drums. Hand sampling with an auger or post hole digger was accomplished in a few areas.

Several areas contained thick waste deposits that were difficult to sample with conventional drilling equipment. We had very good success, however, using a vibracoring technique in these areas. A 3-inch thin walled aluminum pipe was vibrated into the waste and then pulled using an A-frame and winch. The pipe was then cut longitudinally using a power saw to expose a vertical section of the wastes collected. Depths of up to 18 feet were successfully sampled in this manner. Forty-one locations were sampled with the vibracore, both on the Main Waste Pit using a barge and on land using stationary equipment.

One hundred ten samples were collected at 57 of the 227 locations for physical and chemical analyses. The remaining locations were logged and used to visually estimate limits of contamination.

The Remedial Design Sampling Program identified considerably more wastes than had been estimated in the RI. It is now estimated that the site contains approximately 82,900 cubic yards of waste and 131,900 cubic yards of contaminated soil for a total of 214,800 cubic yards of material to be incinerated. This new amount is a 43% increase over the volume identified in the RI. In addition, there are approximately 2600 cubic yards of trash and debris ranging from tires to appliances that were quantified. Given the complexity of the site, we believe that the extra effort expended in the more thorough quantification was worthwhile.

A summary of the physical and chemical characteristics of the wastes and contaminated soils is given in Tables 1 and 2.

PROCUREMENT APPROACH

Early in the design process it was decided to use a two-step procurement approach. This procurement was done under 40 CFR Part 35 and not under the Federal Acquisition Regulations. With a two-step approach, the first step involves requesting and evaluating detailed technical proposals from contractors interested in bidding on the project. At the end of the first stage, a shortlist of contractors that are judged technically qualified to perform the work is developed. The second step is the commercial step where the shortlisted firms are invited to submit bids for the project. The project is awarded to the lowest responsive bidder.

The approach involved the development of a detailed Request for Proposal (RFP). This RFP consisted of a formal RFP, instructions for preparing and submitting the proposal, a proposal form, statement of work, required proposal format and evaluation criteria. In addition, draft contract documents and the entire plans and technical specifications for the project were included in the RFP. All the data collected on the site were made available to the contractors including the RI, FS and Remedial Design Sampling Report. The plans and specifications were specific in the areas that required specific approaches or procedures and were performance based where possible to leave the exact approach up to the individual contractors.

Six detailed Technical Proposals were received in March 1989. After a thorough evaluation, five of the Technical Proposals were accepted and shortlisted for the final bidding.

The plans and specifications were reissued as a bid package for the five shortlisted teams. The list of technical specifications is shown in Table 3.

Table 1
Typical Chemical Analysis of Wastes
Sikes Disposal Pits

	Overflow Area	Main Waste Pit	Small Waste Pit	Tank Lake
GC/MS Volatiles (ug/Kg)				
Benzene	78,000	18,000	4,200	1,400
Chlorobenzene	680	12,000	320	51
Chloroform	660	<370	<320	<9.5
1,1-Dichloroethane	3,200	2,400	<270	410
1,2-Dichloroethane	250,000	<49,000	13,000	<9.5
1,2-Dichloropropane	270	450	660	<9.5
Ethylbenzene	24,000	<52,000	13,000	33
Methylene Chloride	730	1,600	1,500	<9.5
Tetrachloroethene	4,400	3,200	4,700	<9.5
Toluene	24,000	66,000	15,000	23
Trans-1,2Dichloroethene	1,000	<710	<610	140
1,1,2-Trichloroethane	86,000	<700	16,000	<9.5
Trichloroethene	<650	<870	2,200	<9.5
Vinyl Chloride	<390	<530	450	97
GC/MS ACIDS (ug/Kg)				
2,4-Dimethylphenol	NA	52,000	19,000	<2,000
Phenol	71,000	42,000	12,000	<2,000
GC/MS BASE NEUTRALS (ug/Kg)				
Acenaphthene	52,000	58,000	110,000	<2,000
Acenaphthylene	680,000	76,000	60,000	<2,000
Anthracene	46,?00	36,000	38,000	<2,000
Benzo(a)Anthracene	<42,000	<42,000	17,000	<2,000
Benzo(a)Pyrene	<28,000	<31,000	NA	<4,000
Benzo(b)Fluoranthene	<19,000	<21,000	NA	<4,000
Benzo(ghi)Perylene	<40,000	<45,000	NA	<4,000
Benzo(k)Fluoranthene	<19,000	<21,000	NA	<4,000
Bis(2-Ethylhexyl)Phthalate	<17,000	<19,000	17,000	<2,000
Chrysene	22,000	<6,000	10,000	<2,000
Dibenzo(a,h)Anthracene	<49,000	<54,000	NA	<4,000
Di-n-Butyl Phthlate	<11,000	<12,000	NA	<2,000
Di-n-Octyl Phthlate	<11,000	<12,000	NA	<2,000
Fluoranthene	138,000	36,000	77,000	<2,000
Fluorene	230,000	100,000	120,000	<2,000
Hexachloroethane	<72,000	<80,000	NA	<2,000
Indeno (1,2,3-cd) Pyrene	<38,000	<42,000	220,000	<4,000
Naphthalene	1,400,000	570,000	220,000	<2,000
Phenanthrene	260,000	100,000	220,000	<2,000
Pyrene	84,000	30,000	53,000	<2,000

	Overflow Area	Main Waste Pit	Small Waste Pits	Tank Lake
METALS (mg/Kg)				
Beryllium	3.2	1.0	1.1	0.5
Cadmium	0.4	0.8	0.6	0.1
Chromium	34.1	56.9	115	4.0
Copper	17.0	64.0	78	4.9
Mercury	1.0	1.6	2.2	0.6
Nickel	16.0	6.0	5.0	<2.0
Lead	154.0	203.0	174	10
Thallium	9.0	4.1	4.5	<0.5
Zinc	154.0	141	82	19.0

Table 2
Summary of Analytical Parameters
Sikes Disposal Pits

			Wastes			Soils	
Parameter	Units	Average	Maximum Value	Minimum Value	Average	Maximum Value	Minimum Value
Density	g/cm3	1.29	2.11	0.80	2.48	2.65	2.08
Moisture	%	35	78	0	15	45	3
BTU/lb		2396	16600	0	226	907	0
Ash	%	24	83	0	82	96	50
Viscosity	cp	NA	>150	40			
Melting Point	Deg.F				>2700	>2700	>2700
Flash Point	Deg.F	NA	>212	90			
Reactive Cyanide	ppm	<1	<1	<1			
Reactive Sulfide	ppm	NA	288	<1			
Corrosivity	mm/yr	0.46	1.30	0.04			
pH		NA	11.2	1.2			
TOX	mg/kg	819	8100	<10	137	1440	<1
Carbon	%	37.04	75.70	1.90	2.22	10.20	0.09
Hydrogen	%	7.12	10.60	1.60	2.14	5.62	0.52
Nitrogen	%	0.32	2.08	0.03	0.10	3.00	<0.01
Sulfur	%	1.09	3.89	0.06	0.09	0.87	<0.01
Phosphorus	%	0.63	24.00	<0.01	0.02	0.13	<0.01
Total Chlorine	%	0.11	0.88	<0.01	0.01	0.07	<0.01
Sodium	ppm	1399	22900	<1	275	4510	<1
Potassium	ppm	351	1770	<1	238	1470	23
Grain Size % Retained #20 Sieve					3	22	0
Grain Size % Retained #45 Sieve					29	61	9
Grain Size % Retained #60 Sieve					25	44	9
Grain Size % Retained #100 Sieve					23	48	7
Grain Size % Retained #200 Sieve					11	26	2
Grain Size % Retained <#200 Sieve					5	17	0

Table 3
Technical Specification Index

01010	SUMMARY OF WORK
01025	MEASUREMENT AND PAYMENT
01050	FIELD ENGINEERING/SURVEYING
01210	CONFERENCES
01220	PROGRESS MEETINGS
01300	SUBMITTALS
01310	PROGRESS SCHEDULES
01370	SCHEDULE OF VALUES
01380	CONSTRUCTION PHOTOGRAPHS
01390	HEALTH AND SAFETY REQUIREMENTS
01391	SPILL CONTROL
01392	ENVIRONMENTAL PROTECTION
01400	CONTRACTOR QUALITY CONTROL
01410	TESTING LABORATORY SERVICES
01510	TEMPORARY UTILITIES
01540	SECURITY
01550	ACCESS ROADS AND PARKING AREAS
01560	TEMPORARY CONTROLS
01580	PROJECT IDENTIFICATION SIGN
01590	TEMPORARY FACILITIES
01630	PRODUCT OPTIONS AND SUBSTITUTIONS
01705	CONTRACT CLOSEOUT PROCEDURES
01720	PROJECT RECORD DOCUMENTS
02100	GENERAL SITE PREPARATION
02120	TREE AND BRUSH REMOVAL
02130	FENCE AND GATES
02161	TRENCH SAFETY SYSTEMS
02210	GROUNDWATER MONITORING WELL DECOMMISSIONING
02220	GROUNDWATER MONITORING WELL PROTECTION
02230	GROU??TER MONITORING WELL INSTALLATION
02310	WATER TREATMENT SYSTEM
02320	STORMWATER CONTROLS
02330	FLOOD PROTECTION STRUCTURE
02340	VOC AND DUST CONTROLS
02410	EXCAVATION
02420	DRUM AND DRUM WASTE REMOVAL
02430	TRASH AND DEBRIS REMOVAL AND DISPOSAL
02440	VERFICATION SAMPLING AND TESTING
02450	DEWATERING
02510	ASH HANDLING
02520	BACKFILLING
02610	FINAL GRADING AND SITE RESTORATION
13590	INCINERATION FACILITY

DESIGN ISSUES

Flooding

One of the first issues to be addressed during the design was that the entire site is within the 10 year flood plain of the San Jacinto River. LAN had experienced with this directly as our site office trailer had been washed one quarter mile downstream during a flood while we were conducting RI field activities. The site has flooded at least three other times during the last 10 years.

Initial thoughts of diking the entire 185 acre site were dismissed as too costly and impractical. In addition, the Harris County Flood Control District had specific requirements about construction in the flood plain:

- The remedial activities could not raise the level of the 100 year flood plain
- Basin storage could not be significantly reduced

The solution was to require flood protection for only two areas, the Facility Area where the incinerator, major equipment and offices would be located and the Main Waste Pit. Computer modeling of the basin indicated that by clearing the entire site of heavy timber, the "n" value could be reduced during a flood. This enabled us to meet the Harris County Flood Control District's requirements.

The Main Waste Pit requires flood protection due to its size and depth. Remediation of this area will require a considerable length of time. If the site were flooded during remediation of the Main Waste Pit, it would be very difficult to prevent the spread of contamination, potentially off-site.

Excavations outside the flood control structures are required to be designed and managed so that any open areas can be closed with clean, stockpiled material in the event of a threatening flood. No more than a 1-day stockpile of waste will be allowed outside of the flood protection structures.

A series of drainage ditches and berms will be used to segregate potentially contaminated and uncontaminated storm water. The potentially contaminated storm water will be sent to an on-site water treatment facility.

Groundwater

The shallow water table on the site, sandy soil and deep excavations make groundwater management a challenging issue. Excavations in the

Overflow Area will average 8 to 10 feet while excavations in the Main Waste Pit will be more than 30 feet below the top of the pit.

The specifications require that the excavation to be done in dry conditions. This requirement will necessitate significant dewatering.

The ROD relies on natural flushing of the upper aquifer for improving the water quality once remediation is complete. This design decision resulted in a specification that prohibits permanent structures to control groundwater, such as slurry walls, which would impede the natural groundwater movement once the source is removed.

Groundwater that is pumped for dewatering will be tested periodically. Water that does not meet discharge criteria will be sent to the water treatment facility. It is anticipated, however, that much of the groundwater will meet the discharge criteria and can be discharged directly to the San Jacinto River.

Clearing

There are an estimated 43 acres of uncontaminated land and 33 acres of contaminated land that will require clearing for construction, remediation and flood control purposes. Trees on-site range from saplings to 4 ft diameter cypress. The majority of the trees are 6 to 18 inch pines.

The entire site will need to be cleared before the flood control structures can be constructed. Trees and stumps in uncontaminated areas will be removed by normal clearing and grubbing operations. Trees in contaminated areas are to be removed in a manner that prevents them from contacting the wastes. The trees and uncontaminated stumps will be chipped and stockpiled to be used as mulch during final site restoration. Stumps in contaminated areas will be removed during the remediation. They will be chipped and incinerated with the wastes and contaminated soils.

Trash and Debris

There are an estimated 2600 cubic yards of trash and debris on the site composed of:

* Debris from the original Sikes homestead that mysteriously burned
* Discarded furniture such as chairs and sofas
* Discarded appliances such as refrigerators and washers
* Hundreds of tires
* Rolls of tar paper, barrels of tar and shingles
* General household trash

This material is scattered in both contaminated and uncontaminated areas. The material in uncontaminated areas will be buried on-site. Large metal items in contaminated areas may be decontaminated and buried on-site. All other material in contaminated areas will be shredded and incinerated.

Drummed Wastes

Approximately 1500 drums were disposed of on-site while it was in operation. Many drums were apparently stacked in one area and later bulldozed into a large mound. Other drums were buried in various locations and still others were scattered throughout the site.

The drums are in various degrees of disintegration with most of them no longer having any structural integrity. Many drums are now empty and others have solidified residues "holding" the drums together. Some appear to have been lab packs.

All of the drums and drum wastes will be incinerated.

Incinerator Facility

One of the first criteria to be established in the design of the incineration facility was to determine the required incinerator size. A thorough review and evaluation of the technologies available was undertaken. We wanted to develop the specifications detailed enough to ensure that the facility would accomplish the intended job but also open enough to provide for competitive bids. At the time that the specifications were developed, the largest transportable incinerators with demonstrated experience were sized for approximately 5 tons per hour, although the technology was developing rapidly. A decision was made to require a minimum burn rate of 15 tons per hour through either one or more incinerators. This feed rate was based on our review of the technology and a desire to complete the project in a reasonable time-frame.

Other specific criteria were developed for maximum feed size, material handling, VOC controls, etc.

The specifications did not define the specific types of feed preparation equipment to use. The specifications did, however, provide detailed performance criteria and limit the maximum size of material to 2 inches.

Air pollution concerns were addressed in several different ways. Performance specifications were written for the air pollution control equipment that had to be installed on the incinerator to allow it to meet all of the identified ARARs. Concern over VOC emissions from the feed preparation area resulted in a requirement that all feed preparation be accomplished within an enclosure as well as specifying requirements for VOC monitoring. Overall environmental concerns resulted in an extensive air monitoring plan for the entire site.

Ash Handling

Ash will be stockpiled in bins as it comes out of the incinerator. The ash will be tested prior to final disposal to ensure that the organics have been completely destroyed and that the ash passes the EP Toxicity test. Ash that meets both criteria will be backfilled in the excavations. The only limit on backfilling is that the ash must have a minimum of 18 inches of final cover.

Ash that does not pass the organics analysis will be reburned at the contractor's expense. Ash that does not pass the EP Toxicity test will be fixed prior to backfilling. Fixed ash may not be placed below the water table.

FINAL DISPOSAL OF WASTES

The specifications require that all wastes currently on-site must be disposed of on-site. This requirement includes uncontaminated trash, incinerator ash, water treatment sludges, etc. Only normal office trash generated during the remediation may leave the site. Any excess material from the flood protection structures must be disposed of on-site.

Equally important, no waste material may be brought on-site including waste oils for firing the incinerator. Concern from local citizens for this site turning into a Regional incineration facility prompted this specification.

CURRENT STATUS

Bids were taken on Mar. 8, 1990. The four bids received ranged from $89,949,100 to $98,380,176; all bids were within 5% of the Engineer's estimate of $94,529,501. A joint venture of IT Corporation and Davy McKee Corporation produced the low bid.

The current schedule for the project calls for the incinerator to be operational and the trial burn complete in late 1991 and for the entire project to be finished in 1996.

CONCLUSION

The Remedial Design of the Sikes Superfund site addressed many unique and challenging problems. The scope of this paper allows us to touch on only a few of the issues and not give a detailed discussion of any.

Integrated Site Remediation Combining Groundwater Treatment, Soil Vapor Recovery and Bioremediation

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ABSTRACT

Integration of remedial techniques is an effective means of aggressive site cleanup. This was the approach used to respond to a catastrophic 8,400-gallon surface loss of gasoline due to vandalism at a bulk terminal. Rapid delineation of the contamination was accomplished with soil gas surveying and soil borings. Emergency activities consisted of the excavation of the top two feet of gasoline saturated soil to mitigate vapor exposure and installation of an 8-inch recovery well to prevent off-site migration of the gasoline. The excavated soil was treated on-site. To complete site remediation, an integrated in situ system was chosen. This approach was taken to provide rapid site remediation and to minimize disruption of site activities. The system consists of a bioaugmented soil vent system to treat contaminated soils - both excavated and vadose zone; a saturated phase bioreclamation system to treat contaminated aquifer soils and groundwater; and a groundwater/air stripping system to capture and treat contaminated groundwater. The system was installed in phases over three months. In eighteen months of full operation, the degree of contamination has been significantly reduced. This site demonstrated that integration of in situ technologies results in rapid and cost-effective remediation.

INTRODUCTION

The site pictured in Figure 1 is a bulk petroleum distribution plant which handles gasoline, diesel, fuel oil and propane gas. The plant is located in the Pine Barrens area of southern New Jersey between Atlantic City and Camden. This area is a sensitive ecological area.

In October 1988, an apparent act of vandalism caused a large gasoline spill at a bulk petroleum storage plant in southern New Jersey. Approximately 8,400 gallons of premium unleaded gasoline were spilled onto the ground around four underground storage tanks used for bulk petroleum storage. Plant personnel responded immediately with measures to protect groundwater and assure safety of workers in the area. At the request of local fire officials, approximately 700 yd³ of soil were removed from the spill area to a depth of 18-24 inches and stockpiled on 6-mil polyethylene sheeting. To reduce volatile emissions and to reduce the fire and explosion hazard, the excavated area was covered with polyethylene sheeting and clean fill material to cap the spill area. This temporary response provided a safer work area for remediation workers and plant employees and allowed the bulk plant to be reopened for normal operation during further cleanup operation.

SITE INVESTIGATION

The site is in the Pine Barrens region and is underlain by the Cohansey Sand. The Cohansey Sand is a sole source aquifer and is sensitive to any threat of groundwater contamination. Soils encountered beneath the site consist of fine to medium sands with some silts. These soil types have good permeabilities which made immediate response a primary concern to reduce the threat of groundwater contamination due to leaching of contaminant from the soil.
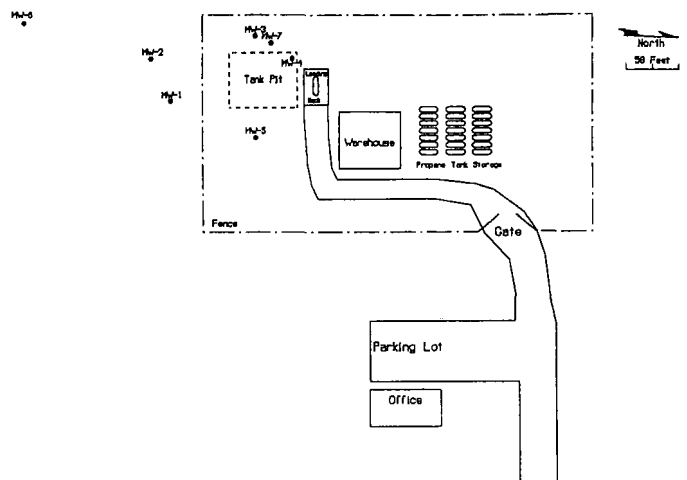
Figure 1
Study Site Bulk Terminal

A soil vapor survey was performed within two days of the loss to assess the extent of contamination. Vapor samples were drawn from probes and analyzed using a portable gas chromatograph. This process gave real-time data which could be used to modify the scope of the soil vapor survey as it was being performed. Vapor samples were drawn from a large number of locations surrounding the spill site and plotted to determine areas of maximum contamination. Figure 2 depicts the results of the soil gas survey. The primary area of contamination was the immediate tank pit area where the gasoline had pooled. High concentrations of gasoline extended to the south and west of the tank pit.

The results of the soil vapor survey were used to select locations for monitoring wells and a recovery system and allowed emphasis to be placed on the area with the maximum potential for groundwater contamination. Based on the soil gas survey, six monitoring wells and two recovery wells were installed surrounding the spill site. Headspace vapor readings were taken during drilling to determine the extent of soil contamination with depth. Additional soil borings were made in the spill area to determine the extent of soil contamination as it varied with depth.
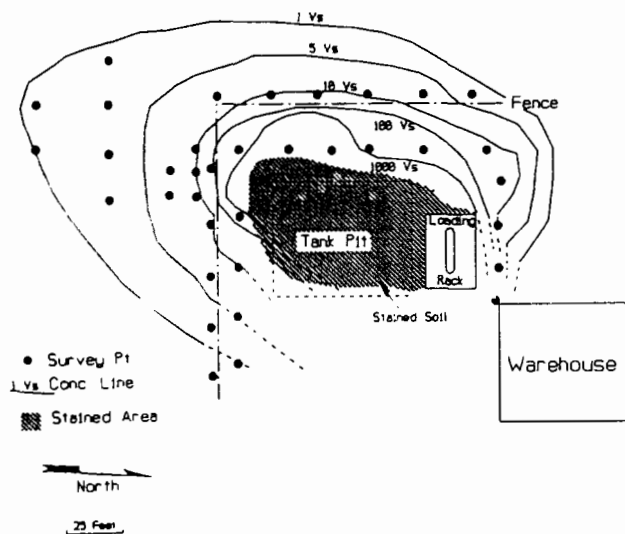
Figure 2
Soil Gas Survey Concentration Lines

Figure 3 presents geological cross sections of the spill area on which the soil contamination results are depicted. The hydrocarbons entered the subsurface through the tank pit. The primary flow direction was vertical leading to a cone of contamination extending to the water table. There was some horizontal spread of product at the bottom of the tank pit along a transition from silty sand to fine sand.
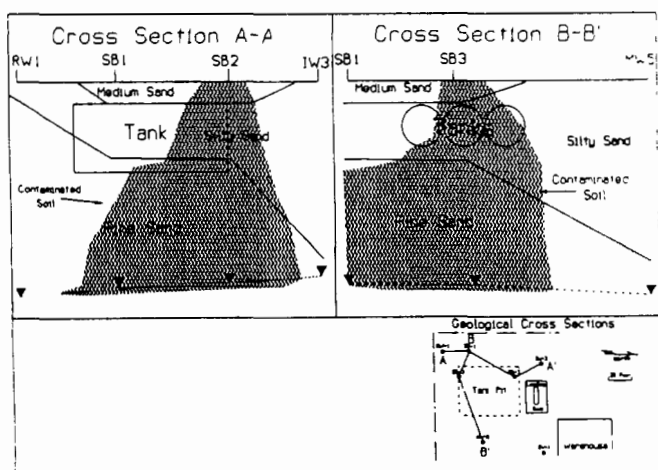
Figure 3
Geological Cross-Sections with
Contaminant Distribution

In all, it is estimated that approximately 6,000 yd³ of soil were contaminated by the spill over an area of approximately 100 feet by 80 feet. An estimate of total amount of gasoline adsorbed in the soil was made using data from the soil vapor survey and soil borings. Based on estimated volumes of contaminated soil and quantitation of contamination with depth, it was estimated that approximately 7,700 gallons of gasoline were adsorbed in the soil of the spill area. An additional estimated 700 gallons were adsorbed in the soil which was excavated and stockpiled immediately following the spill. Due to the significant depth to groundwater (18 to 20 feet) and the quick emergency response actions, it was estimated that initially less than 100 gallons of gasoline reached groundwater under the spill area.

Groundwater samples were taken from the six monitoring wells and two recovery wells. The results, as presented in Table 1, show that the groundwater was contaminated, but that the contamination was confined to the immediate area of the spill.

Table 1
Initial Groundwater Sampling Results, (µg/L)

Well	BTEX	MTBE	Total, VOC
MW-1	BDL	ND	BDL
MW-2	7.9	ND	7.9
MW-3	387.6	290	677.6
MW-4	425	ND	425
MW-5	ND	ND	ND
RW-1	2940	8700	11640

Figure 4 provides an overview of the extent of contamination. Soil contamination is found in the general area of the tank pit and extends from grade to the water table. Groundwater is contaminated and the plume extends to the southeast of the spill area along the direction of groundwater flow. The spread of the groundwater plume was partially blocked by the existence of a trough in the water table elevations running west to east and located south - southwest of the spill area.
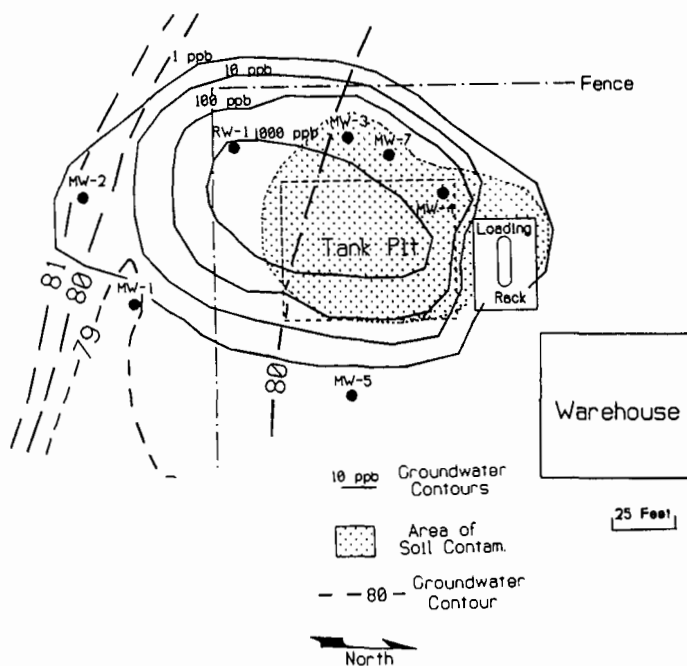
Figure 4
Extent of Soil & Groundwater Contamination

Based on these assessments results, the focus of the remedial program was to:

• Contain the spread of groundwater contamination
• Remediate the contaminated soil to remove the source of groundwater contamination
• Restore groundwater quality

REMEDIAL ALTERNATIVES

Two general alternatives were compared for dealing with the spill. The first alternative involved excavation and replacement of all contaminated soil in the spill area, combined with continued groundwater treatment to remove dissolved contaminants and prevent off-site migration of any contaminated groundwater. The results of the soil vapor survey indicated that approximately 6,800 yd³ of soil had been contaminated. If this soil had been excavated and trucked to a secure landfill, the estimated costs would have approached $700,000. The facility owner would retain perpetual liability for the contaminated soil stored in the secure landfill. In addition, soil excavation would require removal of the storage tanks and loading rack. Estimated cost for this alternative, including groundwater treatment, was more than $800,000 and would have effectively put the facility out of the liquid fuel storage business.

The second alternative was to treat the contaminated soil on-site using soil venting and bioremediation. With this alternative, the petroleum bulk plant could remain in operation during remediation. There would be no off-site liability since no contaminants would leave the site. Using a variety of processes to treat soil, groundwater and vapors, the estimated cost for on-site treatment was $500,000-$600,000. The decision was made to treat the contamination on-site.

IN SITU TREATMENT COMPONENTS

There were two basic types of contaminated media: groundwater and soil. The soil contamination was primarily in the vadose zone, although some contaminated soil existed below the water table.

Gasoline is relatively volatile, having an average vapor pressure of ~50 - 100 mm Hg. It is biodegradable, having a BOD'5 of 0.08 - 0.12 mg/L. It is, however, relatively insoluble, having a maximum solubility of ~150 mg/L. Based on these properties, remediation of significant quantities of gasoline is accomplished best by the use of soil vapor extraction and bioreclamation. However, since the groundwater also was impacted, a groundwater recovery system was necessary to remediate the spill. The groundwater system also aided the bioreclamation system by enhancing transport of nutrients and oxygen through the area.

The components of the treatment system selected were:

- Groundwater recovery and treatment
- Soil vapor extraction
- Bioreclamation

The following sections contain descriptions of the technical aspects of each component of the remediation system.

GROUNDWATER EXTRACTION AND TREATMENT

Groundwater extraction and treatment is a process utilized to maintain hydraulic control of dissolved groundwater contaminant plumes. By estimating site-specific hydraulic characteristics, appropriate pumping equipment, treatment systems and recovery well(s) can be located, designed and installed to maintain the necessary hydraulic control.

Groundwater which is extracted from the subsurface can be treated for organic removal using various technologies. Two of the most common technologies employed for removal of gasoline constituents from a water stream are air stripping and activated carbon. In this case, air stripping was employed because of its low maintenance and lower operating costs.

SOIL VAPOR EXTRACTION

Soil vapor extraction is a process for removing volatile organic contaminants from unsaturated soils by induced air flow. In using soil vapor extraction, a series of vertically screened wells is placed in the area of contaminated soils penetrating the horizon of contamination. A vacuum is applied to the vent wells to induce air flow through the subsurface and to volatilize and remove the contaminant.

Soil vapor extraction systems may require treatment of the vapor effluent. Two basic technologies are available for treatment of vapor effluent - carbon adsorption and thermal treatment. In this case, a thermal treatment system was employed because of its low maintenance and low operating cost.

BIORECLAMATION

Simply viewed, bioreclamation is a two step process:

$$\begin{array}{ccc}\text{Contaminant} & \text{Bacteria} & \text{Cell Material} & \text{Bacteria} \\ \text{------>} & & \text{------>} & CO_2 + H_2O \quad (1) \\ \text{(C,H)} & & \text{(C, H, N, P, O)} & \end{array}$$
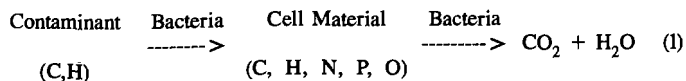
In the first step, bacteria, which have evolved the specific enzyme machinery, use the contaminant, which is mostly carbon and hydrogen, as a food and energy source. A portion of the carbon and hydrogen is "burned," i.e, used as an energy source yielding CO_2 and water directly. Most of the contaminant, however, goes into the production of additional cell material - other bacteria.

In order to make cell material, the bacteria need a proper balance of nitrogen, phosphorous and oxygen relative to the carbon source. In the natural environment, these factors are all in balance. However, when a loss/spill of organic chemicals occurs there is an overabundance of carbon relative to the naturally available oxygen nitrogen and phosphorous. This overabundance of carbon creates a stress situation which cause the bacteria to be dormant. The same thing happens in activated sludge when one gets a shock loading - one loses the culture. Once, through the practice of bioreclamation, a balance is re-established, the bacteria rapidly convert the carbon to cell material which then becomes food for other soil bacteria. This subsequent metabolism takes the partially degraded contaminant ultimately to CO_2 and water - complete mineralization. The key to the successful application is to transport nutrients and oxygen to the areas of contaminated soil and groundwater.

Successful treatment of the gasoline spill required application and integration of all three components. Figure 5 shows a conceptual view of the integrated system. The groundwater system captures and treats contaminated groundwater. It also aids in the transport of nutrients and oxygen for the bioreclamation system. The vent system removes gasoline from the vadose zone by both direct volatilization and by supplying oxygen to the bioreclamation system. Finally, the bioreclamation system degrades gasoline in vadose and saturated zone soils and in groundwater. It also increases the removal of adsorbed organics by solubilizing them so they can be captured and removed by the groundwater system.
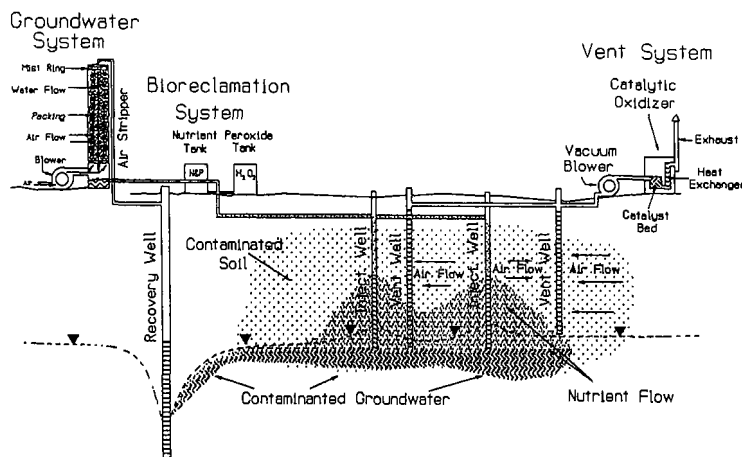
Figure 5
Conceptual View of Integrated Remedial System

SYSTEM DESIGN AND INSTALLATION

Groundwater Extraction and Treatment

Based on the results of the soil gas survey, an initial recovery well location was selected. Recovery well RW-1 was installed in the location indicated in Figure 4. Groundwater was pumped from this recovery well at a flowrate of approximately 20 gpm as an interim measure instituted to assist in establishing hydraulic control of the contaminated groundwater.

The extracted groundwater was treated using air stripping. Air strippers volatilize compounds from the water phase into the vapor phase due to the air-water partition coefficient or the Henry's Law Constant. The air stripper employed at this site was a 24-inch diameter, 22-feet tall unit packed with two-inch media. The air flowrate was 1,000 cfm and hydraulic capacity of the unit was 50 gpm. The treatment efficiency ranged from 98-99.9% removal of VOCs. Influent MTBE concentrations were reduced by 60-85%. The air stripper removed approximately 0.1 lb/hr of hydrocarbon compounds, which represents an equivalent removal of approximately 70 gallons of gasoline per month. The liquid effluent from the air stripper was combined with a nutrient solution and hydrogen peroxide and routed to five nutrient injection wells to assist in the bioremediation process.

Once groundwater monitoring wells were installed and sampled to confirm the results of the soil gas survey, the groundwater pumping was temporarily halted to allow groundwater elevations to return to static levels. A 72 hour pump test was then performed to determine the hydraulic characteristics of the water table aquifer. An approximate transmissivity (T) of 20,000 gpd/ft and storage coefficient (S) of 0.034 were estimated based on site-specific conditions and assumptions. An average daily groundwater flow velocity of 3.0 feet/day was calculated.

The data discussed above were utilized in performing a capture zone evaluation using the following equation:

$$r_{og} = \frac{Q}{(2\pi)\ (T)\ (I)} \tag{2}$$

where:

r_{og} = stagnation point/velocity divide downgradient
Q = extraction rate from recovery well
T = Transmissivity
I = Groundwater gradient
and
r_{ug} (upgradient) = r_{og} (2π)
r_{cg} (cross gradient) = r_{og} (π)

Upon performing the capture zone evaluation on recovery well RW-1 at a flow rate of 20 gpm, we decided that additional hydraulic control was necessary to effectively capture dissolved hydrocarbon compounds.

In order to establish sufficient hydraulic control at the site, an additional recovery well (RW-2) was installed to a total depth of 50 feet below grade at the location depicted in Figure 6. Additionally, Figure 6 depicts the water table elevation under pumping conditions (with RW-2 operational at 25 gpm) versus the originally inferred static water table elevations.
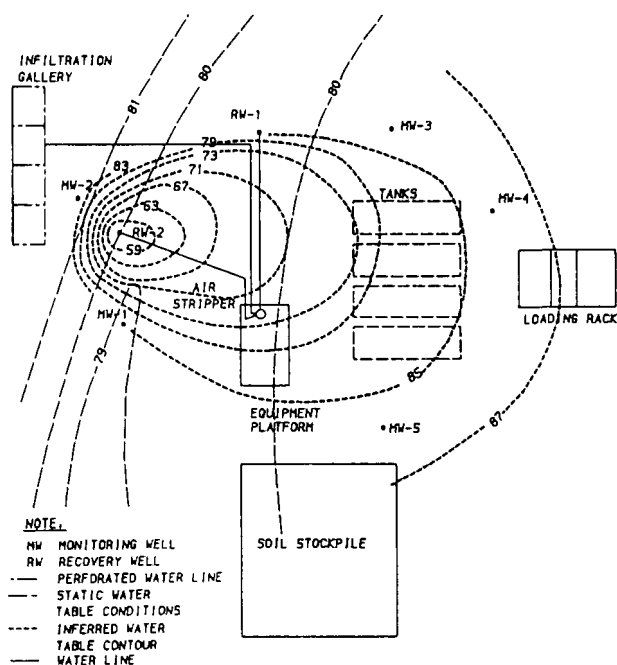
Figure 6
Groundwater Treatment System "RW-2"

The theoretical capture zones created by pumping recovery well RW-1 at 5 gpm and RW-2 at 25 gpm are depicted in Figure 7. The water table elevations depicted in Figure 6 seem to confirm the theoretical capture zones depicted in Figure 7
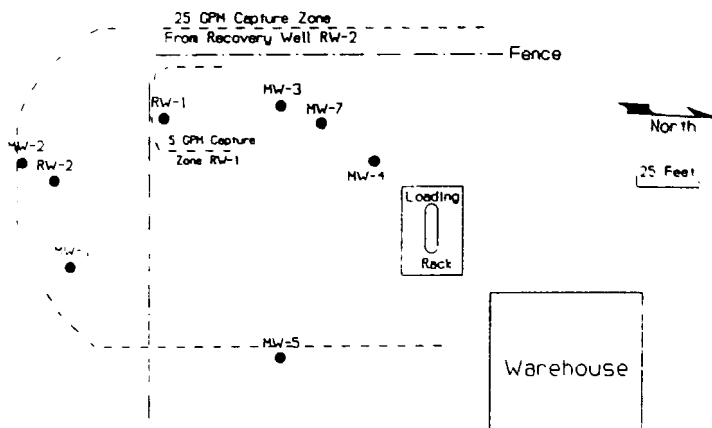
Figure 7
Capture Zones for Recovery Wells

By examining the influent concentrations depicted over time in Figure 8, the effectiveness of the groundwater recovery system can be seen in maintaining hydraulic control of the dissolved hydrocarbon compounds.
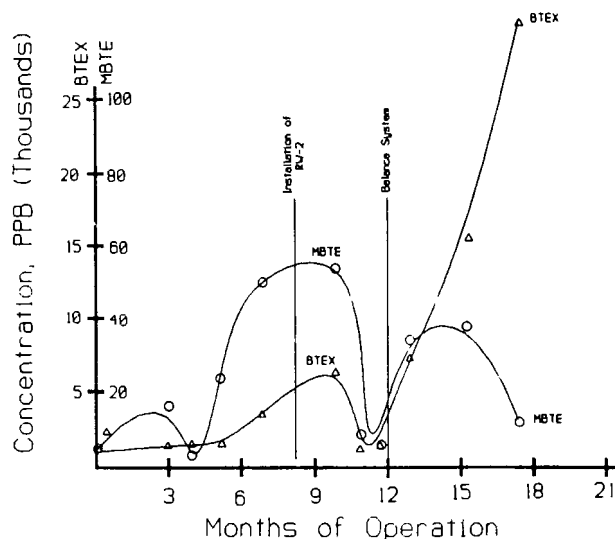
Figure 8
VOC Concentrations in Recovery Well(s)

Upon evaluating the hydraulic conditions of the site while recovery well RW-1 was pumping, we decided to add an additional recovery well (RW-2) to the groundwater recovery system. As indicated in Figure 8, this new well led to the reduction of the combined influent concentrations due to a greater volume of water being recovered by the two recovery well systems. The recovery of dissolved contaminants was increased again after 11 months of recovery system operation by adjusting the flowrates in RW-1 and RW-2 in response to a followup evaluation of hydraulic site conditions. By monitoring and adjusting hydraulic conditions at the subject site, more contaminants have been drawn to RW-2 and hydraulic control of the dissolved hydrocarbons has been established. Hydraulic control is further enhanced by the upgradient injection of nutrient-enriched air stripper effluent. This upgradient injection increases the gradient across the area of dissolved hydrocarbon compounds, thereby increasing the rate at which contaminants can be recovered and nutrients can be circulated.

SOIL VENTING

If ambient soil vapor pressure in a spill area is reduced, hydrocarbons can be removed from soil in the vapor phase. Vacuum blowers

were used to draw air through contaminated soil in the spill area to vaporize adsorbed hydrocarbons and carry them to the surface. Soil venting was utilized in two ways; the first system treated excavated soils from the spill area; the second system treated the remaining contamination in vadose zone soils.

Immediately following the spill, approximately 700 yd³ of contaminated soil were excavated from the spill area to limit volatile emissions and reduce fire and explosion hazards. This material was stockpiled on polyethylene sheeting near the spill site. Perforated PVC laterals were installed in the soil pile and nutrient solution was sprayed on the soil. The entire soil pile was then covered with polyethylene sheeting and the PVC laterals were manifolded to a high vacuum blower, which was operated to remove hydrocarbons in vapor phase from the soil pile.

Separate bail valves allowed adjustment of air flow through the soil pile to optimize removal of hydrocarbons. The operating air flowrate for the soil pile was approximately 100 cfm.

Four vapor extraction wells were installed in the spill area to allow soil venting of approximately 6,000 yd³ of contaminated soil in the unsaturated zone. The vapor extraction wells were 4-inches in diameter and approximately 22 feet deep. Separate laterals from each well were manifolded to a high vacuum blower and separate ball valves on each lateral allowed dedicated control of vapor flow from the different wells to optimize hydrocarbon removal in the vapor phase. The operating flowrate from the vapor wells was approximately 130 cfm.

Hydrocarbon removal through use of the vent system approximately 85 lb/day, equivalent to approximately 14 gallons of gasoline per day. Vapor-phase treatment of the air exhaust was required to meet New Jersey air emission standards. Alternatives for vapor-phase treatment included carbon adsorption and catalytic oxidation. Because site remediation could ultimately result in the removal of almost 50,000 pounds of hydrocarbons (from 8,400 gallons of gasoline), it was determined that catalytic oxidation would be the most cost-effective means of vapor treatment. Catalytic oxidation provides conversion of volatile organic chemicals to CO_2 and water vapor. The process uses a precious metal (platinum) catalyst, operating 600°F to 700°F, which is a significantly lower temperature than used in thermal incineration. Heat released during catalytic oxidation of the hydrocarbon vapors is recovered to reduce the power consumption for heating the catalyst.

A Catalytic Scavenger™ Unit, manufactured by Oil Recovery Systems, Inc., (ORS) was installed to treat vapors at this site. The unit operates on a relatively dilute influent vapor level of hydrocarbons (less than 25% of lower explosion limit) and incorporates safety features to automatically shut the unit down if vapor concentration or operating temperature become too high. At this spill site, this catalytic unit treats approximately 230 cfm of vapors from the soil pile and vapor extraction wells. The unit removes approximately 3.6 lb/hr of hydrocarbons and reduces influent vapor levels by more than 95%.

The layout of the soil vent system is pictured in Figure 9. The figure shows the location and influence of the in situ vapor extraction points.

BIOREMEDIATION

Bioremediation was used to treat adsorbed and dissolved contaminants in the saturated zone. Bioremediation was also used in conjunction with soil venting to accelerate the removal of adsorbed hydrocarbons in the unsaturated zone. An added benefit of the process is that it removes adsorbed hydrocarbons which are not as effectively removed by soil venting from the saturated zone.

Nutrient requirements and optimum conditions for biodegradation were determined by laboratory simulation of conditions using actual soil samples from the spill site. The results are presented in Figure 10. As can be seen, the site required the addition of nutrients at ~100 mg/L level to effectively remove the gasoline.

The layout of the bioremediation system is shown in Figure 11. Nutrient-amended groundwater was independently injected through five injection wells and through a series of shallow infiltration lines. The nutrient peroxide solution was injected continuously through the injection wells and on a batch basis through the infiltration lines. The water content in the vadose zone was kept at ~50% of residual satura-

tion to maintain a balance between bioreclamation and soil vapor extraction.
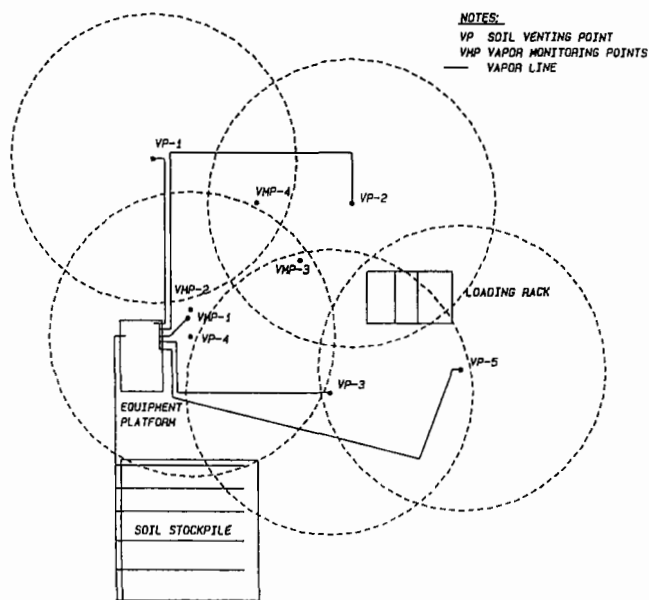
Figure 9
Soil Venting System
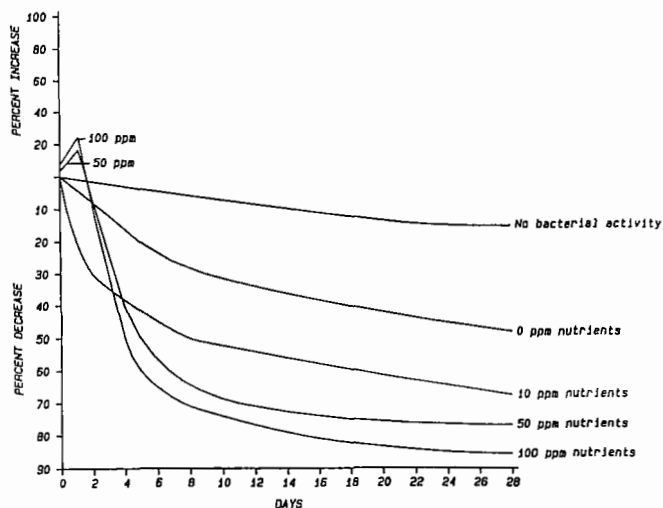
Figure 10
Laboratory Pilot Study BTEX
Degradation with Time

The installed system was a fully balanced and integrated system. As shown in Figure 12, the equipment was laid out so that individual points could be adjusted and the system could be balanced. Groundwater from the recovery wells was air stripped, amended with nutrients and hydrogen peroxide and then reinjected through injection wells. Vapors were withdrawn both from the soil pile and from the in situ points. The vapor stream was sent to the catalytic oxidation unit.

OPERATING RESULTS

The system has been operating for approximately 18 months. Of the approximately 47,000 pounds of gasoline in place after system installation, ~34,000 pounds (or 73%) have been removed/destroyed by the remedial system.

The performance of the different system components is depicted in Figure 13. As can be seen, the bulk of the removal has been due to the vapor extraction system. The soil vapor extraction system provided

a rapid and substantial response to the spill. However, bioreclamation also provided significant removal of hydrocarbons. As can be seen from the data in Figure 13, the removal due to the other processes has increased with time. This result is to be expected as the vapor extraction system removes the highly volatile and mobile fractions leaving a less mobile residue. This residue is more responsive to bioreclamation than it is to soil venting. Hence, the increase in the relative importance of bioreclamation with time.
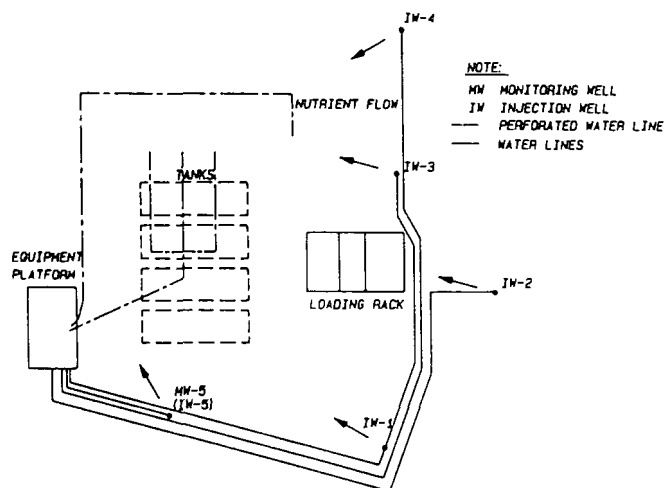
Figure 11
Bioremediation System
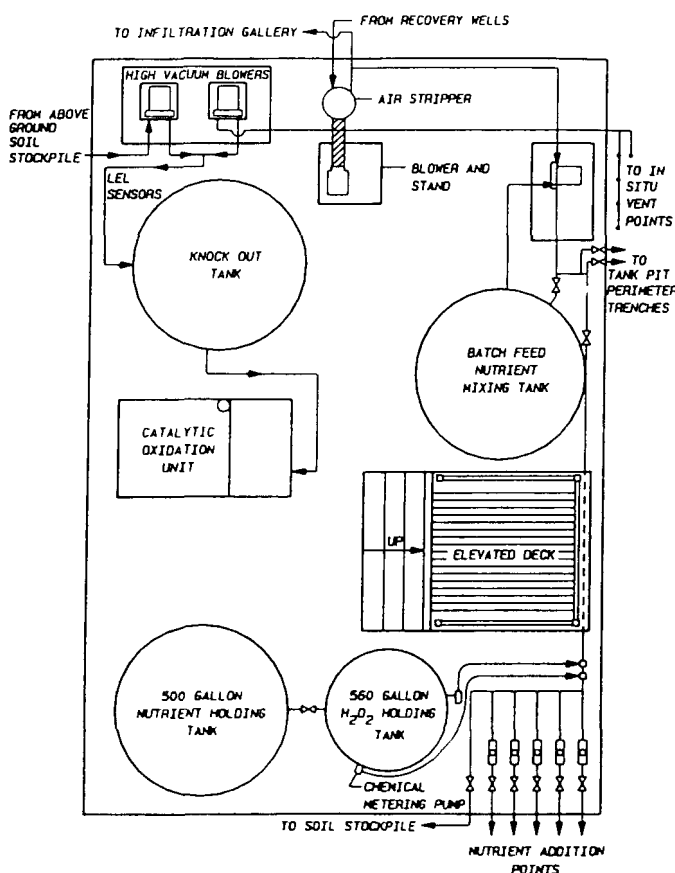
Figure 12
Equipment Schematic
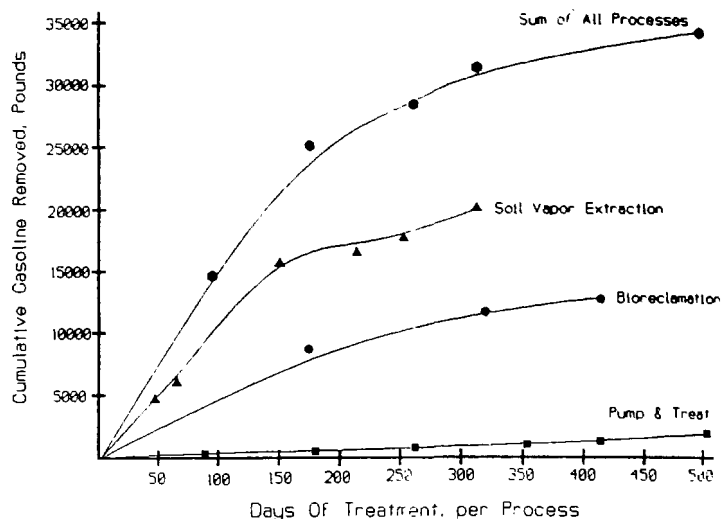
Figure 13
Treatment Performance Integrated System

The driving force for the remediation was the control and reduction of groundwater contamination. The system has had a substantial impact on groundwater contamination in the source area. Two types of volatile organic contaminants were tracked in Figure 14 BTEX (benzene, toluene, ethylbenzene and xylene) and MTBE (methyl tertiary butyl ether). The BTEX level started at about 1200 μg/L and the MTBE level at 4400 μg/L. In the first part of reclamation, both concentrations increased: to ~22,000 μg/L for BTEX and to 88,000 μg/L for MTBE. This increase was due to the solubilization of the adsorbed contaminants due to water circulation through the vadose zone and biological activity. After the system had been operating for approximately 6-9 months, substantial decreases in BTEX and MTBE concentration were observed. As the source area has been remediated, the impact on groundwater has been mitigated.
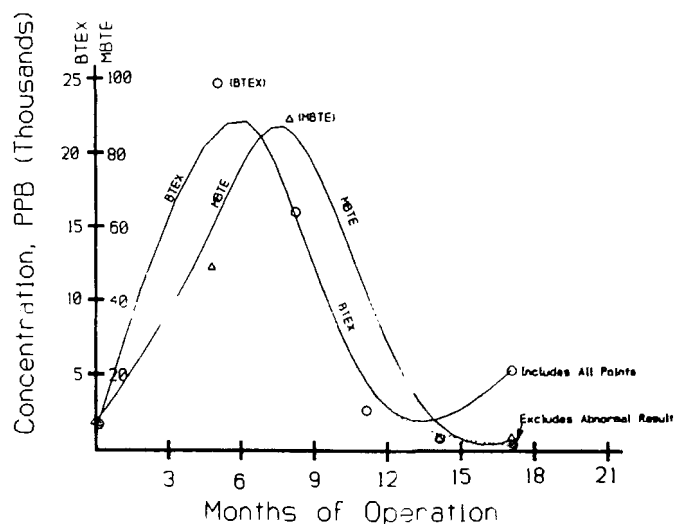
Figure 14
Reduction of VOCs in Groundwater in Source Area

Several things should be noted in Figure 14. First, the BTEX results showed an apparent rise in the last sample due to abnormally high results in one well. All other wells remained low and were in line with previous results. The cause of the aberration may be due to sampling error, and the well will be resampled. A second observation is that the MTBE concentration decrease lags the BTEX because MTBE is less volatile

and less biodegradable than BTEX. Consequently, it has taken longer to reduce the source concentration.

CONCLUSION

Using an integrated system to treat groundwater and soil contamination provided an effective and rapid response to large-scale organic contamination. The combination of bioreclamation, soil vapor extraction and groundwater recovery employed at this site has removed almost 34,000 pounds of gasoline in fewer than 18 months of operation. The system has effectively reduced groundwater contamination in the spill area by more than 90% from the maximum levels. The integrated system has been effective because it has made best use of the properties of the contaminant and the nature of the site in remediation. Gasoline is a volatile, biodegradable contaminant mixture. It is not, however, very soluble. As a result, the application of soil venting and bioreclamation has resulted in substantial removals of gasoline.

The effectiveness of on-site treatment at this spill site demonstrates that use of modern technology can reduce costs and limit liabilities for petroleum companies which experience large spills. At the same time, contaminants can be contained within the spill area to reduce threats to groundwater and air quality.

Restoration of a Refinery Site
For Use as a Commercial Center

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ABSTRACT

There is often concern that petroleum refining operations cause significant soil and groundwater contamination due to spills, leaks, improper design of storage and pipeline facilities and long periods of operation. In some instances, these concerns have been confirmed by the discovery of significant accumulations of hydrocarbons beneath refineries. Yet, the demolition of the 40 year old Golden Eagle Refinery in Carson, California (Site) demonstrated that contamination is not always significant and that through the use of well-designed demolition efforts and enhanced bioremediation, site restoration can be accomplished easily and quickly.

Restoration of the 76 acre Site was accomplished in five phases: (1) cleaning to remove tank bottom sludges and API-type separator bottoms and delivery of all such materials to an approved disposal site; (2) removal of all above surface structures and underground storage tanks; (3) removal of underground pipelines, pits, sumps and clarifiers; (4) removal and disposal of a small volume of soil contaminated with lead; and (5) consolidation of petroleum hydrocarbon-contaminated soil within the old tank farm area where enhanced bioremediation was accomplished. A Site characterization study was completed while the first three phases were being accomplished. The results of this study established the regulatory agencies' requirements for bioremediation.

Semiperched water and aquifer testing demonstrated that the dissolved concentrations of total petroleum hydrocarbons ranged from below laboratory detection limits to 40 μg/L and chlorinated hydrocarbons ranged from below laboratory detection limits to 27 μg/L at the Site. After repeated monitoring of the contaminant levels in the semiperched water and underlying aquifer, no significant changes in concentrations were noted. Monitoring continues on an annual basis. Development of the Site is ongoing.

Petroleum hydrocarbon concentrations in the contaminated soil ranged from 60 to 32,000 ppm. The Solmar Corporation commercial bacterial formulations were tested for efficacy in reducing the hydrocarbon concentrations to acceptable levels. A selected formulation was used and reduction in hydrocarbons to acceptable levels was completed in approximately eight months. Some residual hydrocarbon concentrations (less that 1,000 ppm) remained in the remediated soil, but they were mostly C15 or higher compounds. Such petroleum residuals, largely asphaltic in nature, do not degrade or move easily through the soil even with extensive water infiltration. Six volatile priority pollutants were detected in the soil at the termination of remediation, but all at concentrations well below 1 ppm. Several nonpriority pollutant volatile compounds also were identified at concentrations of 9.5 ppm of less.

The planned use of the Site is for a commercial complex with extensive buildings and related asphalt-covered parking and landscaped areas. Although the residual hydrocarbon concentrations in the soil were not considered to be a problem, requirements were evolved to limit the potential for any significant impacts from the residual hydrocarbons during future site development.

INTRODUCTION

Petroleum refining, storage and transporting facilities have often been cited as major sources of soil and groundwater contamination. It is not unusual to find several feet of free product sitting on top of groundwater and also to find dissolved product constituents in the groundwater. Loss of product can be due to accidental spills and leaks, improper design of facilities and improper or insufficient maintenance and repair. In many instances, the soil and groundwater contamination is the result of decades of Site use for the same general functions. There is one such site in California which for approximately fifty years has been used for two different refining operations, each with separate storage and crude/product transportation facilities and regional transportation of petroleum products and finally used only for short term storage and distribution of products.

The soil and groundwater contamination is extensive and free product can be found in several locations. The problems are compounded by activities at adjacent industrial facilities which have produced napalm and bomb components, processed phosphate materials containing arsenic and produced vinyl chloride-based materials. This situation is almost a classic example of a site where spills and leaks have been common, where an old design was overused and where maintenance and repair were not timely or sufficient to comply with the ever changing rules and regulations. In many instances, remediation of a refinery would bring to mind most of the conditions described above. This was not the case for demolition of the 40 year old Golden Eagle Refinery, Carson, California.

GOLDEN EAGLE REFINERY SITE

The Golden Eagle Refinery Site (Site) occupies 76 acres surrounded by residential developments on two sides and commercial development, inactive landfills and a major freeway on the other sides. The original crude processing units, excluding the existing tank farm (Fig. 1), were constructed by Sunset Oil in 1945. Over the next 10 years additional processing units were added, reaching a production capacity of 4,000 bbl/day. The products produced included kerosene, fuel oil and gasoline. In 1953, a thermal cracking unit was added to increase production of gasoline, but this unit was taken out of service in 1961/1962. Production of leaded gasoline ceased in 1965, but a tetraethyl lead storage tank remained in place until demolition in 1985. In 1980, a third crude processing unit was added which increased capacity to 12,500 bbl/day. The three crude units, in combination with a naphtha stabilizer unit and

a rerun unit, produced JP-4 and JP-5 aviation fuel, fuel oil and diesel fuel until the refinery stopped production on November 12, 1984.
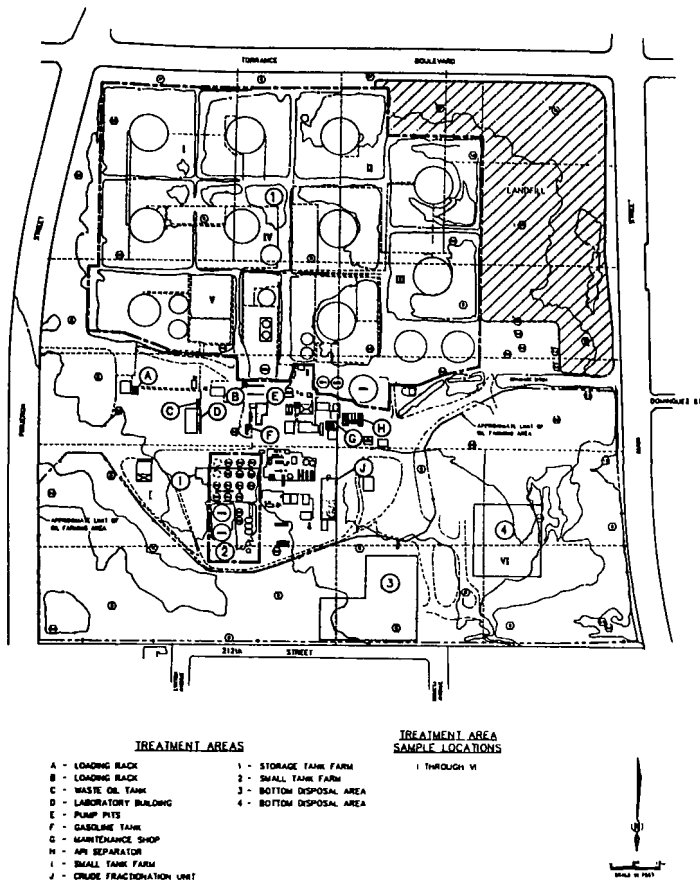
Figure 1
Golden Eagle Refinery, Carson, California

Primary transport of crude and product to and from the refinery was by a system of pipelines connecting the refinery with oil fields, other refineries and terminals at the Port of Los Angeles. There were truck loading racks but they were used sparingly.

Approximately 10 acres on the northeastern portion of the Site were used as a landfill (Fig. 1). This use was very short, beginning in late 1961 and ceasing in late 1962. The depth of the fill material ranges to about 38 ft below grade, with an average soil cover of 2-5 ft. The contents of the landfill range from concrete and asphalt to household wastes. Some methane gas is produced, but the soils around the landfill are relatively impermeable and constitute a natural barrier to gas migration.

Although there were a few areas on the Site with perched water at depths of 35-40 ft, in general the depth to groundwater is greater than 50 ft below the surface. There are several underlying aquifers which provide potable water.

WASTE DISPOSAL

Until about 1971, tank bottom sludges were placed on the southern portion of the Site and farmed (Areas 3 and 4, Fig. 1). The sludges were allowed to dry and then were disced into the soil to allow for natural bacterial break down of the hydrocarbon components. For a brief period of time, refinery wastewater was disposed on-site into a slough which flowed into the Los Angeles Harbor area. After 1950, all wastewater was discharged into the sewer system.

BASIC SITE GEOLOGY

The surface soils at the Site consist of silty clay and clay formations. These formations effectively limited the downward migration of any

residual contamination in the surface soils. It was typical to encounter hydrocarbon concentrations of 10,000 ppm at a given depth with the hydrocarbon concentration 5 ft lower being Not Detected (ND). The low level of contaminant migration also was due to the presence of mostly heavy hydrocarbons, i.e., hydrocarbons with 12 or more carbon atoms.

ANALYTICAL PROCEDURES

Soil samples were obtained from fifty borings and nine monitoring wells were drilled to or just below the groundwater level. One well was drilled into the underlying aquifer. Soil samples were obtained at 5-ft intervals. Soil and groundwater samples were tested using U.S. EPA Methods 418.1, 8015, 8240 and 8270.

GROUNDWATER ANALYSES

Contaminant concentrations in the semiperched groundwater were very low. Several priority pollutants, chlorobenzene, 1,2-dichloroethane, benzene, ethylbenzene, toluene and trans-1,2-dichloroethylene were found at low concentrations. Only the concentration of benzene and 1,2-dichloroethane exceeded the California Department of Health Services Action Levels for Drinking Water.[1] These concentrations were not considered to be a problem because the semiperched zone is not used for drinking water, the clay layers in the soil essentially preclude extensive downward migration of the contaminants and most of the contaminants are heavy hydrocarbons. Further, introduction of additional contaminants is essentially precluded since the refinery has ceased operations and the existing contaminated soil has been treated.

VOLUME OF SOIL TREATED

After extensive geotechnical and hydrogeological analyses, 14 areas were established where treatment was required. Ten of these areas were excavated (Areas A through J, Fig. 1) and approximately 530 yd^3 of soil were transported to Area 1 (Fig. 1). Most of the soil contaminants were within 0.5 ft of the surface, with only the contaminants in Areas C and F extending down to 20 ft below the surface. The soils in Areas 1 through 4 were treated in place. The largest volume, approximately 20,000 yd^3, was in Area 1. Areas 2 through 4 contained about 3,000 yd^3 Collectively, approximately 23,000 yd^3 of soil were treated using bioaugmentation. This low volume is attributed to good housekeeping during refinery operations even before current rules and regulations were implemented. The treatment areas were arranged so that the contaminated soil was approximately 10-12 in. thick.

LEAD CONCENTRATIONS

The surface soil in two small sites within Area 3 contained lead concentrations which exceeded the Total Threshold Limit Concentration (TTLC) value of 1,000 ppm.[1] Soil from these areas was excavated and transported to an approved disposal site. Four other samples were tested using the California Waste Extraction Test (WET) to determine if the lead concentrations below the TTLC were soluble. All of the soluble lead concentrations were less than 0.03 mg/L, which is less than the Soluble Threshold Limit Concentration (STLC) value of 5 mg/L.[1]

BIOAUGMENTATION PROCEDURES

Samples from the treatment areas were obtained and submitted to Solmar Corporation for treatability studies. The hydrocarbons were extracted from the samples with Freon 113 using a Soxhlet apparatus. Portions of the individual extracts were in turn inoculated with various commercially available Advanced Bio Cultures. Formulation L-104 showed the highest degradation capability based on degradation efficiencies ranging from 47% to 64% after 21 days.

The treatment areas initially were watered using a 2000-gal. water truck. When the soil was moist, fertilizer with phosphorus and nitrogen was added using the water truck. When the phosphorus and nitrogen levels in the soil were 5 ppm and 20 ppm, respectively, the bacteria were added. The cultures, supplied in dry form, were reconstituted by adding approximately 2 gal. of water/lb of culture. After soaking, the cultures were added using the water truck. Treatment was based on an initial inoculation of 50 lb of L-104 per acre of treatment area. This

initial application was followed two weeks later with an inoculation of 37.5 lb/acre. Thereafter, inoculations of 25 lb/acre were added monthly. Other than during inoculation of L-104, watering in Area 1 was accomplished using a portable sprinkler system fed from the refinery fire protection system. The soil moisture content ranged from 25% to 30% during the treatment efforts. The 8-foot high tank farm external berms were left in place so that any excess water was contained within Treatment Area 1. Watering in Areas 2, 3 and 4 was accomplished using the water truck.

The L-104 bacterial formulation included some species which were not initially efficient in breaking down the hydrocarbons in the treatment areas. However, as breakdown products are produced, it is important that all species of the consortium be available to handle the metabolites being formed. The subsequent inoculations assure that all species of the consortium are available in suitable numbers to give complete breakdown.

Since the breakdown process is accelerated by the presence of oxygen, about once a month, the treatment surface area was disced to a depth of approximately 10 in.

TREATMENT RESULTS

Sample stations A through F were established in Areas 1 through 4 (Fig. 1). Samples were collected frequently to determine bacterial plate counts and changes in hydrocarbon concentrations. Often, since it is not possible to repeatedly sample in exactly the same location, hydrocarbon concentrations at a given station increased or decreased during successive analyses.

The highest concentration of hydrocarbons in the treated soil was 32,330 ppm. Initially, the soils contained several purgeable priority and nonpriority pollutants and extractable priority pollutants. Concentrations of benzene, toluene, xylene, ethylbenzene and methylene chloride ranged from ND to 800 ppb; concentrations of hexane, methylcyclopentane and 3-methylpentane ranged from ND to 9,500 ppb; and concentrations of bis(2-ethylhexyl)-phthalate, diethyl phthalate and butyl benzyl phthalate ranged from ND to 204 ppm. Initial bioaugmentation treatment started in February 1986, and the levels of hydrocarbons were sufficiently reduced by October, 1986. The fluctuations in hydrocarbon concentrations at Sample Stations A through F are shown in Table 1. Almost all of the short-chain hydrocarbons were eliminated. The residual hydrocarbons were saturated straight-chains, ranging in size from C20 to C27. The initial concentrations of purgeable and extractable compounds were reduced to ND or below 1 ppm. The nonpriority pollutant levels also were reduced to 9.5 ppm or lower. The extractable priority pollutants, primarily phthalates, were detected in final sample analyses but at levels below 1 ppm.

FINAL SITE DISPOSITION

After treatment of the soil, the Site was generally deemed suitable for commercial development based on implementation of at least the following conditions:

• The landfill site was covered with a sufficiently thick cap and use thereof was limited to parking or other passive uses
• Landscaped areas were watered using a drip system
• Protective membranes were placed under buildings

CONCLUSIONS

Based on the results of several Site studies[2-5] which are summarized in the paper, several conclusions can be drawn:

• The Golden Eagle Refinery Site is unique in that the degree and diversity of soil contamination was limited;

• The Site soil conditions limited the migration of the hydrocarbon contaminants both within the soil and into the semiperched groundwater and underlying aquifers;
• Selection of the bacterial formulation is critical to successful reduction of hydrocarbons in the soil;
• Bacterial degradation of hydrocarbons requires optimum concentrations of phosphorus and nitrogen; application of water is critical and discing the soil being treated will enhance the rate of degradation of the hydrocarbons;
• Bioaugmentation using formulated bacteria is an easy and relatively inexpensive way to reduce hydrocarbon concentrations in soils; and
• Residual concentrations of long chain hydrocarbons (C20 or higher) can be left in place provided the design of future developments includes conditions which minimize the potential for the collection of vapors in buildings or percolation of water through the soil into the ground water regime.

Table 1
Hydrocarbon Concentrations in Treatment Areas[1]

SAMPLING DATE	I	II	III	IV	V	VI
2/20/86	1,050	1,150	7,670	2,980	1,270	(2)
2/18/86	300	342	1,972	1,370	(3)	(2)
2/25/86	1,060	510	3,260	210	(3)	(2)
3/4/86	1,460	2,550	3,930	237	2,100	(2)
3/12/86	1,900	300	5,440	2,225	1,040	(2)
3/17/86	530	92	1,560	1,190	1,150	(2)
3/25/86	656	278	3,760	1,340	11,140	(2)
3/31/86	400	390	730	670	800	(2)
4/7/86	1,530	240	770	3,610	770	(2)
4/15/86	82	206	619	196	115	(2)
4/22/86	1,300	840	7,100	2,500	1,650	(2)
4/28/86	330	1,800	1,850	8,800	1,300	(2)
5/5/86	264	478	2,940	3,910	1,290	10,600
5/13/86	725	720	5,300	7,180	2,650	30,500
5/20/86	2,015	1,030	3,430	2,700	260	32,330
5/27/86	2,700	1,180	4,360	3,490	595	25,500
6/3/86	460	170	1,170	1,660	640	6,500
6/10/86	1,310	710	1,570	3,430	1,980	32,000
6/16/86	1,790	1,280	2,780	10,100	1,470	10,600
6/23/86	650	260	1,000	860	274	9,070
7/2/86	480	350	1,200	1,480	530	11,000
7/7/86	810	1,220	3,150	3,130	1,160	6,160
7/14/86	1,470	1,500	2,330	4,070	770	377
7/22/86	1,640	1,010	2,700	1,170	378	694
7/29/86	348	512	702	1,420	117	47
8/5/86	378	332	1,722	2,750	292	912
8/11/86	760	640	90	1,350	170	480
8/20/86	2,100	4,000	7,600	11,000	1,500	2,800
8/28/86	550	665	2,480	290	945	700
9/8/86	490	785	2,800	1,900	298	235
9/15/86	1,320	694	1,220	3,290	672	1,300
9/22/86	419	3,100	604	2,560	101	4,970
9/29/86	1,850	1,930	4,000	3,880	320	60
10/6/86	87	126	560	650	95	2,850
10/14/86	250	680	900	1,000	110	800

(1) See Figure 1 for locations.
(2) Not sampled until 5/5/86
(3) Samples not collected due to flooding.

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1. California Code of Regulations, Title 22, Division 4, Sections 64435 and 66699.
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Successful Approach to a Superfund Site Closure

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ABSTRACT

Have you ever wondered how to close a one-square-mile Superfund site and still have money left in the bank? This task was the challenge that faced Metropolitan Dade County, Florida (County) and its consultants more than five years ago. Early estimates put closure construction costs at approximately $25 million (1985 dollars), today the estimated cost for closure is just $16 million (1990 dollars), or approximately one half the original cost estimate!

The project team accomplished this savings by dividing the site into separate zones with different potentials for contamination. Landfill and groundwater models were used to quantify the impacts of alternative closure plans. Each zone was treated separately in the closure plan and different levels of treatment were applied as appropriate. Thus, closure costs were reduced by selecting the most cost-effective, environmentally-acceptable closure alternative.

Detailed closure design plans are completed now and construction is expected to begin early in 1991. This paper describes the closure process which made this project successful.

INTRODUCTION

The Northwest 58th Street Landfill (Landfill) is a one-square-mile site located in Dade County, Florida approximately five miles northwest of the Miami International Airport. The Landfill was placed on the NPL (NPL rank 174) of potential uncontrolled hazardous waste sites in October 1981.

The Landfill is one of three NPL sites which are included in the Biscayne Aquifer Superfund Study. All three sites have caused some contamination of the Biscayne Aquifer, which is the sole source of drinking water for 2,000,000 people in the Miami-Dade area. Each site represents an operable unit of the entire remedy for this study area and a separate ROD has been issued for each site as well as for the entire Biscayne Aquifer Study Area.[1]

BACKGROUND

The Landfill is owned by the County and was the County's main disposal facility for more than thirty years. Operations at the Landfill began in 1952, with waste placed at or below the groundwater table in shallow trenches. Until it was banned in 1960, open burning for volume reduction was practiced. Daily cover of waste material was not practiced until 1975 and fires frequently occurred in the uncovered refuse.

In 1975, daily cover was applied to the waste in response to new State of Florida regulations. By this time, approximately 70% of the site had been filled with solid waste and there was little natural soil available for cover material.

Cover material had to be imported from outside sources. The cover

sources included: (1) calcium carbonate sludge from water treatment plants; (2) crushed limestone; and (3) spoil materials such as muck, limestone and sand from construction sites.[2]

The type of waste at the Landfill can be described as municipal solid waste. The Landfill also accepted liquid waste from restaurant grease traps, septic tanks and wastewater treatment plants, which were disposed of with the other wastes.

The Landfill was never operated or permitted as a hazardous waste facility, nor is there any evidence to suggest that hazardous materials were ever knowingly accepted.

Both the Florida Department of Environmental Regulation (FDER) and the U.S. EPA have worked with the County to develop final closure plans for the Landfill. The County and FDER entered into a Consent Order in June 1979. Because of widespread low to moderate groundwater contamination in the study area, the U.S. EPA placed the Landfill on the NPL in October 1981. Two public drinking water supply wellfields downgradient of the Landfill were of particular concern.

The Landfill stopped accepting wastes for disposal in October 1982 but it has never been officially closed in accordance with State of Florida regulations. The Consent Order with FDER is still in effect; however, the County must also meet the U.S. EPA's requirements. Although interim cover was provided, a final closure plan had never been implemented.

On September 21, 1987, the U.S. EPA issued a ROD for the Landfill. The ROD is concerned with on-site soil contamination, site-related groundwater contamination and downgradient private well-users. The remedy selected in the ROD requires: (1) Landfill closure in accordance with the technical requirements of Chapter 17-7 of the Florida Administrative Code (FAC, 1985), utilizing the U.S. EPA guidance document *Covers for Uncontrolled Hazardous Waste Sites* and (2) municipal water to be provided to private well-users east of the Landfill.[1]

The ROD further states that the Landfill closure will include leachate control through a combination of grading, drainage control and capping. On April 26, 1988, the U.S. EPA and the County signed a Consent Decree, which is the legal mechanism for enforcing the conditions of the ROD.

A first attempt at developing a closure plan for the Landfill in the early 1980s, treated the entire site as one unit. Plans for grading, drainage and placement of a low permeability cover were developed with an estimated construction cost of approximately $25 million (1985 dollars). However, the County decided to use a different approach to closing the Landfill, with the goals of reducing the cost and achieving an environmentally-acceptable closure plan.

In 1985, the County sold bonds which provided funds for the development and implementation of a final closure plan for the Landfill. During this same time, the County created special taxing districts to finance

plans to put the private well-users on public water supplies. Potable water service has been provided to areas downgradient of the Landfill since early 1988.

LANDFILL CLOSURE APPROACH

The County authorized the Brown and Caldwell project team to initiate work on the Landfill closure project in 1985. The project team began by reviewing existing data and previously prepared reports. During this phase of the work, the project team decided to conduct predictive landfill and groundwater modeling to quantify the water quality impacts of various landfill closure options.

Since landfilling of waste was not accomplished uniformly over the one-square-mile site, waste depth varies from 5 to 10 feet in the southern third of the site to 75 feet in the east mound. Greater potential for leachate contamination is expected from areas on the site where waste is newest and depth is greatest. Therefore, the landfill was separated into five separate zones based on waste depth and varying site characteristics.

Figure 1 shows the five zones which were identified for landfill and groundwater modeling. Zone 1, a 90-acre area, consists primarily of a relatively new 70-foot mound on the east side of the Landfill; it was found to have the strongest leachate concentrations. Zone 2 is a 78-acre area where waste disposal has not taken place. Zone 3 is 61 acres with an older, less well-defined mound than Zone 1. Zone 3 has depths of fill up to elevation 50 feet and lower leachate concentrations than Zone 1. Zones 4 and 5 are 192 and 99 acres in size, respectively, with average fill depths of 15 to 30 feet and 5 to 10 feet, respectively; and as would be expected, there are generally lower leachate concentrations in these zones. The project team required additional information in order to perform predictive modeling of landfill closure options. A data acquisition program was developed to supplement the existing data base. The types of required data can be categorized as: (1) surface and groundwater data and (2) landfill site data.[3]
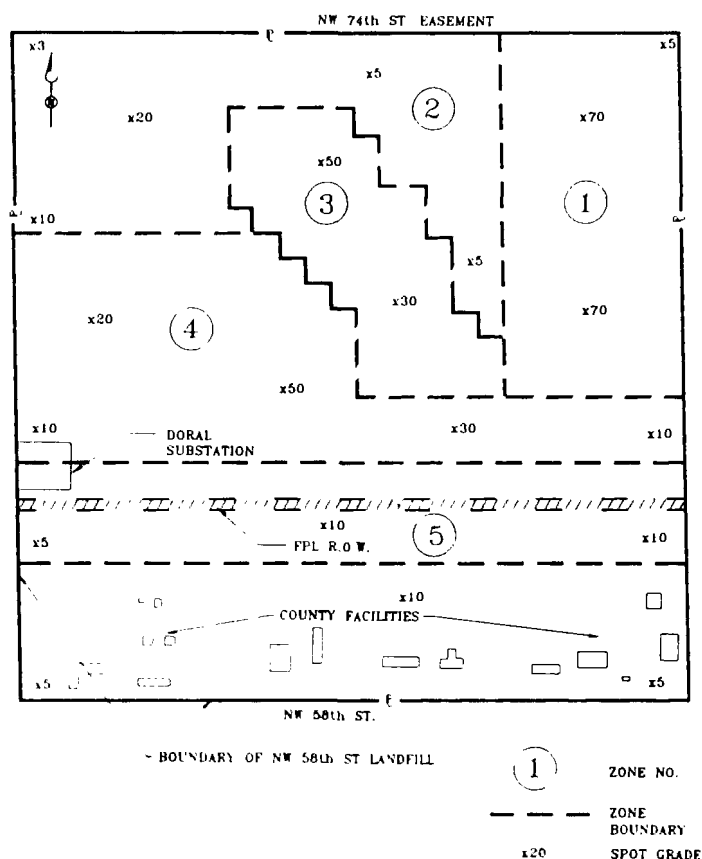
The program was designed to obtain site-specific surface and groundwater data to allow development and calibration of groundwater models. Data identified in the program included water quality, water elevation, aquifer hydraulic conductivity and aquifer thickness. The objectives of site data acquisition were: (1) to develop sufficient information to make water balance calculations, (2) to establish representative leachate quality characteristics and (3) to obtain subsurface information beneath the Landfill to adequately model leachate movement.

DEVELOPMENT OF ALTERNATIVES

During the alternatives development process, Brown and Caldwell team members used engineering judgement and site characteristics (such as topography, age of fill, depth of fill, strength of leachate and percolation rates) to develop alternatives that meet the requirements of the ROD.[4] The Hydrologic Evaluation of Landfill Performance (HELP) model was used to estimate existing percolation rates by zone. The age of fill material, by zone, was estimated based on historical aerial photographs. Leachate samples from each zone were analyzed for typical indicators of municipal solid waste and included parameters such as chloride, sulfate, ammonia, iron, lead and zinc. Leachate concentrations obtained during the data acquisition phase were used to obtain contaminant mass loading rates. Chloride was chosen as the contaminant for groundwater modeling because it is chemically conservative and does not degrade biologically over time. A decay function was developed by plotting chloride concentrations versus age of waste. A chloride loading rate for a forty-year period was then generated for groundwater modeling purposes. The forty-year period covers early site operations through twenty years beyond the closure date.

Because a cover's primary function is prevention or minimization of infiltration, it corresponds to a prevention or minimization of leachate generation from the landfill. The U.S. EPA guidance document refers to a cover that reduces percolation to some acceptable level as a "leaky roof." A cover that intercepts any water percolating toward the waste is referred to as "watertight."[5] These definitions from the guidance document were used to develop alternatives for the groundwater modeling.

The ROD requires leachate minimization through a combination of grading, surface capping and drainage control. Six closure alternatives were developed that include a wide range of "leaky" and "watertight" covers on the various zones of the Landfill. For the purposes of this evaluation, a leaky roof cover was defined as a cover that allows four inches of percolation each year to infiltrate the wastes. A watertight cover was defined as having one inch of percolation per year.[4]

ALTERNATIVES EVALUATION

The technical performances of six alternatives were evaluated with the help of two groundwater models, a flow model and a solute transport model [INTERSAT and Method of Characteristics (MOC), respectively]. The results of the modeling indicated no significant differences in the technical performances between the alternatives over the 20-year period. The greatest differences between alternatives occur during the early years after closure (up to 1995). These differences become less noticeable over time, and the results are essentially the same by the year 2010.[4] The alternatives were also evaluated based on construction costs. The closure costs for the six alternatives ranged from $10 to $30 million. The relative benefits gained by implementing each closure alternative were compared to the construction costs. Alternative 5 was selected as the most cost-effective alternative because of the relative benefits gained (in the early years after closure) per unit cost.

CLOSURE PLAN

Alternative 5 was recommended for closure of the Landfill because it is the most cost-effective, environmentally acceptable alternative. This alternative consists of improvements to Zone 1 only and includes a watertight cover on the mound; leachate interception on the east side of Zone 1, where leachate seeps exist; storm water management on Zone 1; and lateral gas migration control, where necessary. Zones 3, 4 and 5 would remain in their existing state.

Figure 1
Landfill Zones for Modeling

Alternative 5 was accepted by the U.S. EPA and FDER with several modifications. Most significantly, is the fact that storm water management is required for the entire site, not just for Zone 1. This modification was incorporated to satisfy FDER regulations. Due to the large quantity of rainfall South Florida receives annually (more than 50 inches per year), the estimated closure construction cost approximately doubled because of the large area involved. Portions of Zones 3 and 4 will receive additional calcium carbonate (water treatment plant sludge) as cover material. Calcium carbonate has a relatively low permeability which will reduce the amount of infiltration and, thus, leachate generation. Because the County receives this material at no cost, significant savings on the supplemental cover material required for Zones 3 and 4 were realized. In addition, the leachate interceptor trench (LIT) installation was accelerated to maximize its beneficial use. The regulatory agencies agreed that upon completion of the LIT, its performance would be evaluated and future actions would be recommended at that time.

Brown and Caldwell and another national firm were selected to develop design documents for construction of the closure plan in February 1988. The design team expedited the LIT design and in September 1988, a Technical Memorandum was issued that established the criteria for the LIT construction. The LIT was installed on the east side of Zone 1 during the Spring of 1989 and became operational in March 1989.

Pump tests were performed in November, 1989 on the LIT pump station so that flowrates could be estimated. Calculations utilizing the test data estimated the volume of intercepted leachate at approximately 5.8 million gallons per year. A leachate mass balance analysis was performed and a Technical Memorandum was issued in December, 1989.[6] This analysis evaluated the performance of the LIT and recommended a revised closure plan consisting of a reduced watertight cover on Zone 1. All other aspects of the closure plan remained the same. The U.S. EPA and FDER accepted the revised plan early in 1990. The final closure plan, which is shown in Figure 2, consists of a synthetic cap on the top portion of the mound in Zone 1. The area covered by the synthetic is approximately 20 acres. The remainder of Zone 1 (approximately 70 acres) will be covered with two feet of compacted, crushed limerock. By reducing the area covered with a synthetic material, approximately $2 million was saved.

The design utilizes Zone 2, which has never been filled with waste, as a storm water retention basin. The design includes channels, closed conduits, culverts, roadside ditches, benches and site grading to convey storm water to the retention basin. The construction cost is estimated at approximately $16 million dollars for this 520-acre Superfund site.

CONCLUSION

The County was able to realize substantial savings on the Landfill closure by using an approach that divided the site into five separate zones. Landfill closure alternatives that treated the zones separately were developed and evaluated. The modeling results showed no significant differences between the alternatives at the end of a twenty year period. Therefore, the most cost-effective, environmentally-acceptable alternative focused on the zone with the greatest potential for groundwater contamination.

Finally, this project was made successful through good communications between the County, FDER and The U.S. EPA. As data became available, they were interpreted, shared among all parties and incorporated into the final closure plan.
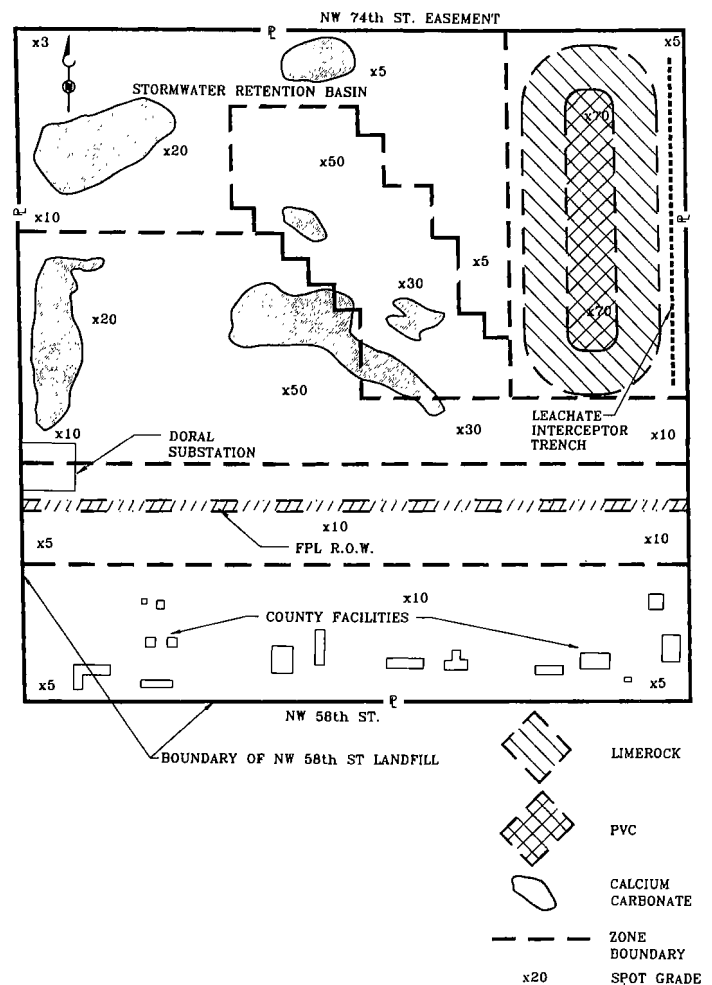
Figure 2
Landfill Closure Plan

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4. Brown and Caldwell. *58th Street Landfill Closure Alternatives Evaluation. Final Draft Report.* June 1988
5. U.S. Environmental Protection Agency. *Covers for Uncontrolled Hazardous Waste Sites.* EPA/540/2-85/002, U.S. EPA, Washington, DC, September, 1985
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Using a Computer-Assisted Site Evaluation System: A Case History

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ABSTRACT

A computer workstation dedicated to characterization and remedial action assessment of uncontrolled hazardous waste sites has been developed. The IBM-PC compatible system is composed of several off-the-shelf software and hardware modules, with software development limited to the creation of utility programs used to transfer data from one software module to another. The component modules include a Geographic Information System, a Data Base Management System, a Computer Aided Design and Drafting System, a Contouring System, a Volume and Mass Calculation System and a Groundwater Modeling System.

The computer system is intended to produce maps and cross sections of the geology, hydrology and distribution of contaminants from data attained at boreholes and sample pits. It is capable of calculating volumes or masses of contaminated material, as well as modeling groundwater flow and contaminant transport.

As part of the development of the system, commonly used interpolation methods were compared to find out which methods are most suitable to use for site characterization. Four surfaces were created to simulate possible plumes at contaminated sites. The plumes were randomly sampled, and the samples were interpolated using 15 different methods. The volumes of the interpolated plumes were then compared with the known volumes of the original plumes.

The system has been implemented in studies of several Superfund sites and Emergency Response sites throughout the United States. The application of this system to the study of a Superfund site in Massachusetts is described.

INTRODUCTION

Data from hazardous waste sites often are collected by several contractors and reported as tables buried in thick reports. The site managers are overloaded with laboratory analyses of contaminants, boring logs, monitoring well logs and survey instrument readings. There is a need to organize and manage these data and present them in easily-understood graphical form.

Beginning in 1986, a project was initiated at the University of Cincinnati to address this problem. The project was centered on the concept that inexpensive, easy-to-use IBM-PC type computer equipment and readily-available commercial and public domain software could be molded into a system useful for waste site characterization. The project was funded by the U.S. EPA, Office of Research and Development, Risk Reduction Engineering Laboratory, in Cincinnati, Ohio. Work is based at the U.S. EPA Center Hill Solid and Hazardous Waste Research Facility, in Cincinnati.

The Computer Assisted Site Evaluation (CASE) system continues to develop and evolve as required by the needs of investigators of con-taminated sites. The specific software and hardware components have changed as new capabilities became available. The results of the interpolation study described in this paper, for example, will enhance the capabilities of the system. The ongoing process of upgrading the CASE system has been concurrent with the application of technical assistance services for U.S. EPA regional offices, other government agencies and contractors.

In the following paper, the current configuration of the system is described, a comparison of different interpolation methods relevant to waste site characterization is discussed, and the application of the system in a recent case is presented.
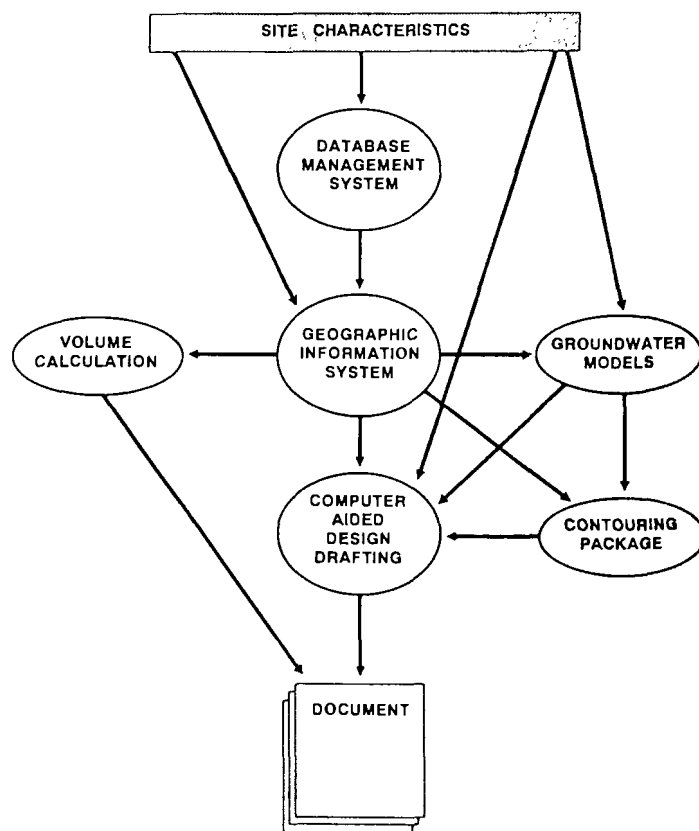
Figure 1
Information Flow Through the CASE System

SYSTEM DESCRIPTION

The system hardware is based on IBM-PC compatible 20 MHz 386 and 12 MHz 286 computers. These machines are equipped with hard disks having capacities of 100 megabytes or more. Core memory capacities range from two to four megabytes of RAM. Standard VGA color graphics monitors are used for display.

Two digitizing tablets are available for input. A 12-in. by 18-in. tablet is used for command templates, freehand drawing and digitizing small maps. A larger 36-in. by 48-in. digitizer tablet is used for entering large maps.

Output devices include a 24-in. by 36-in. multipen drafting plotter, a laser printer, a wide dot matrix printer and a screen camera.

System software is composed of several types of commercial and public domain packages linked with file conversion utilities (Fig. 1). Data transfer linkages are built into some of the packages, such as DXF conversions that permit the contouring package to transfer files to the Computer Aided Design and Drafting (CADD) package. In other cases, small utility programs were developed to facilitate data transfer.

Site characteristics, such as results from soil and water analyses or water levels, are entered into a data base tailored for site characterization. We use the Borland REFLEX Data Base Management System (DBMS). This DBMS, though not as powerful as top-of-the-line packages, is easy to use and capable of meeting all the needs of the project. Since the data base is interactive, rather than programmed and compiled, data files can be extracted, graphs and tables can be created and modifications can be made to the record structure by means of point-and-click operation.

The Geographic Information System (GIS), Spatial Information Systems pMAP, serves as the core of the CASE system. pMAP is a cell-based GIS that is easy to use and well suited for small site studies. It provides an extensive command set that permits precise control of map manipulation. Repetitive operations are facilitated through the use of macros. The GIS is used to create a three-dimensional model of the site hydrogeology. Cross sections showing the geology and hydrology are extracted from this model and ported to the CADD for rendering. The GIS also is used to create contaminant maps, where a spectrum of color hatching indicates level of contamination and black stipple indicates areas where reliable data are unavailable.

Several contouring packages are available for use with the system. Most often we use Golden Software SURFER to make conventional contours, then port the file to the CADD for annotation and final rendering. Radian CPS/PC is used for more elaborate diagrams, and U.S. EPA GEO-EAS is used when kriging is required.

For calculation of volume or mass of contaminated material, a program was developed to work with the GIS to integrate the volume under a surface. SURFER and CPS/PC are also capable of volume calculation.

Groundwater flow and contaminant transport can be modeled using several public domain or commercial packages, depending upon the site requirements. Groundwater modeling within the CASE system typically is done using analytical models and preliminary numerical models. The U.S. Geological Survey MODFLOW numerical modeling system, coupled with the MODELCAD preprocessor, is most often used.

All of the graphical output from the CASE system goes to a CADD system for final production. Three-dimensional drawings are rendered in the Computervision Personal Designer CADD system, whereas two-dimensional drawings are rendered in Generic Software CADD Level Three. These two systems are being superseded by Autodesk AutoCAD 386 version 10.

COMPARISON OF INTERPOLATION METHODS

Many maps, such as those depicting water level, aquifer thickness or distribution of contaminants, are generated by interpolating between a limited number of data points obtained from borings or wells. Computer interpolation programs often are used to generate a regularly-spaced grid of data from irregularly-spaced sample points. There are several interpolation methods available, and each method has several parameters that affect details of the interpolation. Many combinations of parameters are possible for the various methods, resulting in a huge number of possible interpolation schemes. Each possible scheme can produce a unique interpolation, so a large number of different maps could be produced from the same data set.

Selecting the most accurate interpolation method for a given situation is a problem that has been studied in several contexts. In the field of hydrology, comparative studies of interpolation methods have been done with water table elevation data,[1] precipitation data,[2] and aquifer transmissivity data.[3] These studies deal with spatially distributed data that vary gradually, in a "continuous" manner. In contrast to the forgoing studies, contaminant concentration data often consist of a small number of samples having a wide range in value including possible zero values. These data are relatively "discontinuous" and are, thus, more challenging to interpolate accurately.

Because different interpolation techniques can produce considerably different maps for the same set of data, and costly errors can be incurred if inaccurate maps are used for contaminated site characterization, it is important to select appropriate interpolation methods. Therefore, as part of the development of the CASE system, a comparative study of interpolation methods in the context of sparse, discontinuous data sets was initiated.

The objectives of the study were: (1) to measure how accurately various interpolation techniques reproduce a known surface (such as a simulated contaminant plume) by comparing the calculated volumes below the interpolated data fields with the known volumes below the actual fields; (2) to rank the interpolation methods according to their overall accuracy; and (3) to examine how the number of points used in the data sets affects the accuracy of the interpolation.

The following interpolation techniques were evaluated:

- Linear weighted average
- Inverse distance-to-a-power
- Minimum curvature
- Kriging
- Least squares
- Projected (tangential) slope
- Convergent (multi-snap)

Most of the methods require the specification of parameters, such as search radius, extrapolation distance or inverse distance power, all of which can affect the results of the interpolation. Default values for interpolation parameters were used in most instances since the average user is likely to accept the default values and because we needed some rationale to limit the large number of possible combinations of interpolation parameters. Several methods were tested using parameters that differed from the defaults. Fifteen examples of the possible permutations were evaluated in this study.

Four software packages were used to perform the 15 interpolation

Table 1
Key to the Interpolation Methods Used

Packages	Labels	Methods
SURFER	SURK	kriging (linear model)
	INV2	inverse-distance 2nd power
	INV3	inverse-distance 3rd power
	INV4	inverse-distance 4th power
	INV5	inverse-distance 5th power
	SUR6	inverse-distance 6th power
	SURM	minimum-curvature
CPS/PC	RAD1	least-squares (search radius 65 using 10 nearest neighbors)
	RAD2	least-squares (search radius 40 using 8 nearest neighbors)
	RADPS1	projected-slope (search radius 65 using 10 nearest neighbors)
	RADPS2	projected-slope (search radius 40 using 8 nearest neighbors)
	CONV	convergent (multi-snap)
GEO-EAS	GEO	kriging (ordinary, block, fitted models)
pMAP	PMAP	linear, weighted (search rad. 15 using 4 nearest neighbors)
	PMAP2	linear, weighted (search rad. 25 using 6 nearest neighbors)

schemes. These include three commercial packages, Golden Software SURFER version 4.0, Radian CPS/PC version 4.1, and Spatial Information Systems pMAP version 2.6, and one public domain package developed for the U.S. EPA, GEO-EAS version 1.0. A key to the 15 methods is listed in Table 1. The PMAP method differs from the others; it uses a macro program interfaced with a GIS to control the interpolation.

Methodology

Four surfaces labeled B, C, D and P were generated to simulate possible contamination plumes.
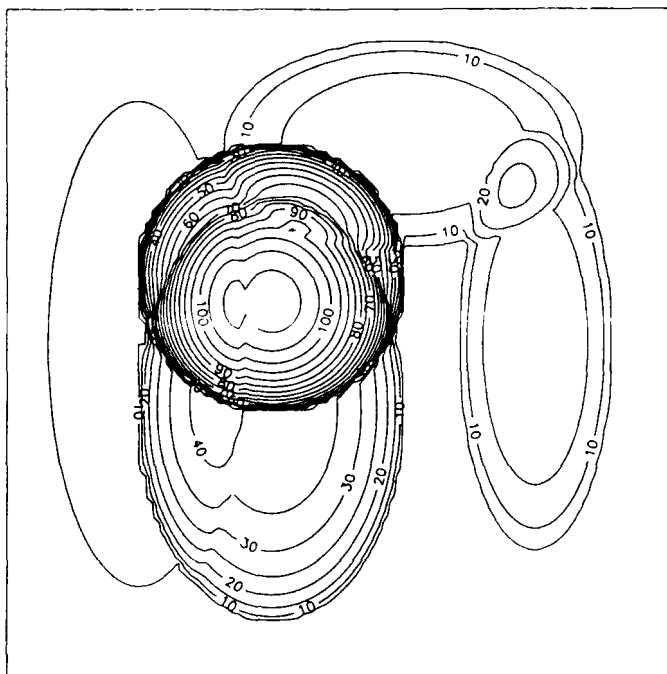
Figure 2
Idealized Geometric Polynomial Surface B
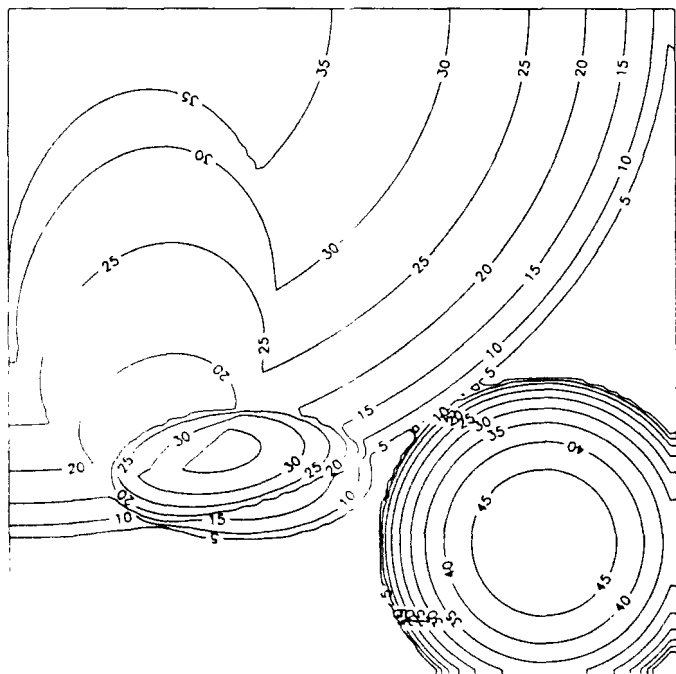
Figure 3
Idealized Geometric Polynomial Surface C
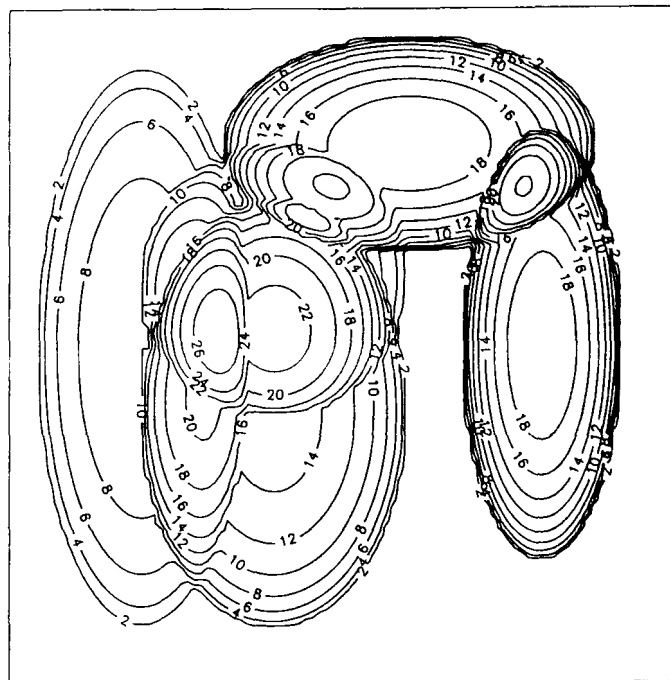
Figure 4
Idealized Geometric Polynomial Surface D
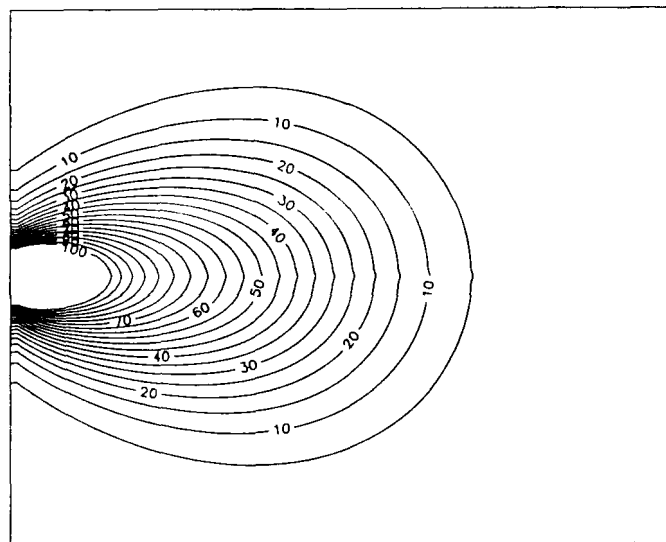
Figure 5
Idealized Contaminant Plume Surface P

Surfaces B and D represent geometric polynomial forms generated by superimposing hemi-ellipsoids of various aspect ratios (Figs. 2 and 3). Surface D differs from B in the amplitude of several of the hemi-ellipsoids (one of the hemi-ellipsoids on the B surface is 8 times higher than on the D surface). Both surfaces B and D are bordered by areas of zero values. Surface C was also generated by superimposing hemi-ellipsoids of varying aspect ratios, but it is bordered partly by zero values and partly by finite values and it is more uniform than surfaces B and D (Fig. 4).

Surface P represents an idealized contaminant plume (Fig. 5). This surface was generated using an analytical solution for the concentration distribution downgradient from a point source having a continuous release rate. The shape of the plume is affected by lateral and longitudinal dispersion in a uniform flow field. The elevation of the P surface tapers gradually toward its edges. Most of the surface is bordered by small,

nonzero values that are less than the resolution of the contours in Figure 5. Thus, surfaces B and D are completely bordered, whereas C and P are only partly bordered by zero values.

Volumes below the B, C and D surfaces were calculated exactly by spatial integration, whereas the volume below surface P was determined by integrating the release rate with time. All the surfaces were discretized into regularly-spaced 100 x 100 grids. One hundred points were selected from each grid using a randomizing algorithm. Data sets were in (x,y,z) format with z representing magnitude at location (x,y). From these 100-point data sets, six subsets were obtained consisting of the first 5, 15, 25, 35, 50 and 75 points.

Task 1

Surfaces were generated from each of the 25-point data sets (PR25, BR25, CR25 and DR25) using the 15 interpolation methods. Data sets with 25 points were selected because waste site data sets often contain 25 or fewer samples, but the expected errors in maps created with fewer than 25 samples are so large that comparing interpolation methods would be meaningless. The grid files generated from each interpolation program were numerically integrated to calculate the volume beneath the interpolated surfaces. The resulting volumes were normalized using the actual volumes, with the results shown in Figures 6-9.

Task 2

The absolute values of the errors for the four surfaces generated from the 25 point data sets were averaged for each interpolation method. This average error was used to provide an empirical ranking of the accuracy of the interpolation methods (Fig. 10).

Task 3

Six representative interpolation methods were used to determine the relation between the number of sample points available for interpolation and the accuracy of volume prediction. Normalized volume was plotted as a function of number of points in the data set for each of the four surfaces (Figs. 11-14).
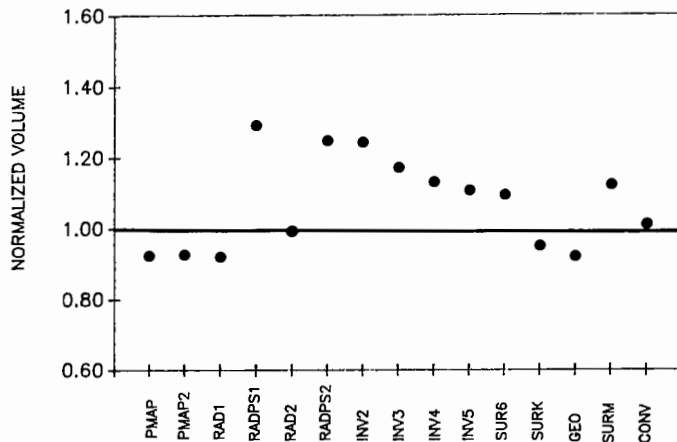
Figure 8
Normalized Volumes For Interpolated Surface D
Using 25 Point Data Sets

Figure 6
Normalized Volumes For Interpolated Surface B
Using 25 Point Data Sets
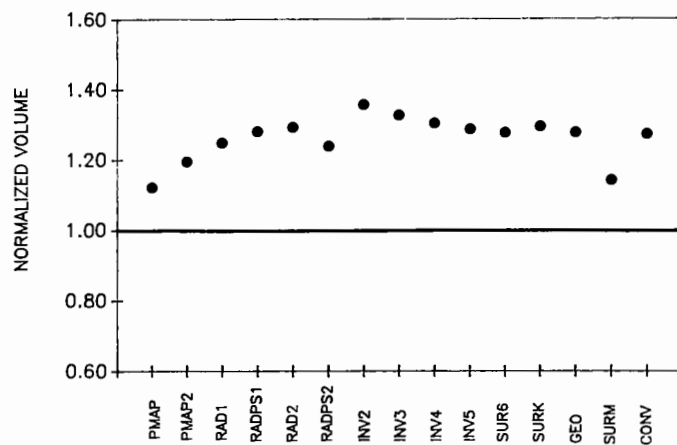
Figure 9
Normalized Volumes For Interpolated Surface P
Using 25 Point Data Sets

Figure 7
Normalized Volumes For Interpolated Surface C
Using 25 Point Data Sets
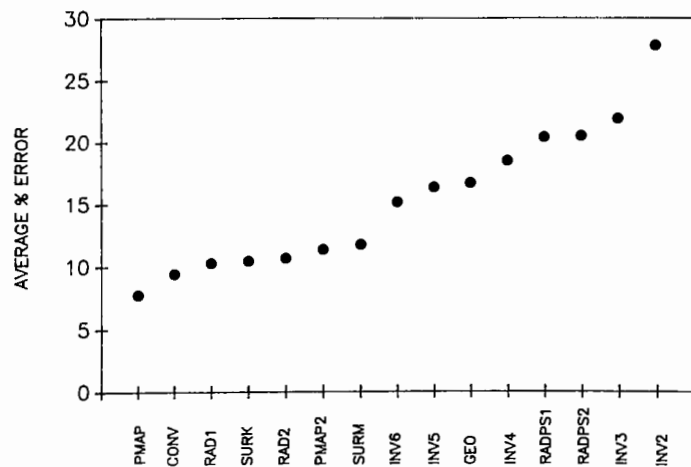
Figure 10
Average Percent Error in Calculated Volumes
For Each of the 15 Interpolation Routines
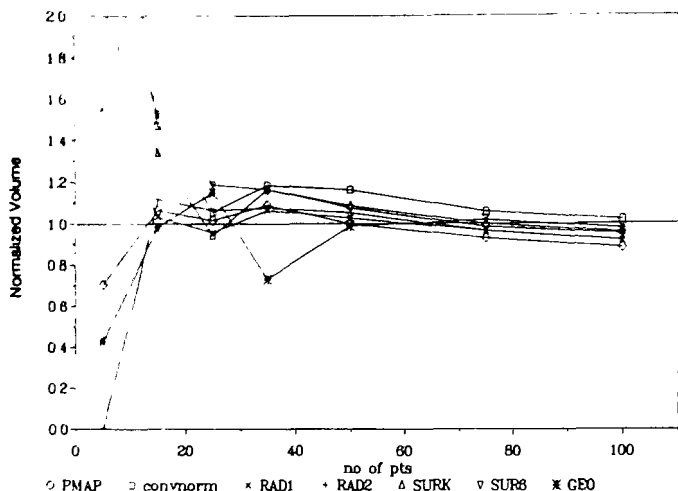
Figure 11
Normalized Volume as Function of Number of
Sample Points For Surface B
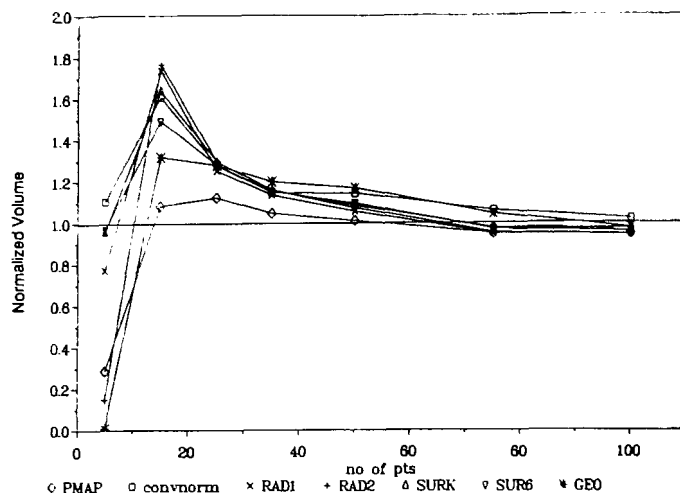
Figure 14
Normalized Volume as Function of Number of
Sample Points For Surface P
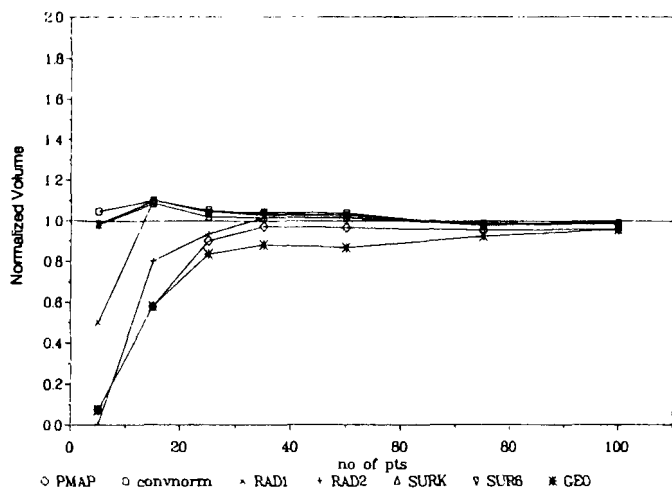
Figure 12
Normalized Volume as Function of Number of
Sample Points For Surface C
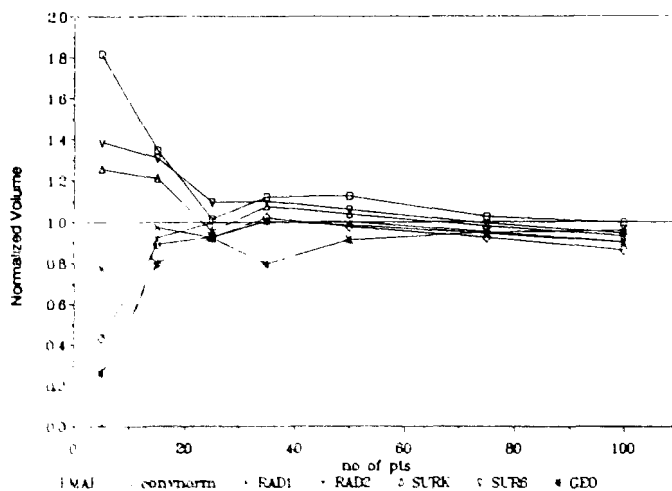
Figure 13
Normalized Volume as Function of Number of
Sample Points For Surface D

Study Conclusions

Volume estimates using the 25 point data sets typically overestimate the actual volumes, although there are some significant differences among the various methods and surfaces (Figs. 6-9). For example, the volume of the P surface is consistently overestimated by all the interpolation methods; normalized volume ranges over a factor of 0.23, from 1.12 using PMAP to 1.35 using INV2 (Fig. 9). Normalized volumes beneath the B and D surfaces (Figs. 6 and 8), however, span a relatively large range, from roughly 0.9 to 1.1 for several interpolation methods (PMAP, CONV, least-squares and kriging) to markedly overestimated volumes (1.25 to 1.5) for other methods (minimum curvature, inverse distance and projected slope). In contrast, volume under the C surface is estimated reasonably well using all the interpolation methods (Fig. 7).

The shape of a surface clearly affects how accurately it can be determined by a particular interpolation method. Our results are limited, of course, to only four surfaces, but it seems that volumes are overestimated when the surfaces are bordered by zeros, as in surfaces B, D and P. Moreover, topographic irregularities appear to result in a wide range of volume estimates, as indicated by results from the highly-irregular B surface. Some interpolation methods, including CONV, PMAP, least-squares and kriging, appear to estimate the volume under the irregular surfaces better than other methods. These observations could be significant because surfaces representing contaminant distributions are expected to be bordered by zero values and possibly highly irregular.

The averaged absolute error of estimated volume ranges from 8 to 28% for various interpolation methods using the 25-point data sets. The PMAP algorithm yielded the least error, although six methods yielded errors that are less than 13% (Fig. 10). Some methods that are highly accurate using one surface are relatively inaccurate using another surface. Only two methods, RAD1 and CONV, were among the most accurate half of the methods for all four surfaces. The PMAP, SURM and SURK each yielded at least one volume estimate that was relatively inaccurate (e.g., surface C for PMAP and surface B for SURM), although on average those methods were among the most accurate (Fig. 10).

In general, the accuracy of the volume calculation increases with the number of sample points (Figs. 11-14). In all four cases, the rate of improvement is large as the number of points increases to roughly 30. Further increases in the number of points improves the accuracy, but the rate of improvement diminishes markedly as the number of points increases from fewer than, to more than 30. Nearly all the interpolation methods yield volume estimates between 0.8 and 1.2 when using 30 points, whereas they are roughly between 0.9 and 1.1 when using 100 points.

The estimated volume may decrease, increase or increase and then decrease, as additional data points are used during interpolation. The particular response probably depends on both the shape of the surface and the locations of the points. This type of behavior has relevance to site assessment, in that changes in the mass estimated in a contaminant plume at various times may be an artifact of a different number of samples available at the different times, rather than an effect of remediation, continued contaminant release, biotransformation or some other process.

Discussion

Among the methods of interpolation used in this study, the CONV method (Radian CPS/PC Convergent Multi-Snap) performed above average on all four test surfaces and had the best overall accuracy for the 100-point data sets (within 2% of actual volume). The CONV method was fairly easy to use and the time of execution was rapid.

The PMAP method was, on average, the most accurate method using the 25-point data sets; however, it underestimated the volume of the 100-point data sets by as much as 15%. This method is flexible, since the macro program that controls the interpolation process can be adjusted. Learning how to run the pMAP program and write the macros is relatively time-consuming, however, and the execution speed is relatively slow.

SURFER methods in general tended to be the easiest to use and fastest programs to run. The SURM method was the most accurate using the CR25 data set and ranked second for the PR25 data set. However, the inverse-distance methods were the least accurate for the PR25 and BR25 data sets.

Although kriging is a popular and powerful interpolation method, we found that the kriging methods were far from the most accurate at volume prediction and can be tedious to use. The U.S. EPA GEO-EAS program requires a trial-and-error model fitting procedure which

is time-consuming to learn and slow to execute. The SURFER kriging method, since it assumed a linear model, is easy to use and usually was more accurate than the GEO-EAS method.

CASE STUDY OF A SITE

The system has been used in several case studies at Superfund sites and Emergency Response sites throughout the United States. The most recent application of the system has been to a Superfund site in Massachusetts.

The site has a history of hazardous waste dumping dating back to 1946. Eight identifiable sludge pits fall within two main disposal aréas, occupying approximately four acres of land (Fig. 15). The sludge contains high levels of toxic metals and is believed to represent untreated products from leather tanneries and other nearby industries. In addition to the sludge pits, an old landfill, a fly-ash pile and several piles of debris have also been identified on the site. To assist in the Treatment Technology Review, our work has involved extracting and summarizing the relevant analytical data from the Remedial Investigation reports in order to present the data to the Superfund Technical Assistance Branch technology team and the site coordinator in a meaningful, concise manner.

For the study, a series of maps and graphs was prepared which presents the distribution of metals, VOCs, semivolatile organic compounds (SVOCs), pesticides and PCBs found in the sludge pits and debris piles at the site.

Contaminant concentration maps were created which show the distribution of total volatile organics (TVOCs) over the site (Fig. 16). A spectrum of five colors of crosshatching is used to indicate levels, or ranges, of contamination. An important feature of this map is the
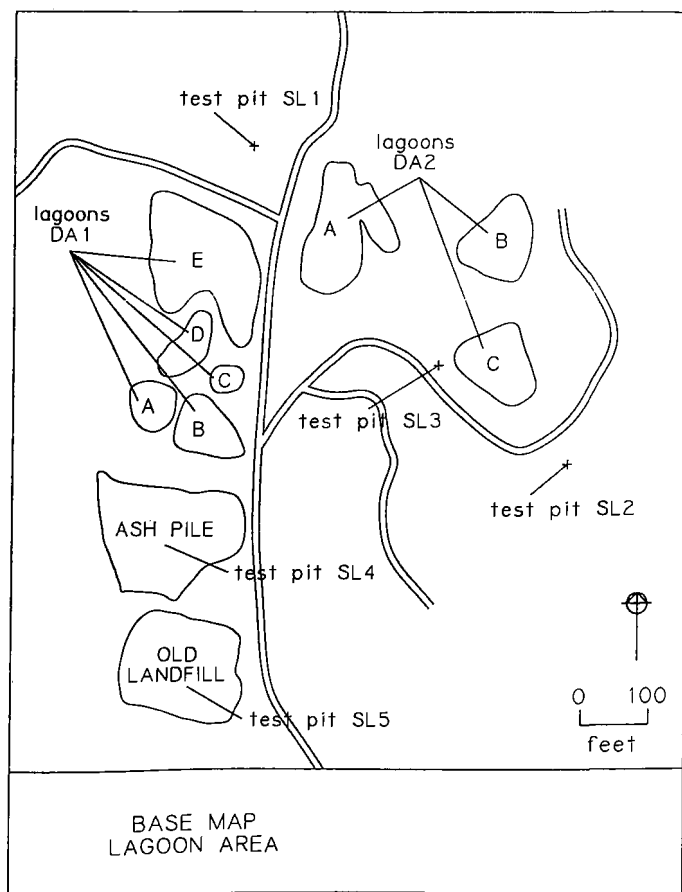
Figure 15
Site Map
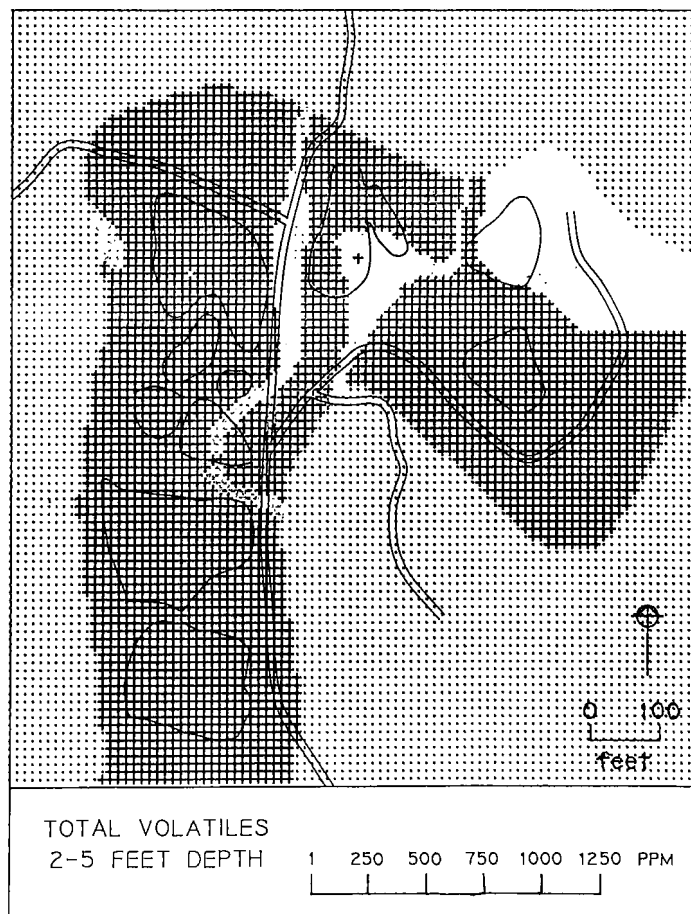
Figure 16
Map of Contaminant Distribution.
Concentrations Are Designated By Color On The Original Map

stipple pattern used to indicate masked areas where extrapolation is unwarranted. Maps were created for three different depth intervals. Figure 16 is an example of a color-coded TVOC map for the interval of 2 to 5 ft.

A second type of concentration map prepared for the study makes use of a logarithmic-scaled histogram to depict the maximum available
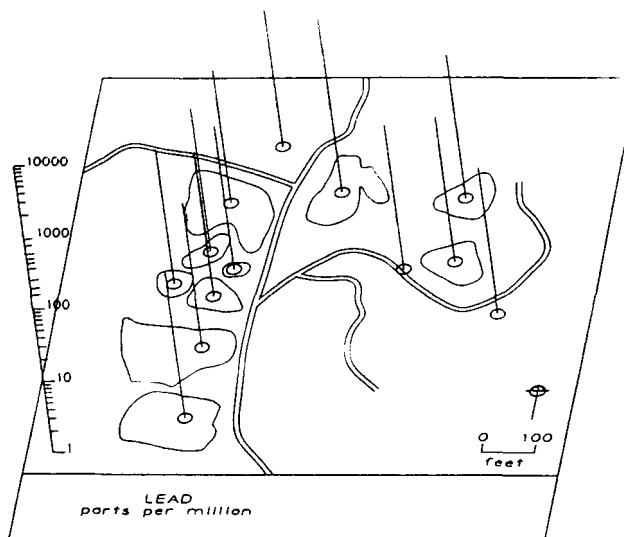
Figure 17
Contaminant Histogram Keyed To Site Layout Map
Histograms Are Color-Coded On Original Maps

concentration of specific metals within each sludge pit and debris pile. An example of this type of map is illustrated in Figure 17, which shows the distribution of lead contamination in ppm units. The histograms are color-coded for easier interpretation and are superimposed on an isometric view of a site map. This type of map is useful in instances where data are sparse and there is reason to believe that interpolation between samples is unwarranted, as in the case of the metals data collected from different sludge pits.

A third type of map created for the study (Fig. 18) uses pie-shaped symbols superimposed on the site map to indicate qualitatively the presence or absence of VOCs, SVOCs, metals and pesticides at locations north of the main disposal areas. A shaded quadrant indicates that the compound was detected.

In addition to the maps mentioned above, tables and graphs were prepared showing the variation in concentration for specific metals and TVOCs both within individual sludge pits and between pits and other sampling areas. Tables were prepared showing the maximum and average concentrations of SVOCs, PCBs and pesticides at the various sampling locations.

The examples given here for the case study do not utilize all the capabilities of the CASE system. The requirements for understanding a site are evaluated for each case, and suitable tools available to the CASE system are applied and developed as necessary. A case study that involved hydrogeologic cross sections and groundwater modeling is described in an earlier paper.[4]

CONCLUSION

A set of computer hardware and software tools has been assembled into a system dedicated to aid in the waste site characterization and
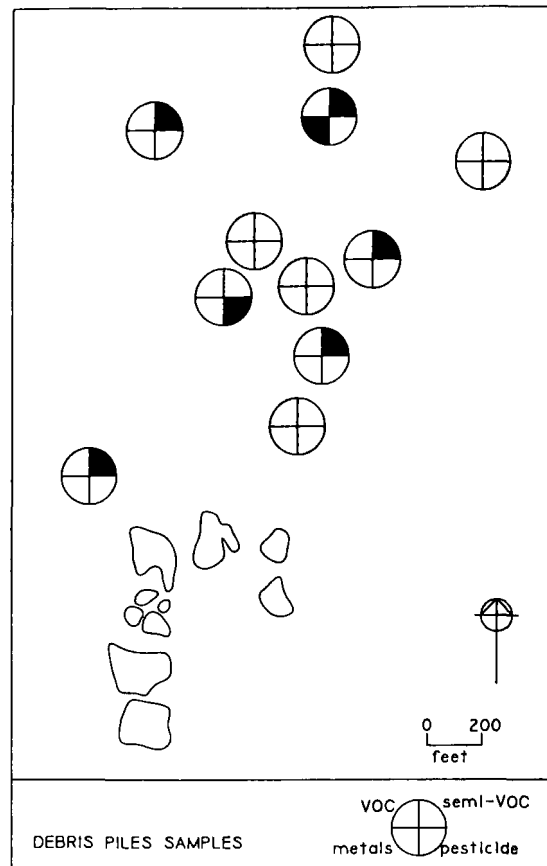
Figure 18
Detected Contaminants At Off-Site Debris Piles
(Shaded Quadrants Indicate Contaminants Present)

remedial action selection process. During the development of this system, a study of interpolation methods was completed to identify methods suitable for use on waste site data sets. The system has been successfully applied to several sites and although the system continues to evolve, it is currently able to supply services on a regular basis.

DISCLAIMER

The mention of names of commercial products was necessary for the purposes of the paper, but it does not constitute an endorsement of those products by us or by the U.S. EPA. The conclusions expressed are solely the authors'. This paper has not been reviewed or approved by the U.S. EPA.

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Thermal Treatment of Oily Soils and Sludges

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INTRODUCTION

There has been a substantial increase in the costs and liabilities associated with off-site disposal of hazardous wastes in the recent years. At the same time, environmental regulations have imposed demanding requirements for acceptable treatment technologies which emphasize waste reduction and recycling in addition to stringent treatment levels. A number of technologies and processes have been developed in the past 1 - 2 years which attempt to address these requirements. Most significant among them are: cement-kiln incineration, thermal desorption, solvent extraction and biodegradation.

This is a brief review of a thermal desorption process applied to hazardous waste treatment. It is based on ReTeC's thermal desorption process that has been used effectively in treating solids and sludges contaminated with organic constituents. The process uses a conventional Holo-Flite^R thermal desorption unit with ReTeC's proprietary modifications, using an indirect heating source.

The thermal desorption process has been shown to be effective for waste minimization, or as a final treatment option to meet the Best Demonstrated Available Technology (BDAT) standards for a variety of wastes contaminated with organic compounds which are subject to the U.S. EPA imposed Land Ban restrictions.

The benefits of this process are:

- Effective for the treatment and mass reduction of a wide range of organic wastes
- Meets BDAT standards for refinery wastes
- Recovery and recycle of organic components
- Reliability and simplicity of operation
- Low capital and operating costs
- Exempt from RCRA permitting due to recovery and recycling of the organic components of the waste
- Safety and environmental acceptability

PROCESS DESCRIPTION

Thermal desorption is the separation of contaminants from a solid matrix through volatilization. Volatilization may be assisted by adding a stripping agent such as steam or an inert gas.

The complete process consists of the following operations: feed preparation and handling, thermal desorption, off-gas treatment, condensate and treated solids handling (Fig. 1).

Feed Preparation

The configuration of the feed preparation and handling system is strongly dependent on the feed and location. It generally is cheaper to remove free liquids by mechanical means rather than volatilization. Therefore, if the feed contains significant amounts of free liquids, it should be filtered before treatment in the desorber. The feed then is

screened to remove particles larger than 1 to 2 inches, depending on the size of the thermal unit. The feed may be conveyed to the thermal unit by mechanical or pneumatic conveyers, feed hoppers, rotary airlocks and other equipment and devices depending on the type of feed and local requirements.

Thermal Desorption

Desorption can be accomplished using different types of directly or indirectly fired equipment. Applications using indirectly fired methods are preferred, since they generate a significantly smaller volume of off-gas than the traditional direct-fired systems. As a result, the capital and operating costs for the system are reduced significantly.

ReTeC uses an indirectly heated thermal desorption/dryer system, the Holo-Flite^R Screw Processor, such as the unit manufactured by Denver Equipment Company, Colorado Springs, Colorado. Hundreds of these heaters have been installed for heating or cooling service throughout the world since the 1950s.

The Holo-Flite^R Processor is commonly used to heat, cool or dry bulk solids/slurries (Fig. 2). The treatment system consists of a jacketed trough which houses a double-screw mechanism. The rotation of the screws promotes the forward movement of the material through the processor. The augers are arranged in the trough so that the flights of the
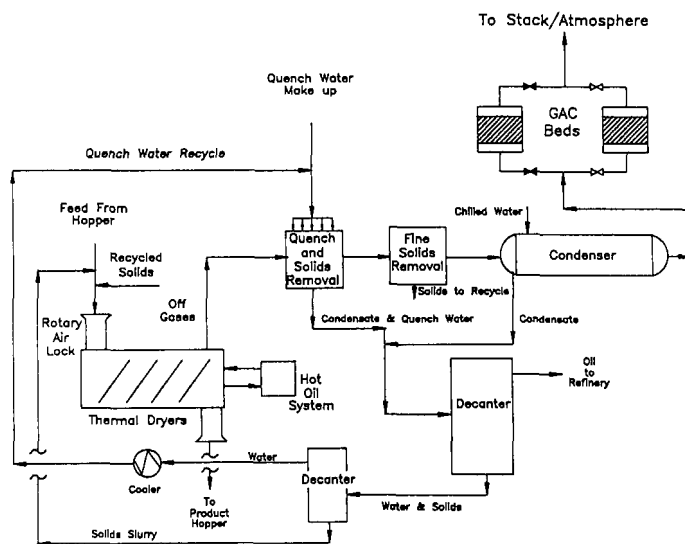
Figure 1
Block Flow Diagram
Dryer System

two screws mesh, facilitating the movement of material and improving heat transfer.

Figure 2
Orientation of Screw Augers

The processor uses a contained, noncontact circulating heat transfer fluid to raise the temperature of the solids/sludges being treated. The heated medium continuously circulates through the hollow flights of the screw augers, travels the full length of the screws and returns through the center of each shaft to the heater (Fig. 3). The heating fluid is also circulated through the trough jacket to provide additional heat transfer surfaces for improved volatilization.

Figure 3
Holo-Flite Processor

In ReTeC's application of this technology, molten salt may be used as the heating fluid in place of hot oil or steam. Molten salt has the

following advantages:
• It is nontoxic and nonflammable
• It does not produce off-gases
• It provides a wide range of operating temperatures, 500-950 °F
• It can easily be cleaned up if spilled

ReTeC has been successfully operating a 1,000 lb/hr thermal desorption unit (Fig. 4) for a number of months utilizing molten salt as the heating medium.
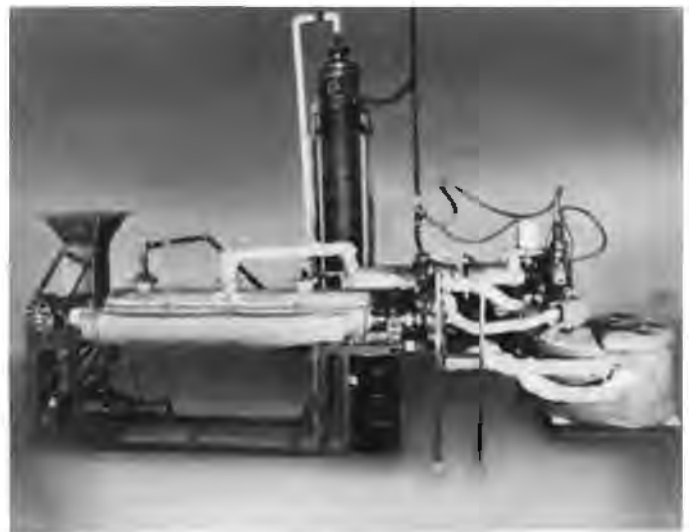
Figure 4
ReTeC's 1000 lb/hr Demonstration Unit

With the support of the vendor of the thermal unit, several proprietary improvements in the standard Holo-Flite® process have been incorporated that substantially increase its efficiency and improve its overall economy. In addition to the use of molten salt, these improvements include the introduction and distribution of an inert stripping gas and improved contacting between the solids, stripping gas and heating surfaces.

Off-gas Treatment

The off-gases leaving a thermal unit generally consist of water vapor, volatilized organics, noncondensable gases and solids. To limit any fugitive emissions, the thermal desorption unit operates at a slight vacuum. Therefore, regardless of whether or not any inert gas is added, some noncondensable gases always will be in the off-gases. Management of these off-gases is a critical factor in the overall treatment process.

Depending on the configuration of the thermal desorption unit, the moisture content and the amount of noncondensable gases, some fine solids are carried over in the off-gases. Therefore, the off-gas treatment is designed to remove solids and VOCs from the noncondensable gases before their discharge.

The off-gas treatment system should be designed with enough flexibility to remain effective in case of process upsets or, more commonly, wide variations in the waste feed. This system typically consists of: gravity settlers, cyclones, filters and solid scrubbers to remove solids; quench drums and coolers to cool the off-gases and condense water and semivolatile organics; and chillers and activated carbon units to remove volatile organics. The treated noncondensable gases can then be discharged to the atmosphere through an activated carbon bed, to the plant's flare or boilers.

Condensate Treatment

Condensate is generated from the moisture content of the feed and quench water. It contains condensed organics in addition to small amount of suspended solids. The bulk of the organics and solids can be separated

by simple gravity settling. The remaining water stream is generally suitable for disposal in a plant's wastewater treatment facility. If quench water is used, the wastewater stream may be further cleaned by filtration, cooled and recycled to be reused as quench water.

TREATMENT RESULTS

The results from a number of tests indicate that the process has significant potential not only for waste minimization but also for the management and treatment of contaminated soils and sludges. ReTeC has per-

Table 1
Typical Mass Reductions in Thermal Dryers

CONTAMINATED SOILS	15 - 25%
REFINERY FILTER CAKE	40 - 60%
API SEPARATOR SLUDGE	60 - 70%

Table 2
Treatment Results - Refinery Vacuum Filter Cake (A)

COMPOUND	ORIGINAL SAMPLE (PPM)	TREATED SAMPLE (PPM)	REMOVAL EFFICIENCY (%)
NAPHTHALENE	<0.1	<0.1	
ACENAPHTHYLENE	<0.1	<0.1	
ACENAPHTHENE	<0.1	<0.1	—
FLUORENE	10.49	<0.1	>98.9
PHENANTHRENE	46.50	<0.1	>99.3
ANTHRACENE	9.80	<0.1	>96.6
FLUORANTHRENE	73.94	<0.1	>99.8
PYRENE	158.37	<0.1	>99.9
BENZO(b)ANTHRACENE	56.33	1.43	97.5
CHRYSENE	64.71	<0.1	>99.9
BENZO(b)FLUORANTHENE	105.06	2.17	97.9
BENZO(k)FLUORANTHENE	225.37	3.64	98.4
BENZO(a)PYRENE	174.58	1.89	98.9
DIBENZ(ab)ANTHRACENE	477.44	10.25	97.8
BENZO(ghi)PERYLENE	163.53	5.09	96.6
INDENO(123-cd)PYRENE	122.27	4.16	96.6

Treatment Temperature: 450°F

Table 3
Treatment Results - Refinery Vacuum Filter Cake (B)

COMPOUND	ORIGINAL SAMPLE (PPM)	TRADITIONAL CONFIGURATION (PPM)	WITH RETEC MODIFICATIONS (PPM)
NAPHTHALENE	56	12	1.9
2-METHYLNAPHTHYLENE	940	73	3.1
ACENAPHTHENE	110	14	0.6
FLUORENE	160	23	0.6
PHENANTHRENE	930	270	13
ANTHRACENE	120	34	1.2
FLUORANTHRENE	46	21	1.3
PYRENE	210	92	4.7
BENZO(b)ANTHRACENE	67	29	1.2
CHRYSENE	81	47	2.6
BENZO(b)FLUORANTHENE	22	11	0.6
BENZO(a)PYRENE	23	14	0.6
OIL & GREASE (%)	20	10	0.3

Treatment Temperature: 550°F

Table 4
Treatment Results - Refinery Filter Cake (C)

COMPOUND	ORIGINAL SAMPLE (PPM)	TREATED SAMPLE (PPM)	BDAT STANDARDS (PPM)
BENZENE	<0.1	<0.1	14
TOLUENE	3.9	<0.1	14
ETHYLBENZENE	14	<0.1	14
XYLENES	129	<0.3	22
NAPHTHALENE	250	<0.7	42
FLUORENE	192	<0.1	
PHENANTHRENE	609	4.6	34
ANTHRACENE	190	<0.6	28
FLUORANTHRENE	2,570	4.1	
PYRENE	1,630	<0.3	36
BENZO(b)ANTHRACENE	714	0.6	--
CHRYSENE	291	<0.1	1.5
BENZO(b)FLUORANTHENE	75	<0.6	--
BENZO(k)FLUORANTHENE	97	<0.9	--
OIL & GREASE (%)	23.8	0.3	
SOLIDS (%)	64.2	99	

Treatment Temperature: 500°F

Table 5
Treatment Results - Creosote Contaminated Clay

COMPOUND	ORIGINAL SAMPLE (PPM)	TREATED SAMPLE (PPM)	REMOVAL EFFICIENCY (%)
NAPHTHALENE	1321	<0.1	>99.9
ACENAPHTHYLENE	<0.1	<0.1	—
ACENAPHTHENE	293	<0.1	>99.96
FLUORENE	297	<0.1	>99.96
PHENANTHRENE	409	1.6	99.6
ANTHRACENE	113	<0.1	>99.7
FLUORANTHRENE	553	1.5	99.7
PYRENE	495	2.0	99.6
BENZO(b)ANTHRACENE	59	<0.1	>99.99
CHRYSENE	46	<0.1	>99.8
BENZO(b)FLUORANTHENE	14	2.5	82.3
BENZO(k)FLUORANTHENE	14	<0.1	>99.8
BENZO(a)PYRENE	15	<0.1	>99.9
DIBENZ(ab)ANTHRACENE	<0.1	<0.1	—
BENZO(ghi)PERYLENE	7	<0.1	>99.4
INDENO(123-cd)PYRENE	3	<0.1	>99.3

formed treatability tests on numerous wastes contaminated with different high-boiling organics from the petroleum refining, gas utility, wood preserving and chemical process industries. These tests have been carried out at relatively low temperatures, 450-600°F.

Table 1, shows typical mass reductions for a variety of waste feeds. Tables 2, 3 and 4 present results of treatment tests performed on listed petroleum refinery wastes. Table 3 compares results from a conventional Holo-Flite[R] dryer with one with ReTeC's proprietary modifications. It can be seen that ReTeC's modifications substantially increase the efficiency of the standard dryer. Tables 5 and 6 present test results from the treatment of contaminated soils from a wood-treating plant and a manufactured gas plant, respectively.

LIMITATIONS OF THERMAL DESORPTION

There are a number of requirements which limit the range of applicability of thermal desorption:

• *Feed Condition* - The feed has to be sufficiently friable to be fed into the thermal unit. At the same time, low viscosity or watery feeds, < 20% solids approximately, are also unsuitable since they tend to cause bypassing and thus reduce the efficiency of the unit.

• *Metals* - Thermal desorption does not remove or stabilize any metals that may be present in the feed. However, since these units operate at relatively low temperatures, they do not oxidize metals, therefore, in general, the metals do not become more mobile or leachable after treatment (unlike incineration).

• *Dust Control* - The solid product of thermal desorption is a dry material with less than 1% moisture. This material can cause substantial handling problems due to dust formation. The dust formation may be controlled by adding wetting agents/water and using covered conveyers and transportation bins.

TREATMENT COST

Thermal treatment costs vary considerably and ReTeC's pricing typically has been in the range of $100-$300/ton of feed. The cost is strongly dependent on the quantity of the waste, length (period) of the contract, moisture and organic content of the waste stream. Typically the installed cost of a complete thermal treatment system, with off-gas treatment and condensate handling, is 2-4 times the cost of the thermal unit(s).

Table 6
Treatment Results - Coal Tar Contaminated Soils

COMPOUND	ORIGINAL SAMPLE (PPM)	TREATED SAMPLE (PPM)	REMOVAL EFFICIENCIES (%)
BENZENE	1.7	<0.1	>94
TOLUENE	2.3	<0.1	>95
ETHYLBENZENE	1.6	<0.1	>93
XYLENES	6.3	<0.3	>95
NAPHTHALENE	367	<1.7	>99
FLUORENE	114	<0.2	>99
PHENANTHRENE	223	18	91.9
ANTHRACENE	112	7.0	93.8
FLUORANTHRENE	214	15	93.0
PYRENE	110	11	90.0
BENZO(b)ANTHRACENE	56	<1.4	>97
CHRYSENE	58	3.7	93.6
BENZO(b)FLUORANTHENE	45	<1.4	>97
BENZO(k)FLUORANTHENE	35	<2.1	>94
BENZO(a)PYRENE	47	<0.9	>98
BENZO(ghi)PERYLENE	24	<1.1	>95
INDENO(123-cd)PYRENE	27	<6.2	>77

Treatment Temperature: 450°F

Selection of Cover and Gas Collection for Municipal/Industrial Landfills

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ABSTRACT

This paper evaluates the selection of cover and gas collection alternatives using a number of criteria related to performance and aesthetics. Case history results are reported for a large (200 acre) southern California municipal/industrial Superfund site. Test results from on-site demonstration plots are highlighted. Cover alternatives included natural materials (i.e., clay), reinforced earth concepts and several synthetic options using both high density polyethylene (HDPE) and very low density polyethylene (VLDPE). Gas migration control alternatives included various well configurations and several surface collectors such as gravel filled trenches.

Performance data were evaluated for 18 parameters including efficiency of gas collection systems, constructability of the overall system selected, cost, vegetation reliability, time to install, maintenance costs, stability and susceptibility to landfill settlement. Due to the proximity of homes in the area aesthetics of the final remedy was also a factor in selection of an alternative.

INTRODUCTION

The remediation of mixed waste (municipal/industrial) landfills has received special emphasis by government agencies in recent years. Not surprisingly, a recent review of sites on the U.S. EPA's NPL indicated that 231 or 19% of the sites on the NPL are mixed waste landfill sites. Mixed wastes sites generally are unique in their size. Because they accepted household wastes or trash and commingled that waste with other types of wastes, mixed waste sites are generally of larger proportions. Small mixed waste landfill sites average on the order of 40 acres while large sites can occupy as many as 250 acres. At many of these sites, much of the waste prism is above ground or above the original ground surface. These "mountains of trash" are often visible to adjacent communities.

The difficulty in selecting an appropriate remedy for these sites is typified in the following excerpt from the U.S. EPA's ROD from the Belvidere Landfill in Belvidere, Illinois:

"The size of the landfill and the fact that there are no on-site hot spots that represent major sources of contamination preclude a remedy in which contaminants effectively could be excavated and treated."

This statement adequately characterizes the fundamental decision which must be made at mixed waste sites. Namely, how best to control the large volumes of wastes at a landfill site which will provide long-term protection of human health and the environment.

At many of these mixed waste landfill sites, because of the similarity of the waste type, site characteristics and size, regulatory agencies have been requiring encapsulation and gas collection as the key elements of the remedy. The focus of this paper is to give a broad overview of encapsulation (cover) and gas recovery from these mixed waste sites and to present an evaluation of some of the alternative solutions or designs which may be considered when remediating a site.

A number of common issues need to be addressed when considering remedial alternatives at these sites, specifically, final cover must minimize infiltration of rainfall and cover and gas recovery must capture methane gas with any associated toxic constituents prior to migration off-site.

In addition to these issues, the chosen remedy for a mixed waste landfill site must consider which standards need be applied. Many of the mixed waste sites on the NPL operated before November 19, 1980, the effective date of RCRA Subtitle C and while these sites may have accepted hazardous wastes as currently defined, the standards of RCRA Subtitle C for landfill design and closure cannot be automatically applied to remediation of the site. At the same time, experts cannot agree that the standards of Subtitle D for design and closure of solid waste landfills are applicable. Since both sets of standards have provisions for landfills, it is reasonable to assume that portions of the standards contained in both Subtitles may apply.

In the following discussion, we present various options which may be considered viable alternatives or solutions for the selection of cover and gas collection at mixed waste sites. In doing this, we make no judgement as to the degree any of these options meet the standards for landfill closure contained in either Subtitle C or Subtitle D.

For purposes of illustration, many of the issues discussed in this paper will be presented with a case history from the Operating Industries Landfill (OII) in Los Angeles. The OII site is a large (190 acre) NPL site located approximately 15 miles east of downtown Los Angeles. The site, which closed in 1984, rises almost 200 feet above its surrounding terrain and is situated adjacent to two housing tracts.

GAS COLLECTION SYSTEMS

Mixed waste sites typically generate landfill gases containing roughly equal amounts of methane and carbon dioxide. Left uncontrolled, these gases can migrate through the subsurface or vent through thin cover on the landfill into the atmosphere causing odor and nuisance problems. These gases quite often carry trace contaminants off-site and therefore pose a potential exposure risk to the surrounding environment. In extreme circumstances, the buildup of explosive concentrations of methane in nearby foundations, sewers and other subsurface structures can also be of concern.

Remediation of the gases generated is split into two distinct pathways of concern: the potential subsurface migration of gas and the emission of gas through the landfill surface.

Deep Well Extraction Systems

Subsurface gas which migrates from the mixed waste landfill through permeable zones to nearby environments is typically addressed or

remediated with the installation of deep wells into the trash prism. A survey of landfills in the Los Angeles basin has shown that various system designs and individual well configurations/spacings have been used to remediate gas. Table 1 summarizes some of the varied designs that have been used.

Table 1
Comparison of Deep Gas Collection Systems
Mixed Waste Sites

Item	Site A Prism	Site A Perimeter	Site B	Site C
Borehole Diameter	6"	12"	30"	14" & 18"
Casing Diameter	6"	6"	4-6"	6"
Well Depth (typ.)	100'	100'	80'	40-80'
Well Spacing	100'	100'	150'	150'
Construction Technique	"Drill/ Drive"	Simple Air Rotary	Continous Flight Auger	Pile Driven

Well spacings are typical. However, closer spacings are many times used in areas of severe gas migration.

Source: Los Angeles County Sanitation District, 1989

The various well configurations or layouts generally fall into two categories of alternatives. In the first alternative (the "gas extraction" method), deep wells are installed throughout the landfill prism at a spacing of approximately 100 feet. The wells are many times installed to the depth of waste in the landfill. The concept of this gas extraction design is premised partly on the assumption that mixed waste landfills are constructed in cells that these individual waste cells within the landfill site are generating gas at various rates and that these cells generally are not communicating significantly with each other. Installing the deep wells throughout the landfill prism allows for collection of the gas near the point of generation so that the gas can be extracted without relying on significant gas movement from cell to cell.

To minimize the capture of excessive oxygen while extracting the gas, the deep wells are not screened near the surface of the waste prism. In the gas extraction well system, to compensate for the deep wells not being screened near-surface, shallow (40 ft maximum) or surface wells are installed. These wells, which can be operated at minimal vacuum, collect gases that build up beneath the cover but do not operate at sufficient vacuum to allow oxygen intrusion to become a concern. Using the combination of deep and shallow wells thereby increases operational flexibility by allowing the operator to independently vary the amount of vacuum applied to the deep and shallow wells.

The second typical design for subsurface recovery uses a well configuration in which the wells are clustered along the periphery of the landfill boundary, with few or no deep interior extraction wells. In this design, referred to as the "gas capture" method, the remediation design may include a combination of wells at various depths. The concept of the gas capture system is to capture only that gas which is moving off-site at the point of escape, the property boundary. In addition, this general design assumes that individual waste cells are in communication with one another which allows gas to move relatively freely through the landfill mass.

The design of individual wells located in trash has been a developing science. The older sites used a traditional rule-of-thumb which called for larger (18 to 36 inches) bored holes with gravel packed perforated casing in the hole. Many of these wells were installed to the depth of trash. The rationale for employing large boreholes was to ensure a long life for the well and minimize plugging. More recent practices (BKK Corporation Landfill and Operating Industries Landfill) have used much smaller wells (6 to 12 inches). These wells have the capability to be installed with either a traditional auger rig or with a "drill/drive" technique which allows the casing to be driven into the waste during drilling to provide more efficient installation of the well through saturated zones in the trash. To date, these smaller wells have not been subject to the same test of time as their larger counterparts, but a simple cost

analysis comparing the capital cost shows that the smaller wells are overwhelmingly more economical to install. For purposes of illustration, Table 2 is included giving a cost comparison of various individual well designs.

Table 2
Estimated Costs for Various Gas
Collection Wells for Mixed Waste Landfills

Borehole (dia.)	Casing (dia.)	Rig Time (cost $)	Cuttings Disposal ($)	Materials ($)	H&S Cost ($)	Total ($)
36"	8" PVC	17,400	9,400	9,100	7,100	43,000
24"	8" PVC	13,800	4,200	7,000	5,600	30,600
14"	6" PVC	7,000	1,400	4,200	4,000	16,600
12"	6" PVC	5,800	1,000	4,100	4,000	14,900
12"	4" PVC	5,800	1,000	2,300	4,000	13,100
6"	6" Steel	6,000	300	4,500	4,400	11,200

Notes:

(1) 12", 14", 24", 36" well costs based on installation using auger technique
(2) 6" well costs based on installation using "drill/drive" technique
(3) Health & safety costs estimated as increased cost for using added respiratory protection and includes added supervision of drilling activities

Source: Environmental Solutions Inc. and Bryan A. Stirrat & Associates, 1989

As mentioned above, in most cases well spacing is still determined by a rule-of-thumb approach using wells on 100-foot centers. The actual required interval can sometimes be determined more scientifically through gas interference testing (similar to that used in natural gas production fields) to determine the boundary of influence a well of given proportions and vacuum may achieve in the waste conditions specific to a given mixed waste landfill.

Shallow Well Gas Recovery Designs

Near-surface gas must typically be addressed separately from deep gas collection in order to prevent excessive oxygen intrusion. The surface gas design must be integrated as much as possible with the selection of cover type as cover is actually an element of any shallow collection network. Without shallow gas collection, gas can build up significant pressure (up to 20 psig) beneath the landfill cover. At the same time, without the installation of at least some cover, the efficiency of the shallow collection system will be low and oxygen infiltration will be dramatic. Various types of shallow gas collection networks are listed in Table 3.

Table 3
Shallow Well Collection Systems
for Mixed Waste Landfills

Type	Description
Vertical Wells	Shallow (40 foot) collection wells, screened interval approximately 5-40' below landfill surface.
Horizontal Collectors	
Gravel-filled Trenches	2'X2' trenches backfilled with gravel, slotted PVC collection pipe embedded in trench.
Slotted Pipe	Slotted PVC pipe laid directly on landfill surface. Can be installed on overlapping criss-cross pattern for added collection efficiency.
"Geo-grid"	Sections of HDPE "geo-grid" material laid directly on to landfill surface. Collection pipe tied to grid provides vacuum source.
"Geotextile"	One layer of geotextile laid beneath the cover. Collection pipes laid on wide spacing to provide vacuum source.

Surface gas collection networks typically fall into two major types, "vertical well" designs and horizontal "gas collection grids." In the vertical well designs, small diameter wells are installed to depths of approximately 40 feet below land surface and perforated from the bottom of the casing to within 5 feet of the land surface. The wells are operated using small vacuum (3 to 5 inch water column) to sweep the gas out of the waste prism while minimizing the potential for oxygen intrusion into the waste fill.

In gas collection grids horizontal collectors are installed immediately beneath the cover to allow for removal of gas as it collects beneath the impermeable cap. These horizontal collectors may be gravel-filled trenches using slotted pipe collectors (i.e., French drains), slotted pipes installed directly on the waste surface (sometimes laid in a criss-cross pattern), or they may be made up of geogrid, a commercial HDPE product used primarily for liquid drainage layers above the cover. Other designs which provide sufficient space beneath the cover to allow for gas collection also are possible.

In tests of these various designs at the OII site, three approaches (gravel-filled trenches, slotted pipe and geogrid) were compared. The tests showed that all three designs were capable of achieving sufficient collection to qualify them as candidates for the final design. The actual design can therefore be made based on the economics of the construction, which favors options which do not require penetration (trenching) into the waste prism.

LANDFILL COVER SYSTEMS

In determining the appropriate gas collection system, the type of cover must also be evaluated, with the reverse also being true. Integration of both gas collection and cover is mandatory to achieving the best alternative for the mixed waste landfill site. Cover can actually be considered a part of the gas collection network in that it allows for buildup of the gas within the trash prism and increases the efficiency of the collection network. Cover also minimizes oxygen infiltration into the gas collection system, which allows better operating performance, particularly at sites utilizing resource recovery of the methane.

Table 4 lists 18 design considerations that may be used to determine the most appropriate cover system. Cover types may include the more traditional clay cover, clay with soil (either with or without reinforcing structures) or, with the improvements in the production and use of synthetic flexible membrane liners (FML), covers using either high density polyethylene (HDPE) or very low density polyethylene (VLDPE) designs.

Table 4
Design Factors for Mixed Waste Landfill
Cover and Gas Collection Systems

```
                 Capital Cost

              Constructability

               Time to Install

      Gas Collection Method (Perimeter)

       Gas Collection Method (Surface)

     Infiltration (Leachate Minimization)

                  Drainage

            Settlement Resistance

                  Stability

     Vegetation Requirements (Irrigation)

            Vegetation Reliability

                 Aesthetics

              Erosion Control

                  Lifetime

            Freeze/Thaw Protection

     Long-Term Operation & Maintenance

   Health & Safety (During Construction)

      Integration (Cover with Gas System)
```

Table 5
Design Alternatives for Cover and Gas
Collection - Operating Industries Landfill

Option	Type
A	Clay cover with hydroseeding directly on to clay (no cover soils). Gas collection using combination of deep and shallow wells.
B	Clay cover with top soil vegetation layer. Additional stability with installation of buttress at certain locations. Gas collection using combination of deep and shallow wells.
C	Flexible membrane liner (FML) with surface "grid" gas collectors. Vegetation using reinforced earth layer above FML.
D	FML with surface "grid" gas collectors and vegetation using "geoweb" soil stabilization system.
E	FML with surface "grid" collectors and vines grown over a trellis mesh.
F	FML with surface "grid" collectors and using synthetic grass (possibly with vines) for aesthetics.

Source: EPA, Region IX, 1990

In recent years, the U.S. EPA has moved toward multilayer (FML plus clay plus soil) designs as remedial options. Part of the rationale for these multilayer concepts for mixed waste landfill sites is the reliance on the RCRA Subtitle C standards for design and closure. As discussed earlier, since most mixed waste landfills operated before the passage of RCRA, it may not be appropriate to automatically impose Subtitle C standards as the design criteria for remediations at these sites.

Multilayer designs may be appropriate at a number of these sites and are constructable under certain situations, such as sites with generally flat terrains and stable wastes. However, in many cases multilayer designs are unnecessary and/or may be impractical because of existing steep slope conditions, waste instability, storm water run-off concerns or excessive long-term operation and maintenance requirements.

At the OII landfill in Los Angeles, the alternatives listed in Table 5 have been evaluated by the U.S. EPA, the U.S. EPA's contractors and a group of PRPs. While a final decision has not yet been made by the U.S. EPA, we are using this work as a basis to discuss various alternatives for the remediation of mixed waste sites. The OII site is unique because of its steep slopes (generally >2H:1V) and its location in the seismically active Los Angeles basin. These factors make reliance on multi layer concepts less desirable. As part of the evaluation of cover and gas collection, several demonstration areas were constructed on-site to fully evaluate some of the options.

Until the relatively recent development of synthetic materials, clay has been the material of choice for cover construction. Clay has the attractive features of being relatively impermeable, naturally available and handled with relative ease using normal construction techniques. Clay can be considered the traditional cover material.

A concern with clay as a cover material, particularly in semi-arid parts of the United States, is the need to keep the clay moist to prevent desiccation and cracking of the cover requiring periodic corrective maintenance. Since desiccation of the clay is a concern, the use of surface grid collectors for gas collection under the clay is not advised; the collectors may enhance desiccation by drawing air through and moisture out of the clay.

Because clays generally have poor nutrient content, it is difficult to sustain vegetation and top soil is required as a medium to support final vegetation at the site after closure. It is noted, however, that one large mixed waste landfill in southern California has successfully supported final vegetation directly on the clay cover.

On steep slopes the volume of clay and top soil needed may raise concerns over the long-term stability of the cover system as the trash settles over time or during seismic events.

At the OII site, because of uncertainties over the long-term stability

and the proximity of off-site structures (homes and roads), using clay may require the use of additional support such as buttress walls to provide stability and the area needed to construct clay alternatives. This additional construction combined with some uncertainty over the availability of clay within the Los Angeles basin and long-term irrigation needs has prompted the evaluation of other options, including the use of synthetic cover.

During the 1980s, the use of flexible membrane liners has increased substantially. Their use has been primarily for liner systems at landfills, but their use as cover materials at mixed waste landfill sites (e.g., Charles George Landfill) is also on the rise. FMLs have the desirable characteristics of being lightweight, impermeable, generally chemical resistant and easy to install, even on steeply sloped areas.

Since the FML designs are not susceptible to desiccation as are the clays, these designs allow for a broader range of shallow gas collection options, including the horizontal grid collectors that are not advised for the clay concepts.

Some disadvantages of FMLs can be their susceptibility to weather (sunlight and temperature variations) if left exposed and their failure to provide any aesthetic quality to the final closure. Also, since the use of FMLs as cover material is still relatively new, the long-term performance of FML systems is unknown.

At OII, several synthetic cover options have been evaluated in an attempt to develop an alternative to the buttressed clay option which may be needed in certain areas. A high priority issue at OII was the need for the final solution to be aesthetically pleasing to the community. Consequently, the options using FML (in this case VLDPE) each contained some variation to provide this aesthetic quality. Two options evaluated employed the use of commercially available soil erosion protection products, including reinforced soil using geogrid and soil stabilized with geoweb. These stabilized soil concepts were developed to provide the soil base needed to support final vegetation.

Another variation in design utilized vines which would eventually drape over the FML and provide the final vegetation. Finally, a totally synthetic option was developed using synthetic grass as a means to provide a natural looking final cover. The advantage of the synthetic grass is that it does not require irrigation or large amounts of maintenance.

The two stabilized soil alternatives and the vine cover and synthetic grass option were all constructed as small (40 ft x 40 ft) demonstration plots. The soil plots were successful, but, the vine cover could not be sustained on the black FML/geotextile underbase. Each test plot was constructed, although long-term monitoring of these areas has not yet been completed. All these options are still deemed to have a potential for use on the site. Since these tests are being conducted in southern California, no attempt was made to evaluate the potential affect of freezing on these systems.

CONCLUSION

This paper has provided an overview of various alternatives to the design of cover and gas collection systems at mixed waste landfill sites. With new products and techniques being constantly developed, many options are available. These options must be evaluated in light of the specifics of the individual landfill, the objectives of the remediation and the standards, both federal and state, in effect at the time. However, the integration of gas collection and cover in determining the most appropriate system is critical to the development of the most cost-effective and technically appropriate system to be utilized.

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Gas In A Hat

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ABSTRACT

Soil vapor extraction (SVE) is an integral part of the remedy selected for the Seymour Recycling Corporation Superfund site in central Indiana. Site conditions created several interesting problems for the design of the SVE system. First, the unsaturated zone, which contains the bulk of the volatile organic constituents (VOCs), is thin relative to the areal extent of the site. Second, site soils are fine-grained with a high moisture content and relatively low air permeability. Finally, the site has internal drainage, and ponding of water on the site provided a strong incentive to cap the site as soon as possible.

The SVE design consisted of horizontal vapor "drains." The system is designed to operate at relatively low air flow rates to minimize exhaust gas treatment costs. The unalterable nature of the drain installation required a predesign study to collect data needed to confidently design the system. The predesign investigation included a soil gas survey, in situ testing of the air permeability, laboratory treatability studies and numerical modeling to determine appropriate drain spacings. The drain spacing evaluation required analysis of the effect of cap loading and soil drainage on the effective air permeability of the soil. The results allowed the drain spacing to be increased, lowering construction costs. The soil gas survey revealed extensive vinyl chloride in the soils which must be vented prior to drain construction.

INTRODUCTION

The Seymour Recycling Corporation site is located in central Indiana approximately 60 miles south of Indianapolis (Fig. 1). The site was a Federal-led cleanup with the RI/FS being performed under U.S.EPA contract. Geraghty and Miller, Inc. is managing Remedial Design/Remedial Action (RD/RA) for the Seymour Site Trust Fund. Geraghty and Miller also acted as primary consultants to the Trust during negotiation of the Consent Decree for the site. Hydro Geo Chem, Inc. acted as a consultant to Geraghty and Miller on soil vapor extraction during the negotiation phase, developed the conceptual design for the SVE system and performed the SVE predesign investigation.

SITE BACKGROUND

The Seymour site is located approximately 2 miles southwest of Seymour in an industrial park surrounded by agricultural land. The primary portion of the site covers approximately 12 acres (Fig. 2). The site was operated as a processing center for waste chemicals from about 1970 to 1980. By March 1980, approximately 50,000 drums, 98 bulk storage tanks and tank trucks were located on the site.[1]

Surface cleanup of the site began in December 1982. The cleanup consisted of removal of containerized waste, surface soil removal, regrading to control surface run-off and installation of a clay cap.
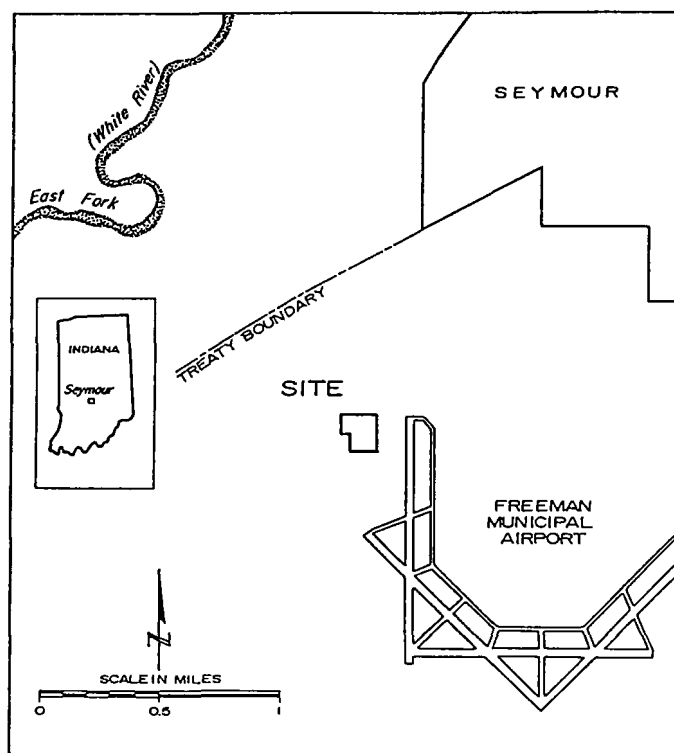
Figure 1
Site Location Map

Contaminant Site

Soils at the site are contaminated with a wide variety of volatile and semivolatile organic compounds as well as some metals and other inorganic constituents. The results of soil analyses performed as part of the predesign investigation indicated that the most abundant VOCs are benzene, toluene and xylenes. The VOCs of most environmental concern and those targeted by the SVE system are chlorinated hydrocarbons, primarily tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1 trichloroethane (TCA), 1,1 dichloroethane (1,1 DCA) and chloroform. As will be discussed later, the degradation products of these constituents also are abundant at the site. A histogram showing the relative distribution of VOCs at the site based on soil analyses is shown in Figure 3.
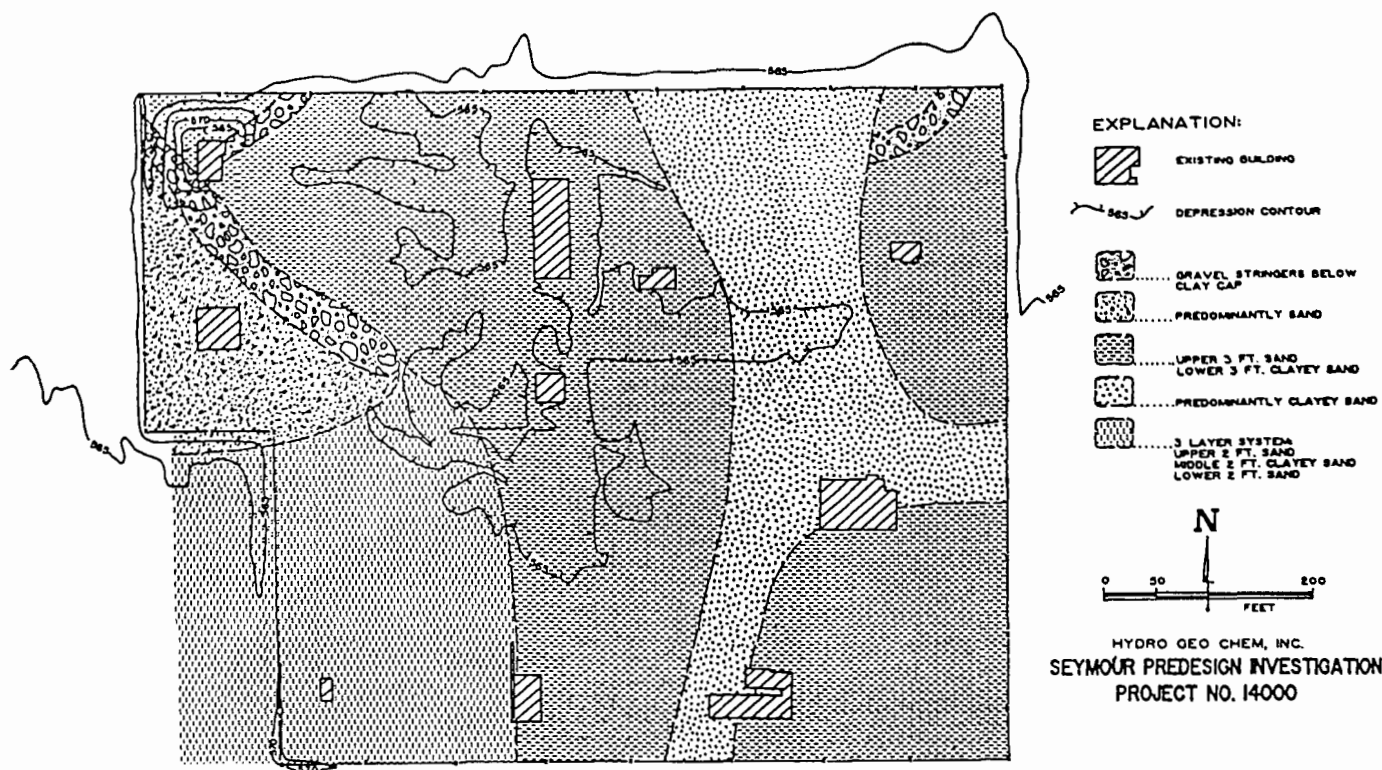
Figure 2
Site Map Showing Major Soil Types
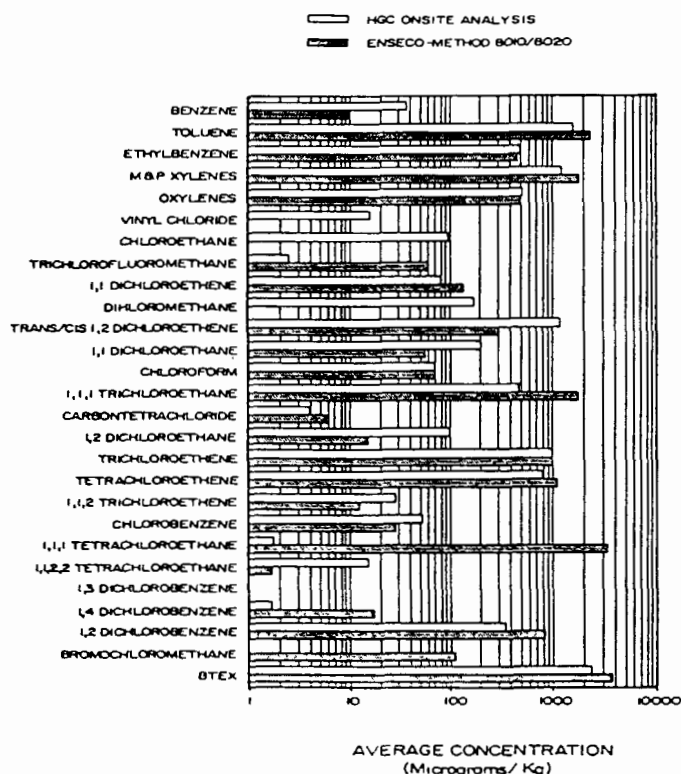
Figure 3
Relative Abundances of VOCs Based
on Soil Analyses

Soil Conditions

The shallow (to 10 feet below land surface) soils at the site consist of: the surficial clay cap, approximately one foot thick; discontinuous zones of coarse gravel fill; fine- to medium-grained sands; and clayey sand to sandy clay. The lateral distribution of these units is shown in Figure 2.

Hydrologic Conditions

The water table beneath the site occurs at a depth of approximately 7 feet below current grade. The direction of groundwater flow is generally to the north beneath the site. Since the initial site cleanup, a condition of internal drainage has existed at the site. Ponding of water has often occurred and nearly saturated conditions exist during parts of the year near the center of the site.

SELECTED REMEDY

The Remedial Action Plan (RAP) provides for installation and operation of a groundwater extraction system to contain and remove contaminated groundwater, a vapor extraction system to remove volatile organic constituents (VOCs) from the soils above the water table, enhanced bioremediation to reduce the volume and toxicity of semivolatile organic constituents and construction of a multimedia, RCRA cap over the site to eliminate further leaching of contaminants from the soils. The work described here deals primarily with the design of the vapor extraction system.

Soil Vapor Extraction

Soil vapor extraction and enhanced bioremediation were proposed in the Feasibility Study report to meet the requirements of SARA calling for remedial actions which reduce the volume, toxicity and mobility of hazardous constituents at CERCLA sites. As proposed in the FS, the SVE system would have consisted of a conventional system of more than 100 vapor extraction wells and was designed to operate for several years prior to installation of the cap. No site-specific data had been

collected at that time to support the design of the SVE system. This design was found to be undesirable because: (1) it delayed installation of the cap for several years allowing continued leaching of contaminants to the groundwater, (2) calculations showed that the air permeability of the soils was likely to be too low to sustain the airflow rates proposed for the well system, (3) high pressure drops near individual wells would result in significant upconing of the water table and (4) extensive off-gas treatment would be required because of the high mass emission rates from the system.

An alternative SVE design was developed utilizing a network of horizontal "vapor" drains to circulate air through the unsaturated soils and withdraw VOCs. The final drain layout, shown in Figure 4, consisted of 19 drains, with alternating drains maintained at subatmospheric pressure and at atmospheric pressure. The system was designed to be installed beneath the cap (hence the title of this paper), to be operated at low pressure drops and airflow rates and to be operated over the lifetime of the cap (nominally 30 years). This alternative conceptual design avoided long delays in installation of the cap, provided for treatment of low-permeability soils, eliminated the problems with upconing and greatly reduced the mass emission rates from the site. A risk assessment showed that off-gas treatment could largely be avoided by reducing the rate of VOC emission from the site. As will be discussed later, however, a soil gas investigation revealed significant concentrations of vinyl chloride which indicated a need for off-gas treatment during the early stages of SVE operation.

The RAP established technology-based performance standards for the SVE system rather than specifying target soil concentrations. The technological performance standards were: (1) that 500 pore volumes of air be circulated through the soils within 30 years of system installation and (2) that no fewer than 2 pore volumes and no more than 35 pore volumes be circulated in any year. In addition, the RAP stated

that the goal of the SVE treatment was to remove 80% of the vapor extractable VOCs.

The rationale for not specifying particular target soil concentrations was that the cap would prevent any direct exposure to the contaminants. The goal of removing 80% of the vapor extractable VOCs was based on preliminary calculations performed as part of the conceptual design report. Establishing such a relative goal was reasonable because: (1) the actual mass of VOCs was uncertain, and (2) the mass removal rate of an SVE system is approximately directly related to the mass of VOCs present in the soil. The 500 pore volume performance standard was selected based on conceptual design calculations using an exponential dilution model which showed that this volume would reduce the initial contaminant mass by 80%.[2]

The RAP also provided for the use of vapor phase tracers to monitor the sweeping efficiency of the SVE. The selection and application of these tracers will be discussed later.

Finally, the RAP required that a predesign investigation be performed to collect data needed to develop a formal engineering design for the SVE system. Of particular importance were an updated description of the spatial distribution of VOCs and measurements of the effective air permeability of the soils. The predesign investigation also provided for a vapor phase tracer test to test tracers which might be used for performance monitoring and to supplement other techniques for measuring air permeabilities. Also to be determined were total and air-filled porosities of the soil and their organic carbon content. Based on the data collected during the predesign investigation, numerical modeling was performed to evaluate appropriate drain spacings and locations for the SVE system to be capable of meeting the requirements of the RAP.

SVE DESIGN PRINCIPLES

The design and evaluation of the SVE system for the Seymour Site
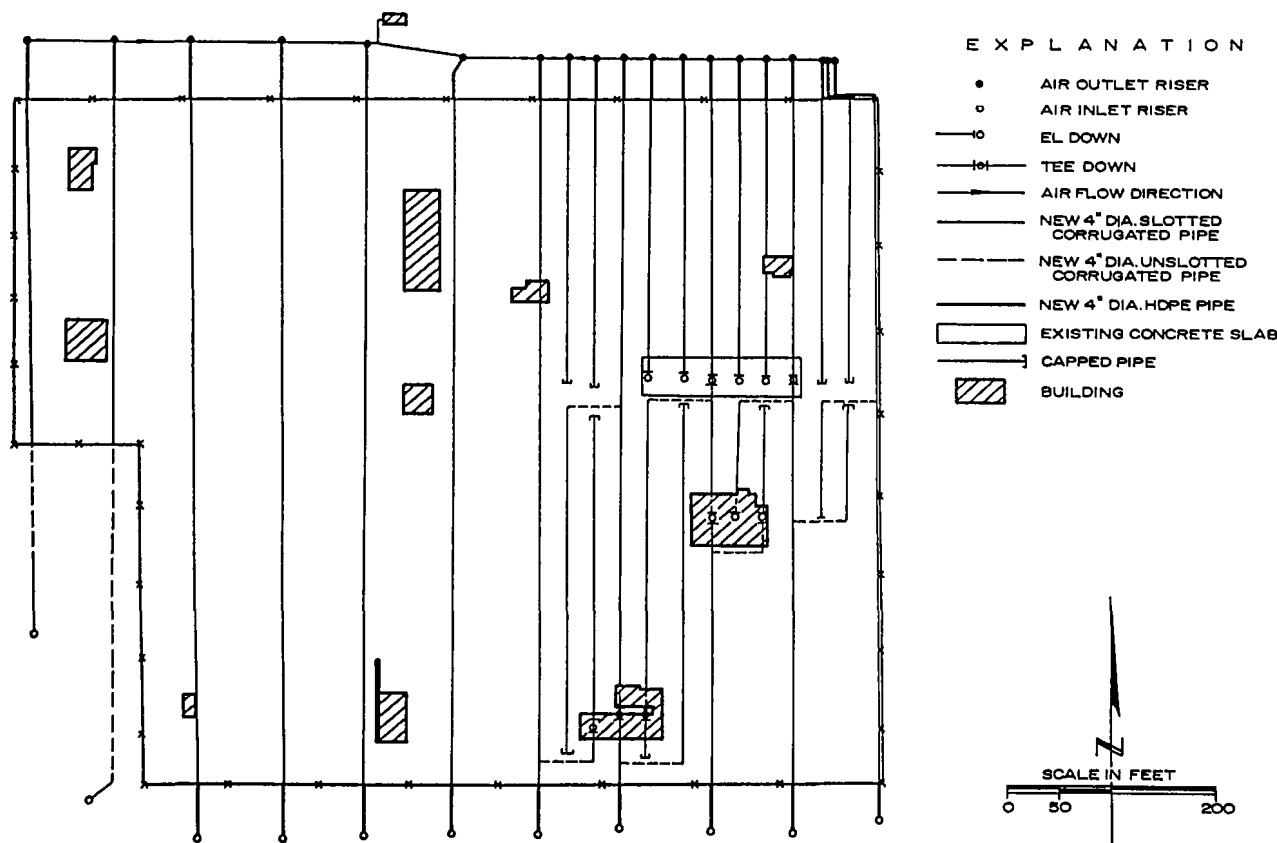
Figure 4
Schematic Showing Final Layout of the
SVE Drain System

were based on an equilibrium thermodynamic description of the partitioning of volatile organic compounds between the solid, liquid and vapor phases in the soil and on well-established physical principles describing the movement of gases through porous media. The various constitutive relationships and models used in the analysis and design of the Seymour SVE system are described briefly below.

The air-strippability of a particular VOC depends on its concentration in the soil gas phase relative to its concentration in the liquid and solid phases. The vapor phase concentration depends on the compound's physical-chemical properties, its state in the soil and the physical and chemical properties of the soil. The vapor extractable compounds at the Seymour site will be distributed among three-phases in the subsurface: (1) as a vapor in the soil gas phase, (2) in solution within the porewater of the unsaturated soils and (3) adsorbed onto organic matter in the soil (including biofilms). Nonaqueous phase liquids are not believed to be present in the soils at the site.

The vapor phase concentrations will be controlled, in part, by their dimensionless Henry's Law coefficients, H_D, which relate the concentration of a compound in the vapor phase to its concentration in the soil water. The water concentration will, in turn, be controlled by the distribution of contaminants between water and the solid soil matrix.

The strippability of constituents can be evaluated by computing the ratio of their concentration in the soil gas to their total concentration in the soil according to Thomas:[3]

$$\frac{C_g}{C_T} = \left[\frac{K_D \rho_b}{H_D} + \frac{\phi_w}{H_D} + (\phi_T - \phi_w) \right]^{-1} \qquad (1)$$

where C_g is the concentration in the gas [M/V air]
C_T is the total concentration in the soil [M/V bulk volume soil]
K_D is the water-solid distribution coefficient [M/M solid/M/V water]
ρ_b is the bulk dry soil density [M/V solid]
H_D is the gas-water distribution coefficient [M/V air/M/V water]
ϕ_w is the water filled porosity
ϕ_T is the total porosity

The gas-water distribution coefficient is:

$$H_D \approx \frac{C_g}{C_w} = \frac{H}{RT} \qquad (2)$$

where H is Henry's Law coefficient
R is the ideal gas constant
T is absolute temperature

The water-solid distribution coefficient is:

$$K_D = \frac{C_s}{C_w} \approx K_{oc} \cdot foc \qquad (3)$$

where C_s is the concentration in the solid [mass VOC/mass soil]
C_w is the concentration in the water [mass VOC/volume water]
K_{oc} is the water-organic carbon distribution coefficient
foc is the fraction organic carbon in the soil

PREDESIGN STUDY

The purposes of the predesign investigation for the SVE system were: (1) to collect site-specific data on soil properties and contaminant distributions needed for the final system design, (2) to evaluate tracers proposed for use in performance monitoring and (3) to determine drain spacings and locations. An evaluation of the mass of VOCs present in

the soils at the site was also included in the scope of work for the predesign investigation.

VOC Distribution and Mass

Soil gas sampling was the primary technique used to determine the current spatial distribution of VOCs at the site. In addition, soil borings were made at nine locations to collect soil samples for chemical analysis as well as for use in laboratory treatability studies. The locations of the soil borings were selected to yield three borings in areas of low contamination, three borings in areas of moderate contamination and three borings in areas of high contamination, based on the soil gas survey.

Soil gas samples were collected on approximately 100 foot centers using a regular grid designed to coincide as closely as possible with the locations of soil samples collected during the RI. Sixty-eight locations were sampled, most at a depth of three feet below grade. Selected locations were also sampled at a depth of five feet. The soil gas analyses were performed in a close support laboratory (CSL) by thermally desorbing the VOCs from the collection cartridges and analyzing the desorbed compounds by gas chromatography with both Hall and photoionization detectors.[4] Twenty-six constituents were included in the on-site analyte suite. Selected gas samples were also collected in evacuated stainless steel bombs and sent to a contract laboratory for confirmatory analysis by GC-MS.

The results of the soil gas investigation are summarized in Figure 5 in terms of the spatial distribution of total VOCs and in Figure 6 as a histogram showing the relative abundance of the various analytes. The VOC distribution revealed by the soil gas survey was consistent with that based on the CSL soil analyses reported in the RI. The soil gas survey revealed significant concentrations of highly volatile compounds, particularly vinyl chloride and chloroethane, believed to be degradation products of the primary solvents, such as TCE and TCA.

The presence of vinyl chloride, which had not be reported in soil samples analyzed during the RI, was significant because its toxicity and low trapping efficiency on activated carbon indicated that the initial off-gas from the SVE system would require incineration. The presence of vinyl chloride also complicated the construction of the SVE drain system. The spatial distribution of vinyl chloride, shown in Figure 7, was similar to that of the other VOCs, although the center of the vinyl chloride mass appears to be displaced slightly to the north in the direction of groundwater movement.

Of particular interest are the VOC mass estimates based on the soil gas analyses, the predesign soil analyses and the analyses reported in the RI and FS reports. The mass estimates from the soil gas analyses were made using Equation 1 and laboratory determinations of total organic carbon, porosity and moisture content to convert soil gas concentrations (mass VOC/volume gas) to total soil concentration (mass VOC/mass soil). The soil gas mass estimates are summarized in Figure 6. The soil gas survey indicated that approximately 4,000 pounds of vapor extractable compounds were present at the site. A similar estimate based on the soil analyses performed during the predesign investigation indicated less than 3,000 pounds of these constituents.

The mass estimates based on the predesign investigation results were less than the 200,000 pounds suggested by the CSL data in the RI or the 50,000 pounds indicated by the CLP analyses reported in the RI. These latter two estimates were the only ones available during development of the RAP, however.

Although the differences between the mass estimates remain unresolved, it is important to note that the predesign investigation samples covered the same area as the RI samples and some were collected in areas were the RI reported total VOC concentrations of greater than 100 mg/kg, yet showed generally much lower concentrations. Given that the RI was performed in 1984 and that the site has been subject to periodic flooding, was well as losses due to volatilization and biological degradation since then, the lower contaminant levels found during the predesign investigation are not surprising. Ultimately, the actual mass of VOCs currently present at the site is of importance only in terms of the need for off-gas treatment because the rate of VOC

TOTAL VOLATILE ORGANICS (ug/l)

Figure 5
Lateral Distribution of Total VOC Analytes
Based on Soil Gas Sampling

Figure 6
Relative Abundances of VOCs based on
Soil Gas Samples

removal by SVE will be proportional to the mass present and the 80% mass removal goal will be achieved regardless of the initial mass.

Air Permeabilities

In addition to the spatial distribution of VOCs, the air permeability of the various soils at the site was a major factor controlling the design of the SVE system. The air permeability of a soil depends both on the intrinsic permeability of the soil and on the moisture content of the soil, because air can flow only through the interconnected voids which are not occluded by water. Air permeabilities at the Seymour site were measured under field moisture conditions by four different means: (1) laboratory tests on soil samples collected using a thin-walled sampler;

(2) step-rate tests performed using the soil gas drive-point in conjunction with soil gas sampling; (3) step-rate tests on individual wells installed in the soil borings; and (4) interference tests performed as part of the field tracer test. Each test measured the air permeability on a different volumetric scale, from smallest to largest. The test results are summarized in the exceedance probability plot in Figure 8. Both the drive-point tests and the laboratory tests indicated a range of air permeabilities over several orders of magnitude, with median values of approximately 2 and 15 Darcies, respectively. The single well tests and interference test results had medians of 10 and 20 Darcies, respectively.

The difference in results is a scale effect resulting from the fact that the single well and interference test results tended to reflect the permeability of the most permeability units penetrated by the extraction wells, whereas the drive-point tests reflected the local permeability of the particular soil in the immediate vicinity of the gas sampling probe and the laboratory test results were dominated by the lowest permeability material in the soil sample. Despite the range in results, the tests all indicated median permeabilities higher than those on which the conceptual design was based.

An interesting special problem which was not considered during the conceptual design of the system was that loading of the native soils by the cap would result in consolidation and a reduction in air permeability. Cap loading was estimated to reduce effective air permeabilities to approximately 20% of their unloaded values, and this reduction in permeability was taken into account in the final system design.

Vapor Phase Tracers

An interesting, but non-critical, aspect of the predesign investigation was the testing of vapor phase tracers to be used in system performance evaluation. The tracers are intended to be injected into the soils at strategic locations to monitor the sweeping efficiency of the SVE system. This process will be accomplished through the use of permeation tubes buried in the soils prior to construction of the cap.

Six tracers were selected for testing: sulfur hexafluoride (SF_6), dibromodifluoromethane (DBDFM), iodotrifluoroethylene (ITFE),

Figure 7
Lateral Distribution of Vinyl Chloride
Based on Soil Samples

Figure 8
Exceedance Probability Plot of Air
Permeability Measurements

Freon 114 (F114), bromotrifluoromethane (BTFM) and bromochlorodifluoromethane (BCDFM). A convergent flow tracer test was performed by injecting the tracers through drive-points located five feet from a air extraction well at the test site shown in Figure 9. Two tracer tests were performed by injecting tracers after pressures around the extraction well had stabilized for nominal flow rates of 5 and 2.5 scfm. Breakthrough curves for five of the six tracers are shown in Figures 10 and 11. The omitted tracer is ITFE, the analysis of which was compromised by an interfering, unidentified compound.
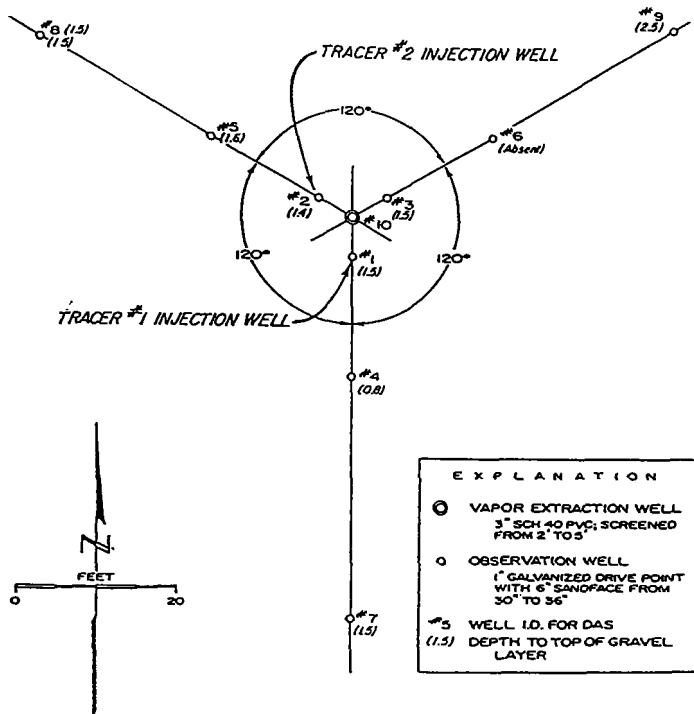
Figure 9
Layout of the Tracer Test Site
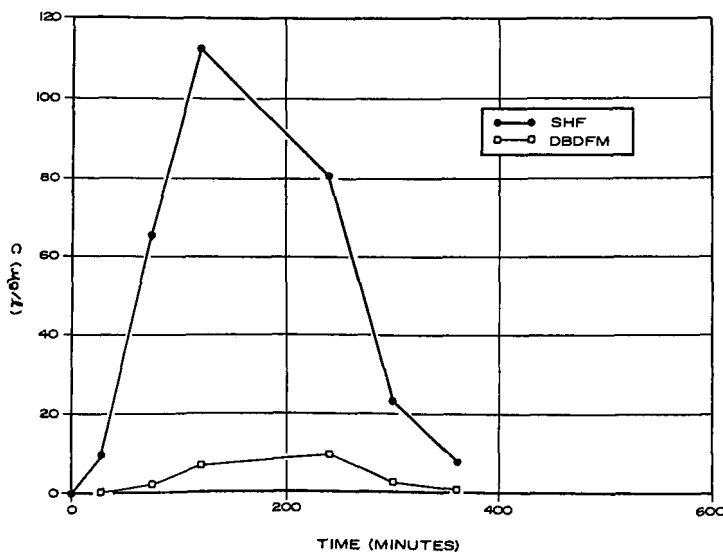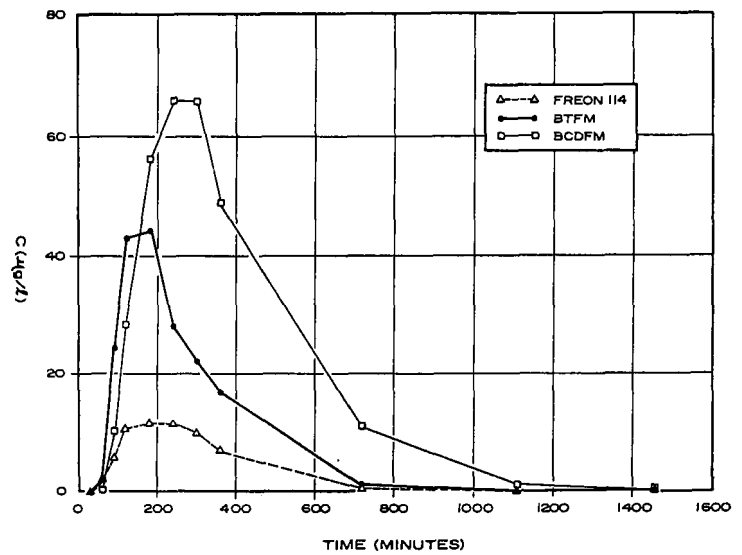
Figure 11
Tracer Breakthrough Curves for Test 2

Analysis of the tracer tests using an analytical model[5] indicated apparent retardation factors between 10 and 20 for all of the tracers. Laboratory column experiments and theoretical calculations indicated, however, that the movement of these tracers should be retarded by a factor of less than two relative to air. The reason for the difference between the field and laboratory results is that the soils at the test site were heterogeneous and that the tracers were injected into lower permeability soils during the field test.

SVE Drain Spacings

Based on the results of the air permeability tests and the spatial distribution of soil types at the site, drain spacing recommendations were developed to assure that the SVE system would be capable of meeting the air circulation requirements of the RAP. An analytic equation was developed for computing the drain spacings required to circulate a specified number of pore volumes in a specified time at a given pressure drop:

$$L = [(k_a t \Delta P^2) / (2\mu P_a N \phi_T \sigma_a)]^{1/2} \qquad (4)$$

where L is the drain spacing
  k_a is the air permeability
  t is extraction time
  ΔP^2 is the difference in operating pressure between the drain and the atmosphere ($P^2 - P_a^2$)
  μ is the viscosity of air
  N is the number of pore volumes to be circulated
  ϕ_T is the total porosity of the soil
  σ_a is the air saturation of the soil
  P_a is local atmospheric pressure.

For the conditions at the Seymour Site and the requirements of the RAP, Equation 1 reduced to the following relationship involving only air permeability:

$$L = 280\sqrt{k_a} \qquad (5)$$

where L is the required drain spacing in feet and k_a is the air permeability in Darcies.

CONCLUSION

A numerical model (TRACRN[6]) was used to test the ability of the

Figure 10
Tracer Breakthrough Curves for Test 1

SVE system to achieve the goal of 80% mass removal. The mass removal goal incorporated into the RAP was based on simplified design calculations using an exponential dilution model which assumed a well-mixed soil volume. The use of a numerical model for the final design calculations allowed consideration of nonuniform soil properties and did not require that the soil volume be assumed to be well-mixed. Three numerical models were constructed, each considering different soil stratigraphies and permeabilities characteristic of the site (Fig. 12).
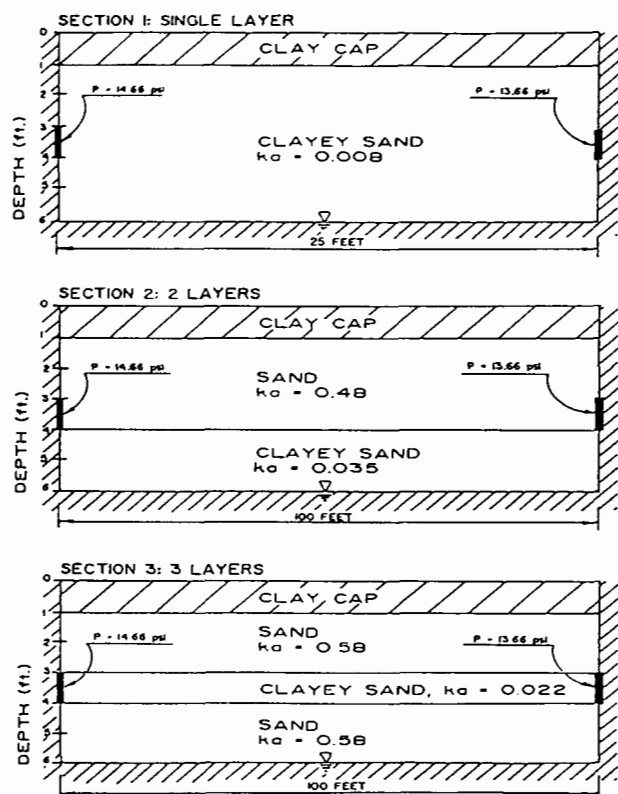
Figure 12
Conceptual Drawing of the Three Type
Sections used in the Numerical Models

The number of years required to achieve the 80% mass removal goal for typical VOCs is listed in Table 1, along with the times based on the exponential dilution model applied to a clay soil. The results indicated that the exponential dilution model yielded conservative results in terms of soil cleanup times.

Table 1
Seymour SVE Predicted Cleanup Times
(time to remove 80% of mass (yr))

COMPOUND	EXP DILUTION CLAY[1]	SINGLE CLAY LAYER (section 1)	2 LAYER SAND/CLAY[3] (section 2)	3 LAYER SAND/CLAY/SAND[3] (section 3)
Vinyl Chloride	0.8	0.5	0.3	0.2
Dichloromethane	3.6	1.9	1.6	0.7
1,1 Dichloroethane	2.8	1.5	1.2	0.6
1,1,1 Trichloroethane	2.5	1.4	0.6	0.5
Trichloroethylene	4.3	2.3	0.9	0.8
Toluene	9.8	5.0	2.0	2.0
Drain Spacing (ft)	---	25	100	100
Average Pore Volumes (per year)	19.7	19.7	48	65

Notes:

(1) Results based on soil properties and flow rate obtained from the single clay layer simulation.
(2) Pressure drop of 1 psi assumed in all simulations.
(3) In the 2 and 3-layer systems, maximum drain spacing was set at 100 feet to provide flexibility in system operation. This resulted in flow rates which exceed the maximum recommended in the Seymour RAP.

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The Trouble With DNAPLs

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ABSTRACT

Sites contaminated with Dense Nonaqueous Phase Liquids (DNAPL) present unique challenges during investigation and remediation, not only for the environmental consultant, but for the regulators as well. Unlike lighter-than-water compounds, where soil contamination generally is limited to the unsaturated zone above the water table, residual DNAPL can coat the soil from the ground surface down to the first confining layer, where pools of DNAPL can form. The residual and the pools of DNAPL combine with the relatively low solubility of the DNAPL compounds to provide an almost endless source of contaminants to the groundwater. The large volumes of soils involved and the depths reached by these dense organic liquids, often make source control an unachievable goal. In addition, movement of DNAPL independent of groundwater flow significantly complicates identification of the extent of contamination and limits the effectiveness of traditional remedial techniques.

Addressing DNAPL sites requires not only a thorough understanding of the physical and chemical characteristics of the chemicals present and the hydrogeologic setting of the site, but it also requires creativity in the development and selection of remedial alternatives. For many DNAPL sites, it can be argued that the emphasis for remediation should be placed on preventing future migration, minimizing the impact on human health and the environment and encouraging the development of new technologies to clean up these sites.

INTRODUCTION

Groundwater monitoring, spurred by RCRA and CERCLA, has resulted in considerable interest in the contamination of groundwater by organic chemicals. Several of these chemicals fall into the class of Dense Nonaqueous Phase Liquids (DNAPL) due to the fact that they are immiscible in water and have densities greater than that of water.[1] DNAPL compounds include halogenated solvents commonly used in industries (such as electronics manufacturing, automotive repair and dry cleaning) and creosote, a wood preservative derived from coal tar, which contains hundreds of individual compounds.[2] Approximately one fourth of the organic compounds on the U.S. EPA Priority Pollutant List are DNAPL compounds and DNAPL compounds have been identified at hundreds of Superfund sites.[1,2] Considering the common use of DNAPL compounds, as well as their widespread occurrence as groundwater contaminants, it is important that regulators, industry and consultants develop an accurate understanding of the implications of groundwater contaminated with DNAPL compounds.

This discussion begins with a presentation of the physical characteristics of typical DNAPL compounds, followed by the current understanding of the transport and fate of these compounds in the subsurface. In regards to transport and fate, it should be noted that significantly more information is available for chlorinated solvents than for creosote compounds. After the presentation of this somewhat theoretical information, a series of four case studies involving DNAPL sites is presented. The sites involve either chlorinated solvents or creosote in various hydrogeological settings. These case studies illustrate observed DNAPL migration in the subsurface and some of the difficulties that have been faced in the investigation and remedial alternative selection for these sites. Although there is some discussion regarding the transport in fractured media, the emphasis is on porous media.

PHYSICAL AND CHEMICAL PROPERTIES OF DNAPL COMPOUNDS

The behavior of a fluid in the subsurface is dependent on the physical and chemical properties of both the fluid and the subsurface environment. Table 1 presents a list of common DNAPL compounds along with physical and chemical properties which affect their behavior in the subsurface. These compounds are grouped by their class; the upper portion of the table relates to chlorinated solvents and the lower portion of the table relates to polynuclear aromatic hydrocarbons or creosote compounds. These four compounds account for 20 to 50% of the creosote mixture.

As the name implies, DNAPL compounds are characterized by densities greater than water (1.00 gm/cm^3) and by relatively low solubilities in water, typically less than 5000 mg/L for the chlorinated solvents and less than 1.0 mg/L for many of the creosote compounds. These two properties allow the DNAPL to pass downward through a column of water as a separate phase. They also allow the DNAPL flow to follow the contours of the top of a confining layer as opposed to

Table 1
Physical and Chemical Properties of Selected DNAPL Compounds

	DENSITY (g/cm³)	VISCOSITY (cP)	VAPOR PRESSURE (mm)	VAPOR DENSITY[a]	SOLUBILITY (mg/L)	LOG (s) (K_ow)
Chlorinated Solvents(2)						
Methylene Chloride	1.33	0.44	349	1.89	20,000	1.30
Chloroform	1.49	0.56	151	1.62	8,200	1.95
Carbon tetrachloride	1.59	0.97	90	1.51	785	2.83
1,2-Dichloroethane	1.26	0.84	61	1.19	8,690	1.48
1,1,1-Trichloroethane	1.35	0.84	100	1.47	720	2.48
1,1,2-Trichloroethane	1.44	na	19	1.09	4,500	2.18
1,1-dichloroethylene	1.22	0.36	590	2.54	400	1.48
Trans-1,2-dichloro-ethylene	1.26	0.4	326	2.01	600	2.09
Trichloroethylene	1.46	0.57	58	1.27	1100	2.53
Tetrachloroethylene	1.63	0.90	14	1.09	200	2.60
Creosote(7)	1.04	72	-	-	-	-
Napthalene[6]	1.15	-	5.4x10⁻²	-	30	3.36
Phenanthrene[6]	1.18	-	2.1x10⁻⁴	-	0.8	4.46
Fluorene[6]	1.20	-	1.0x10⁻²	-	1.7	4.18
Fluoranthene[6]	1.25	-	1.0x10⁻²	-	0.3	5.22

a Relative to the density of air

flowing along the top of the water table, as is the case with lighter-than-water immiscible liquids.

Beyond the similarities described above for the chlorinated solvents and creosote compounds, the physical characteristics differ fairly widely between the two groups. The chlorinated solvents have viscosities less than water, which suggests that pure chlorinated solvent will move faster through porous media than water [viscosity of 1.005 Cp at 25 °C[3] and the creosote compounds, with higher viscosities, will move more slowly than water. The difference in viscosity between the chlorinated solvents and water also affects their migration through the saturated zone, resulting in fingering of the chlorinated solvent as it displaces the water.[4] This fingering effect may not be as significant for creosote. The high vapor pressures for the chlorinated solvents make groundwater contamination via sinking vapors a concern. This phenomenon is not a significant problem for the creosote compounds. The log K_{ow} values indicate that the movement of dissolved chlorinated compounds will

FIGURE 1a. GROUNDWATER CONTAMINATION FROM A RESIDUAL DNAPL SOURCE IN THE UNSATURATED ZONE.

FIGURE 1b. GROUNDWATER CONTAMINATION FROM RESIDUAL DNAPL SOURCE IN THE UNSATURATED AND SATURATED ZONES.

Figure 1
Scenarios for DNAPL Migration

be retarded somewhat and that the creosote compounds will be significantly retarded when compared with the velocity of water through the soils.

TRANSPORT AND FATE OF DNAPL

Figure 1 presents a series of diagrams illustrating three different scenarios for the migration of DNAPL into the subsurface. Figure 1a represents a scenario in which the volume of DNAPL spilled is less than the retention capacity of the unsaturated zone. The downward migration of the DNAPL, therefore, stops before the water table is reached, resulting in an immobile mass of DNAPL in the unsaturated zone. This is not to say however, that the spill will not impact the groundwater. Organics dissolved in infiltrating rainwater have the potential to continue migrating toward the water table.[2] In addition, vapors from the chlorinated solvents can descend through the unsaturated zone to the water table, where they can dissolve into the groundwater. Due to the low vapor pressures of the creosote compounds, the vapor concentrations in the unsaturated zone would not be as likely to affect the groundwater.

Based on laboratory tests using chlorinated solvents, the quantity of DNAPL which will be retained by the soil (residual saturation) is dependent on the hydraulic conductivity of the soil and the physical characteristics of the DNAPL. For these chlorinated solvents, the residual saturation in the unsaturated zone ranges from 3 to 30 L/m^3 for soils with hydraulic conductivities of 1x10^{-2} to 1x10^{-4} cm/sec, respectively.[2] This figure is equivalent to 1 to 10% of the pore space.[1] It should be noted that Schwille's work was based on laboratory experiments using single contaminant systems in columns of clean homogeneous sand. As a result, these values likely are lower than what would be encountered in a natural depositional setting where subsurface heterogeneities could increase the retention capacity of the system.[2] Work completed by Karikoff[5] indicates that organic compounds will adsorb more strongly to soils containing natural organics. Although his work was based on organic compounds dissolved in water, it is assumed that soils with higher natural organic content would have a higher retention capacity for phased organic compounds as well.

As shown in Figure 1b, if a spill exceeds the retention capacity of the unsaturated zone and if sufficient pressure exists, the DNAPL will penetrate the water table. The behavior of the DNAPL as it reaches the water table is considerably different than that of a dissolved contaminant. Unlike the dissolved contaminant, which will immediately alter its course in the direction of the horizontal groundwater flow, the DNAPL will continue its downward migration apparently unaffected by the groundwater flow.[2] This downward migration will continue through the saturated zone until the residual saturation of the soil is reached. Residual saturation values for the saturated zone differ from those for the unsaturated zone due to differences in interfacial tensions between air and DNAPL and water and DNAPL. These values for chlorinated solvents range from 5 to 50 L/m^3 for soils with hydraulic conductivities of 1x10^{-2} to 1x10^{-4}, respectively.[2] This is equivalent to 2 to 15% of the pore space.[1] As in the unsaturated zone, this residual mass of DNAPL in the saturated zone is essentially immobile. The permeability of the porous media containing the residual mass will be affected by the presence of the mass; however, groundwater will flow through the immobile residual and, theoretically, emerge at concentrations equivalent to the solubility of the DNAPL compound.[1]

As shown in Figure 1c, when the quantity of DNAPL spilled exceeds the retention capacities of both the unsaturated zone and the saturated zone, the DNAPL will accumulate on the top of an underlying confining layer or low permeability lens. This DNAPL accumulation will migrate down the slope of the top of the confining layer regardless of the direction of groundwater flow. This migration will continue until the DNAPL either forms a pool in a depression on top of the confining layer or migrates through the confining layer via root holes or fractures. The downward migration through a confining layer can also occur through improperly installed monitoring wells or ungrouted boreholes. Groundwater flowing across the top of the DNAPL pool will not affect the movement of the pool; however, as this occurs, DNAPL will dissolve from the pool into the groundwater.[1]
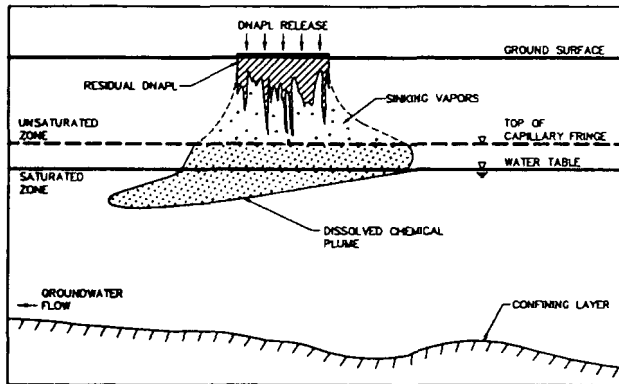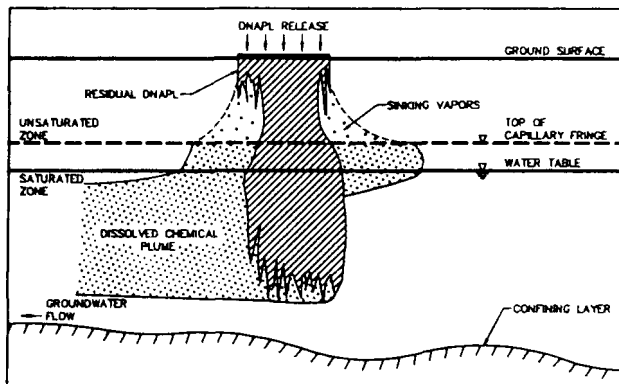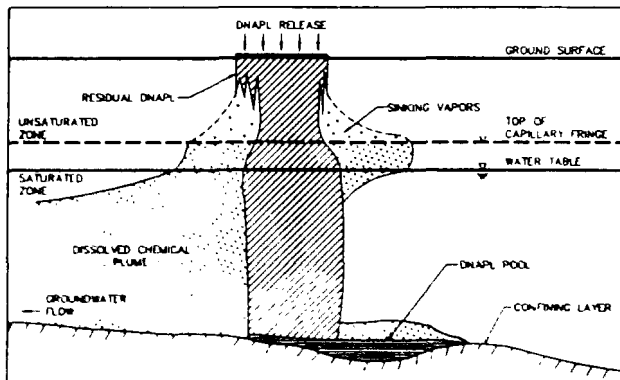
Significant observations based on the laboratory work with chlorinated solvents are that the migration through the soil can be very rapid and that even small changes in the permeability of apparently homogeneous material can completely divert the DNAPL flow.

IMPACT ON SITE CHARACTERIZATION

There are three general problems associated with the investigation of sites contaminated with DNAPL: (1) defining the source area, (2) determining whether or not free-phase organics are present and (3) determining the depth of contamination without contributing to further downward migration. The importance of each problem is discussed below.

Defining the Source

Typical site remediation includes source removal. The objective of the remediation is to eliminate a large percentage of the contaminant mass so that remediation can be accomplished in a reduced period of time or in a less costly manner. With DNAPL, the area of residual saturation and any pools, in effect, are part of the contaminant source. As has been discussed previously, the mass of contaminants immobilized in the soil, coupled with the low solubility of the DNAPL compounds, provide an almost endless supply of contaminants to the aquifer.

As with other contaminants, the search for DNAPL begins at the point of release. However, since low permeability lenses and the top of the confining layer will affect the migration pathway, residual saturation can be present upgradient or crossgradient of the original source. This migration path can be erratic and small volumes of soil can retain significant quantities of DNAPL. Even a fairly closely spaced grid may miss fingers of DNAPL that continue to act as a source. The closer the grid, the higher the confidence that the extent of DNAPL has been defined. This type of investigation becomes expensive.

In areas without rock or gravels, cone penetrometer testing can be extremely useful to map the low permeability soils and confining layers. This technique, however, generally is limited to depths of 100 ft or less and would not be used to investigate below an upper-water bearing zone unless casing was used.

Determining the Presence or Absence of Free-Phase DNAPL

If it could be proven that the DNAPL present existed only as residual saturation, an extraction well system could be used to contain the dissolved contaminant plume. However, if DNAPL pools are present, an extraction well system will not be adequate. This inadequacy is due to the fact that pumping water will not significantly impact the migration of DNAPL pools, which may continue to migrate, providing more source material outside of the well network. Determining the presence or absence of free-phase DNAPL is not trivial. Soil samples at residual saturation levels can appear to be very oily. Due to the problems with laboratory analyses at high levels of concentration in the soil, even analytical results may not be conclusive. The best indication of free-phase DNAPL, if seeps or other manifestations are not present, is an increase in concentration just above a confining layer.

As stated previously, laboratory tests have indicated that groundwater flowing through residual DNAPL theoretically can become saturated with the dissolved DNAPL compound. Dissolved concentrations as high as these are seldom observed in the field and typically are less than 10% of the solubility.[1,4] This problem is believed to result partially from aquifer heterogeneities and the mixing of clean and contaminated groundwater during sampling.[4] As a result, the location or presence of residual or free-phase DNAPL normally cannot be determined strictly from dissolved concentrations in the groundwater.

Determining the Depth of Contamination

In the absence of a known confining layer, drilling to define the lower extent of contamination is risky. Although casing can be used to isolate upper zones, there still is concern about creating artificial pathways for downward migration. One approach that has been used is to install wells outside of the area of shallower contamination to the depths of interest. Deeper borings closer to the source would not be completed unless these wells indicated contamination was already present in the lower zones. Defining the depth of DNAPL becomes a moot point in fractured rock or depths below approximately 150 ft since not much can be done to remediate DNAPL in these situations.

Considerable care must be taken when drilling and installing monitoring wells at sites potentially contaminated with DNAPL. First, improper selection of a screened interval within an aquifer can result in incorrect information regarding the presence or quantity of a DNAPL. If a well screen is set too deep into a confining layer, the result can be an over-estimation of the thickness of the free-phase DNAPL. Conversely, if the well screen is set too shallow, the result can be an under-estimation of free-phase thickness or collection of a groundwater sample too far above the DNAPL pool to reflect the presence of the dissolved contaminant. Secondly, drilling a boring through a DNAPL pool and through a confining layer can introduce the DNAPL to deeper strata, potentially leading to disastrous results. At best, this cross-contamination will result in erroneous conclusions regarding the concentrations and depths to which the DNAPL has migrated. At worst, it could result in the contamination of a previously unaffected aquifer.

IMPACT ON REMEDIATION

The movement of the organics in the subsurface and the presence or absence of phased organics becomes important in the evaluation and selection of remedial alternatives. Furthermore, the presence of DNAPL can seriously impact remediation costs and the amount of time required for remediation. It is possible for DNAPL compounds to penetrate into the subsurface to depths beyond the reach of normal excavation techniques and, due to the low solubility of DNAPL compounds, pump-and-treat remediation methods may require centuries to attain dissolved concentrations below the drinking water standards.[1]

For example, assume that an extraction well has been installed in an aquifer contaminated with residual and pooled trichloroethene (TCE). Assume also that groundwater can be extracted from this well at a rate of 10 gpm, which is not uncommon for shallow alluvial aquifers, at an average TCE concentration of 10 mg/L (approximately 1% of the solubility of TCE). At this pumping rate and concentration, only 36 gallons (less than two-thirds of a drum) would be removed from the aquifer in a year. For large spills, it becomes easy to see how pump-and-treat remediation scenarios could take hundreds of years to clean up an aquifer contaminated with DNAPL.

The use of surfactant, alkali and polymer to enhance the removal of the DNAPL has been tested in bench-scale and pilot-scale studies; however, limited information exists regarding the large-scale application of these technologies.[8] Furthermore, it is uncertain whether the use of surfactants alone will facilitate the cleanup of soils to within U.S. EPA guidelines.[9]

Another problem concerning sites contaminated with DNAPL compounds is the depths to which the DNAPL can migrate. In the absence of any shallow confining layer, a DNAPL spill could potentially migrate several hundred feet into the subsurface if the quantity of the spill was sufficient. This deep migration makes excavation of the DNAPL residual and pools impractical and containment at these depths also may not be feasible. In these cases, the best solution may be long-term monitoring and treatment of any contaminated groundwater which must be withdrawn from the aquifer for use.

There appear to be two potential approaches to remediating DNAPL sites. The first approach is to increase the solubility of the DNAPL in water so that pump-and-treat alternatives are more efficient. Although some work with surfactants has been done, additional testing is needed along with investigation of other options such as the use of organics which are miscible with water to increase the apparent solubility of DNAPL in the water. Another option to be considered is the introduction of materials which would effectively seal the affected soils. More research is needed to develop technologies to better address DNAPL sites.

CASE HISTORIES

The following contains four case histories of DNAPL-contaminated sites. The first two of the sites involve chlorinated solvents and the second two sites involve creosote compounds. Each case history includes a brief
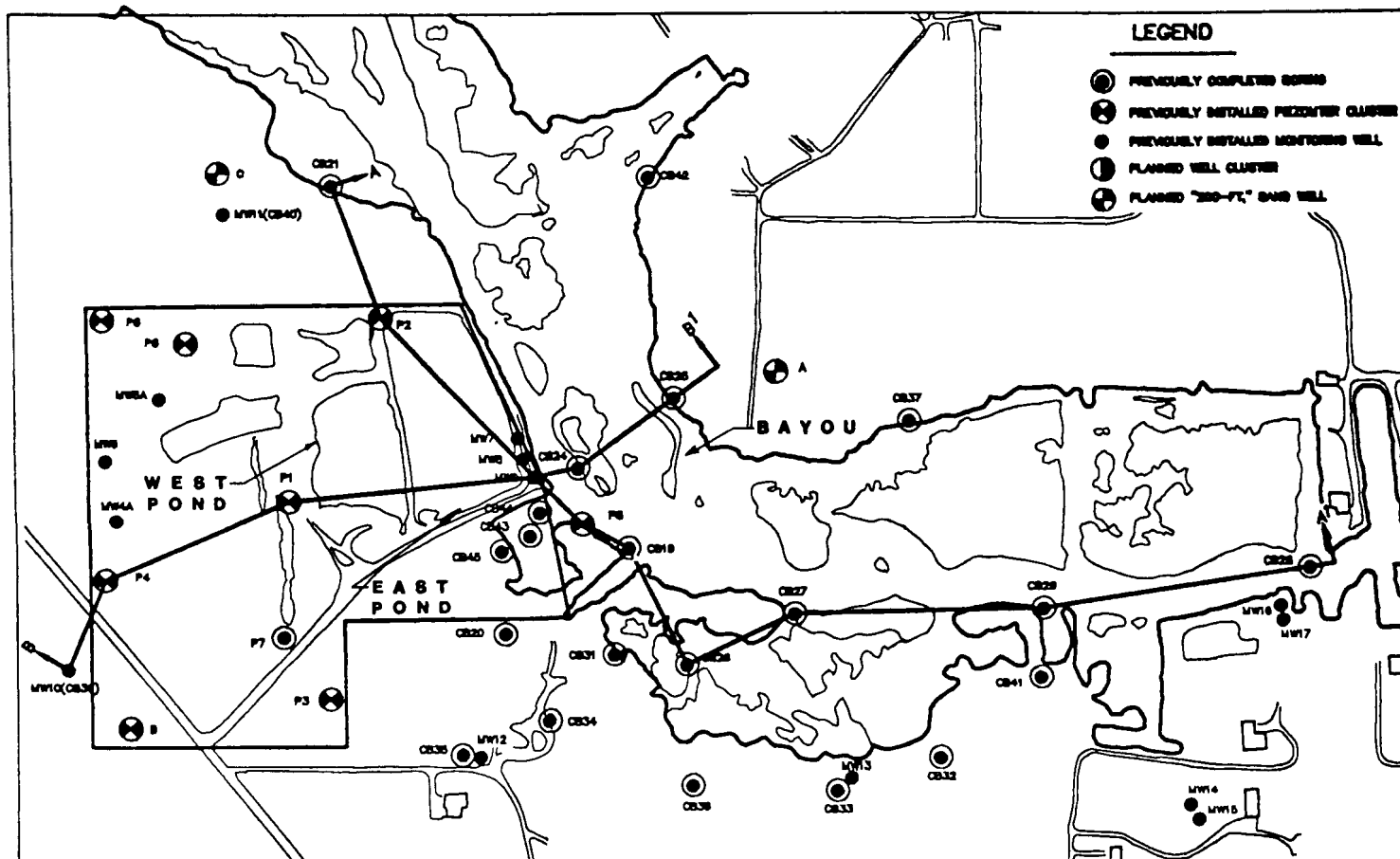
Figure 2
Case History A
Site Map

discussion of the site history, site geology, results of the site investigation, remedial alternative selection and current project status.

Case History A - Uncontrolled Chlorinated Hydrocarbon Disposal Site

From the early 1950s until the early 1970s wastes were brought to this site from a nearby industrial complex by an independent disposal company. A site diagram is shown in Figure 2. Liquid wastes consisting primarily of chlorinated hydrocarbons were discharged into the large ponds. In 1985 and 1986 a Remedial Investigation was conducted at the site. Among other things was the discovery of approximately 1,000,000 gallons of chlorinated solvents in the West Pond. The chlorinated solvents were composed of ten different compounds with 1,2-dichloroethane and 1,1,2-trichloroethane accounting for approximately 60% of the material present.

The site is located in the Gulf Coastal Plain. In the site area, Pleistocene Age deposits outcrop, while Recent deposits are confined to narrow belts along streams and wider belts in river basins. The Recent deposits are alluvium, consisting of fine sand, silt, clay and thin lenses of coarser sand. A geologic cross-section of the site is shown in Figure 3. Private wells in the site vicinity are screened as shallow as 150 feet MSL.

In an effort to determine the extent of contamination, borings and wells were completed. The borings were sampled continuously and screened in the field with an OVA. When elevated total readings were identified in a headspace analyses, a gas chromatograph was run with the same instrument for a positive identification of site contaminants. In addition, visual signs of contamination were noted. For this phase of the investigation, soil samples were not submitted for laboratory analysis. Based on the work plan, drilling at a particular location would

continue to a depth of 100 feet MSL or 10 ft into clean soils, which ever was deeper. In areas where contaminants were found, casing was used to prevent cross-contamination of lower strata.

A problem that was encountered with this approach is illustrated with the boring log shown on Figure 4. The graph on the left side shows the OVA readings with depth. Clean samples (OVA reading < 10 ppm) were identified at depths of 67, 82 to 92, 103, 118 and 124 feet, with significant contamination in between. As shown, this occurred several times. Although this boring was terminated at 124 ft due to limitations of the rig, there is not a high degree of comfort that the vertical extent of the contamination was identified.

A cross-section across the site is shown in Figure 3. The areas of apparent free-phase chlorinated solvents are illustrated with hatching. The results of the site investigation supported a number of the concepts of DNAPL research work including the diversion of chlorinated solvents by layers of less permeable soils. Significant fingering was apparent along with the identification of differing contaminant foot prints with depth. Another interesting aspect is the appearance that the chlorinated solvents migrated through the thin clay layers. This finding was not supported by the laboratory data and the migration may have been through holes or fractures in the clay layer and not as bulk migration through the clay. Since drilling has not been completed directly beneath the pond, it is not known whether a true confining layer is present.

The most significant problem encountered during the Site Investigation was how to determine the vertical extent of migration of the chlorinated solvents directly below the impoundments. For technical reasons, there has been no desire to drill through the bottom of the pond for fear of encouraging the downward migration. The options being considered include deeper borings adjacent the impoundments, although,
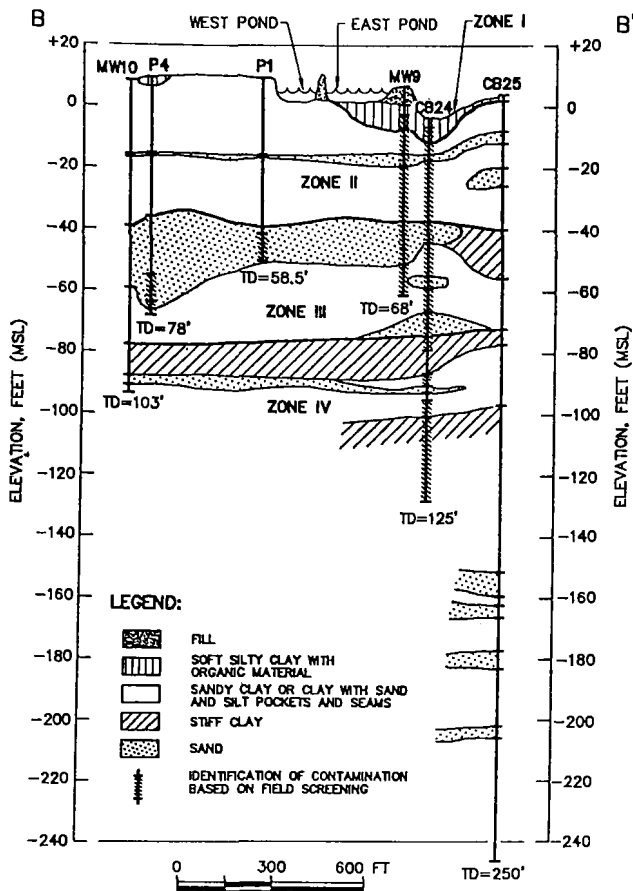
Figure 3
Case History 3
Stratigraphic Cross-Section B-B'
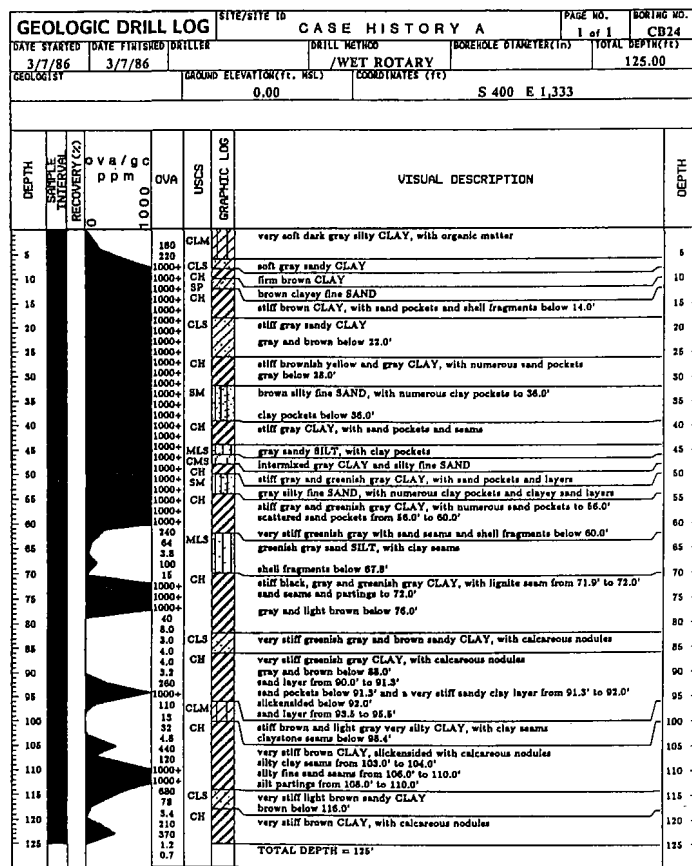
Figure 4
Case History A
Boring Log
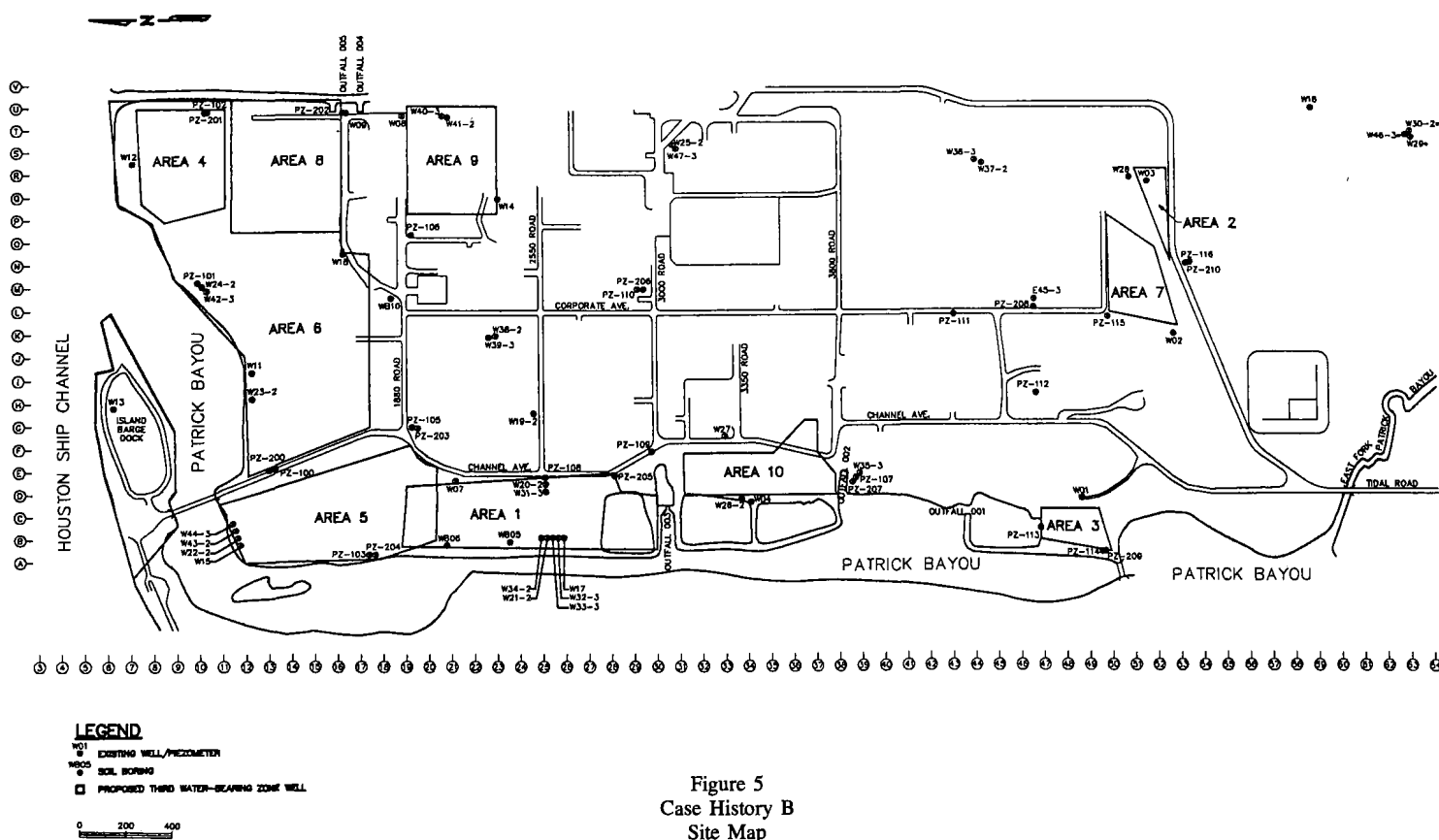
Figure 5
Case History B
Site Map
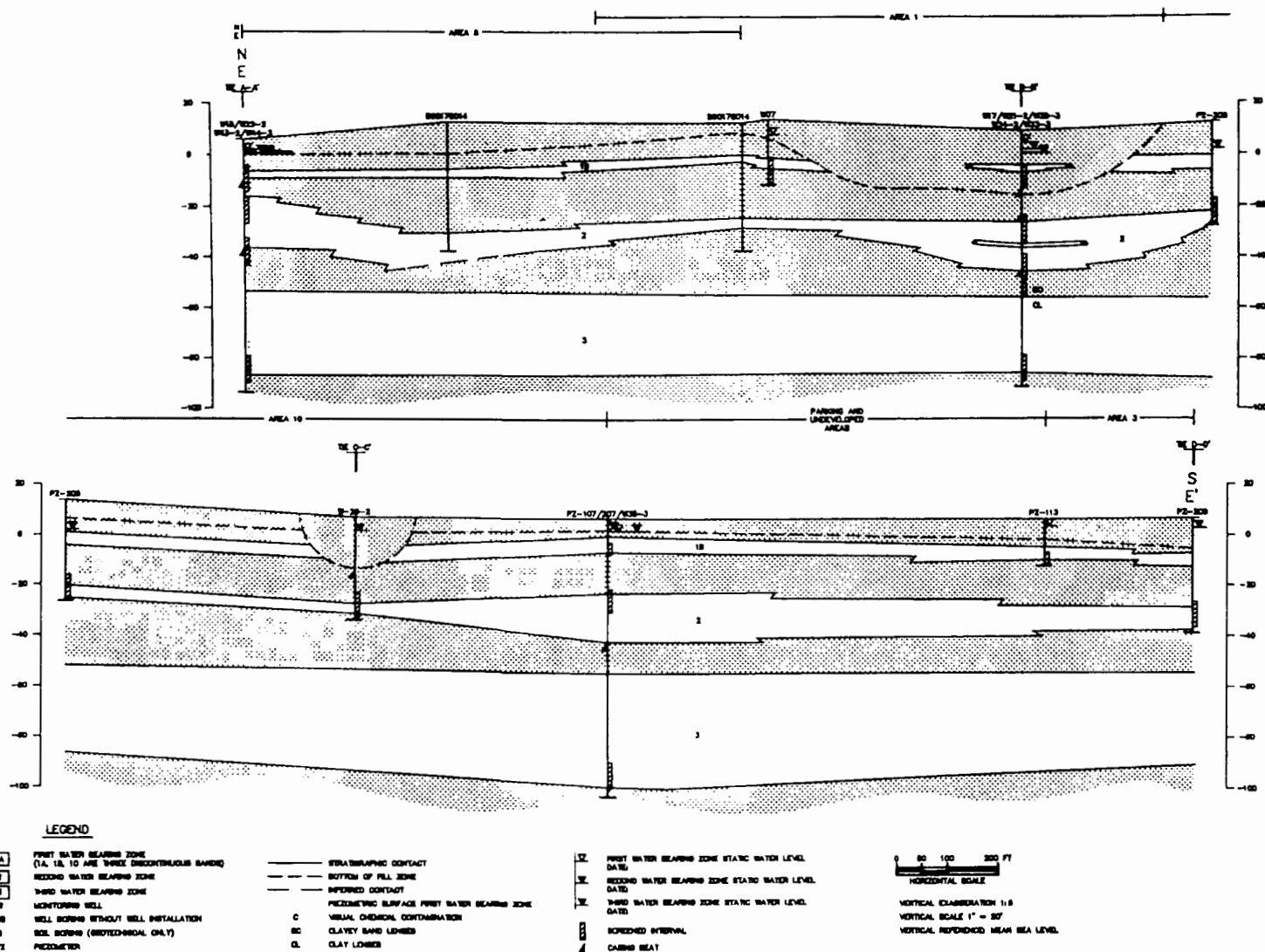
Figure 6
Case History B
Geologic Cross-Section

to some degree, this approach potentially has some of the same problems as drilling through the bottom of the pond. A second option is the use of directional or horizontal drilling where the vertical portion of the boring would be in a clean area. The drawback to this approach is the expense and the fact that current technology allows only one sampling depth beneath the pond. The third option to investigate the depth of migration is to install wells around the site screened in deeper formations. This option is being implemented currently and the need for additional investigation will be determined based on the results of sampling from these wells. Although not definitive, it will provide additional information regarding the depth of contamination.

In terms of potential remedial options, this site is complicated for a number of reasons. A portion of the migration has been beneath the adjacent bayou and chlorinated solvents have been identified to depths of at least 125 ft. If a confining layer is discovered, it may be possible to isolate this area with interceptor trenches or slurry walls. Without a confining unit, or a with a confining unit at a depth beyond the physical capabilities of any type of barrier, remediation likely will include institutional measures to prevent usage.

Case History B - Chlorinated Solvents Plant

This site is a currently operating, 60-acre chemical plant located along the Houston Ship Channel. A map of the site is shown in Figure 5.

Over the past 25 years, the plant has produced, among other chemicals, carbon tetrachloride, dichloroethene, trichloroethene and perchloroethene. These DNAPL compounds were generated both as products and as components of the plant's waste streams.

The site geology consists of fluvial and deltaic deposits of the Beaumont Formation. As shown in Figure 6, three water-bearing zones have been identified in the upper 120 feet. These include: a five-foot thick discontinuous silty sand at a depth of 20 feet; a five- to ten-foot thick silty sand at a depth of 40 feet; and a 40-foot thick silty sand at a depth of 70 feet. These water-bearing zones are separated from each other by leaky confining layers consisting either of clay or sandy clay. The shallowest known aquifer used in the area for drinking water is located at a depth of 400 feet.

During the investigation, chlorinated solvents were found in all three water-bearing zones, both in dissolved form at concentrations as high as 2000 mg/L (total chlorinated hydrocarbons) and as free phase pools on top of the underlying confining layers. The source of the contamination is believed to be a combination of historical releases from process areas and leakage from former waste management areas. While it is possible that the DNAPL migrated to the lower two zones via natural pathways, such as fractures in the confining layers, it is possible that the numerous geotechnical borings which had been drilled previously at the site contributed to the downward migration. These borings
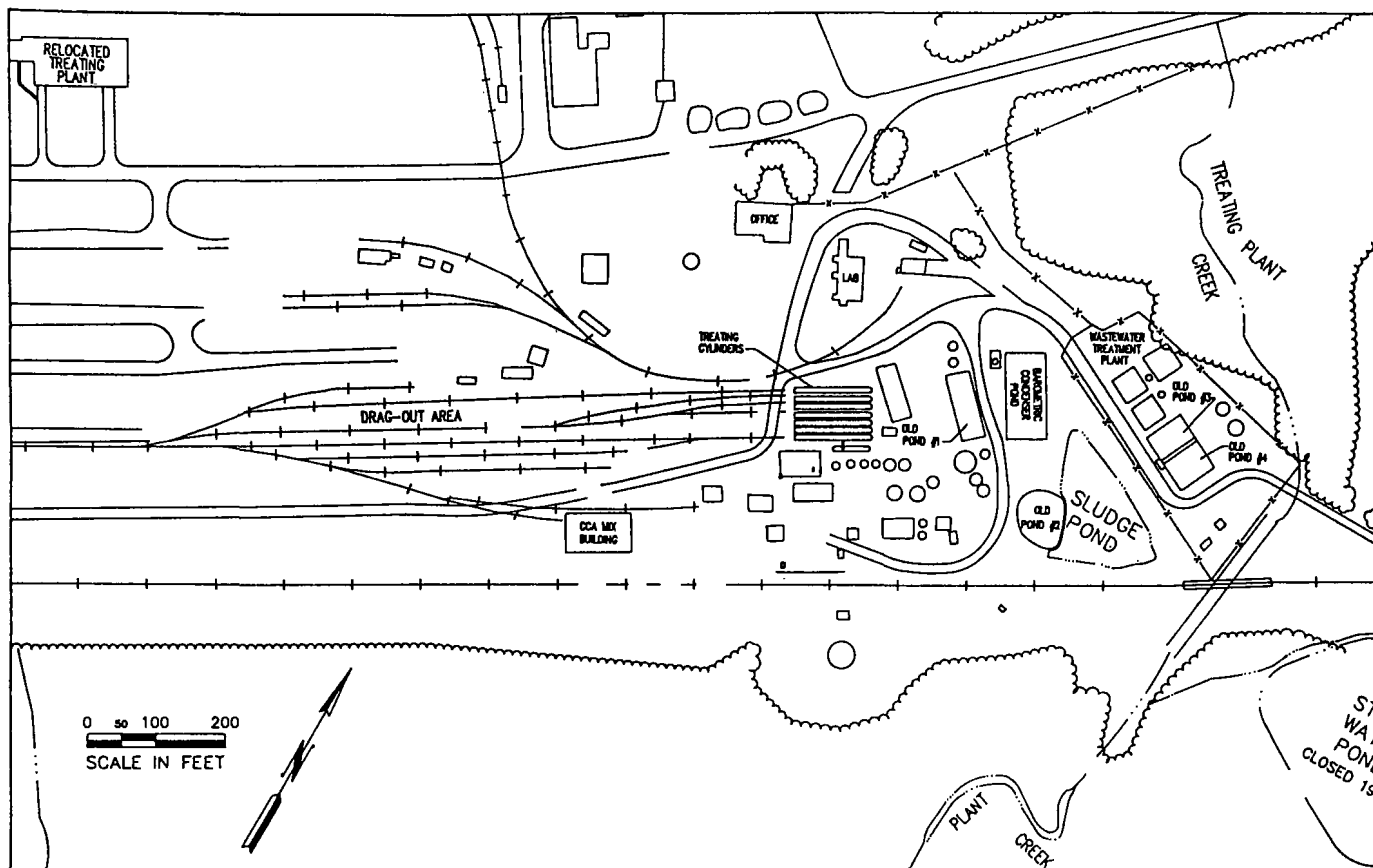
Figure 7
Case History C
Site Map
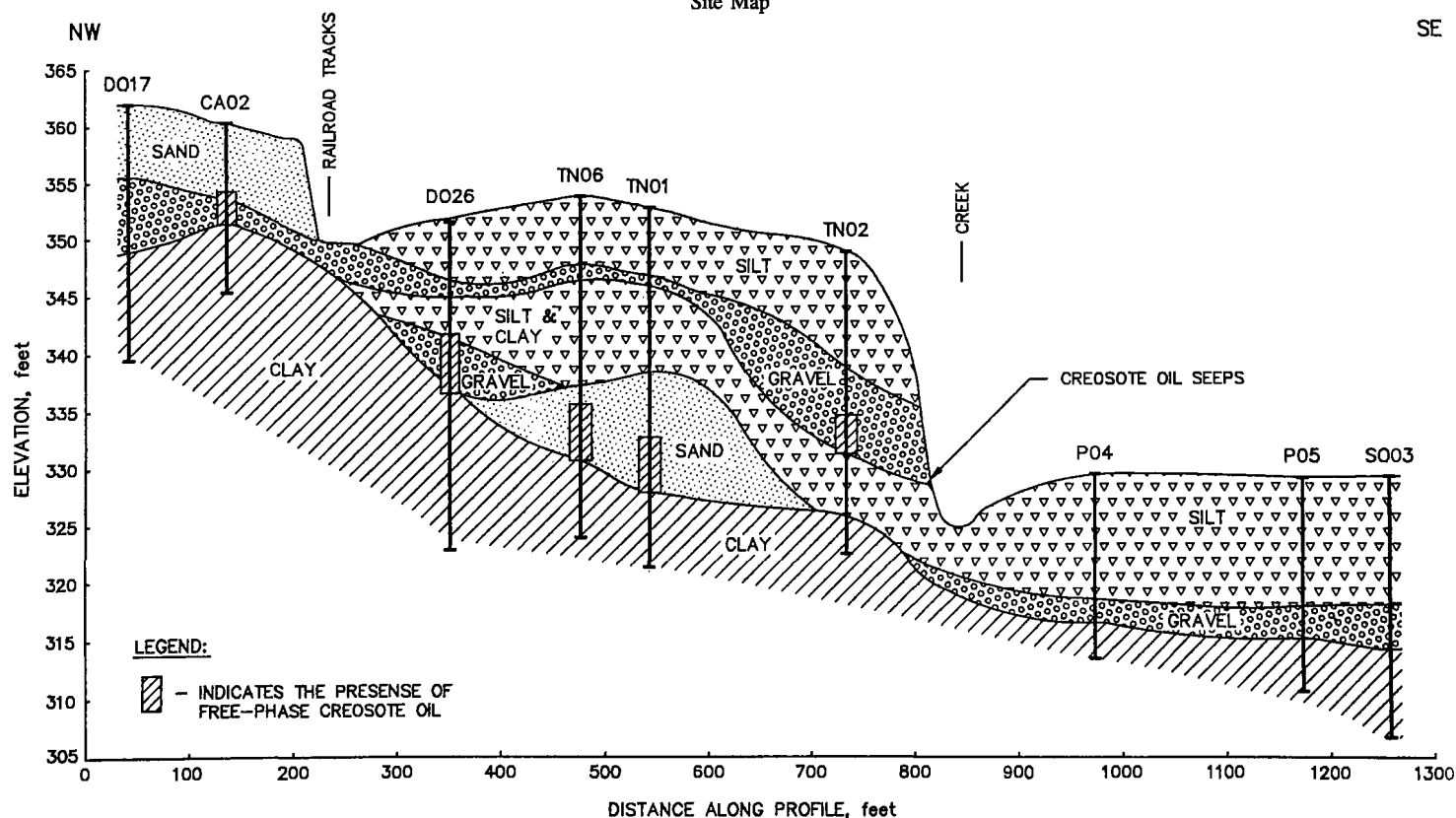
Figure 8
Case History C
Wood Treating Plant
Northwest-Southeast Geologic Cross-section

extended as deep as the third water-bearing zone and reportedly had been left ungrouted.

Subsequent work at the site has concentrated on preparing detailed maps of the top of each confining layer in an effort to predict the potential future migration of the DNAPL. Based on these maps and on the known locations of free-phase DNAPL, it appears that the DNAPL pools are migrating in a direction opposite that of the groundwater flow. Geophysical borehole logging has been utilized on nearby water-supply wells in order to characterize the stratigraphy beneath the third water-bearing zone without risking possible cross-contamination of any deeper zones during drilling activities.

Due to the depths to which the free-phase DNAPL had migrated (120 feet), many remedial alternatives, such as excavation, were determined to be impractical. Plans for remediation have focused on the containment and control of the free-phase DNAPL and dissolved DNAPL compounds. Plans are to install a slurry wall to the bottom of the second water-bearing zone in order to prevent further migration of the DNAPL pools in the upper two zones. Groundwater pumping will occur to maintain a negative hydraulic head on the slurry wall as well as to prevent migration of dissolved contaminants. Due to the depth of the third water-bearing zone, a remedial alternative for this zone has not yet been selected.

Case History C - Wood Treating Plant

This site is a currently operating 300-acre wood treating plant located in southwest Arkansas. A map of the site is shown in Figure 7. The plant has been in operation for more than 40 years, during which time wood products were treated either with chromium-copper-arsenate, pentachlorophenol or creosote. As was the practice at many wood treating plants, wastes generated during the wood treatment process were stored in unlined surface impoundments where free-phase treating solutions could be separated from the water and returned to the process area. This method of operation resulted in significant quantities of sludge, a major component of which was creosote oil.

The site geology consists of 15 to 25 feet of alluvium which generally of 12 to 20 feet of interbedded clays, silts and sands interbedded with a three to five foot thick discontinuous gravel unit. This gravel is underlain by the Paluxy Formation which consists of stiff clay with localized lenses of gravel, sand and limestone of depth. A cross-section of the site is shown in Figure 8. The upper-most water-bearing unit is a semi-confined aquifer, which is located in the alluvium and confined from below by the clays in the Paluxy Formation. Most of the water supply wells in the area are set in gravels and sands at depths below 150 feet.

During the investigation, free-phase creosote oil was identified in the gravel unit to the extent shown in Figure 9. The oil appears to have originated from the former impoundments and migrated down the slope of the top of the clay. A small creek, which runs through the site, intersects a portion of the oil-saturated gravel unit and creosote has been observed seeping from the stream bank. Much of the creosote, however, has migrated well beyond the creek by way of the gravel unit which, in places, passes beneath the creek. It is estimated that approximately 1,900,000 gallons of creosote oil are present in the gravel unit beneath the site. Groundwater generally flows in the same direction as the oil migration. This contamination is evidenced by a plume of dissolved creosote compounds which extends beyond the mass of creosote oil. Unlike the two sites previously discussed, a competent confining layer (thickness >20 ft) is present at the site at a depth of 15 to 25 feet. Migration of creosote into this clay is limited to no more than two feet.

Several Interim Remedial Measures (IRM) have been implemented to limit the migration of the oil, including: removal of sludges from several of the impoundments, closure of two of the three main impoundments, diversion of stream flow in the creek through a culvert which bypasses the oil seeps, construction of sumps in the stream bed to collect oils, and an installation of French drains to collect oils from the gravel in some areas.

The presence of a relatively shallow confining layer allows a variety of remedial alternatives which were not possible for the other sites.

The remedial alternatives currently being evaluated include: passive remediation, in situ treatment, excavation and containment/stabilization. Both the passive remediation and in situ treatment alternatives would use a series of extraction trenches to drain the oil from the gravels. In situ treatment would include the injection of surfactants and/or nutrients to flush out the residual oil and promote biodegradation. Although passive remediation would have a capital cost of only $2 million dollars, treatment of the groundwater and oils over 30 year period would cost an estimated $10 million. It is estimated that the injection of surfactants using current technologies would increase the removal rate of the creosote compounds but might not significantly reduce the time required for remediation; therefore, long-term operating costs would not decrease.

Excavation and on-site treatment of all of the contaminated soils would require only 4 years to complete but would cost in excess of $40 million. Containment of the migrating oils with slurry walls and capping to reduce infiltration appears to be the most viable alternative. This process would cost an estimated $4 million in capital costs, but the operating costs could be reduced by 75%. This alternative could be used to prevent further migration until more appropriate remedial technologies can be developed.

Case Study D - Arkwood Superfund Site

Wood treating at the Arkwood site was performed from 1962 to 1984. During this period both creosote and pentachlorophenol were used as preservatives. A map of the Arkwood site is shown in Figure 10. Also shown are the locations of borings and wells completed during the Remedial Investigation.

A geologic cross-section is presented in Figure 11. As shown, the geology is very irregular with soils above karst limestone. Present in the limestone are multiple fractures, joints, fissures and solution channels. This particular stratigraphy would have caused problems during the remedial investigation regardless of the contaminants present. The presence of DNAPL complicated the typical investigation problems
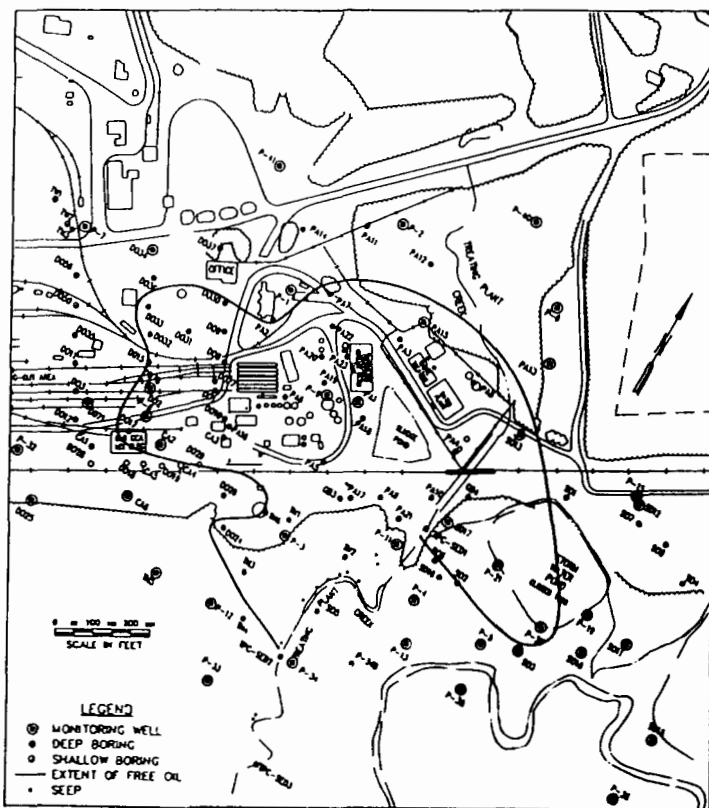
Figure 9
Case History
Extent of Creosote Oil Migration
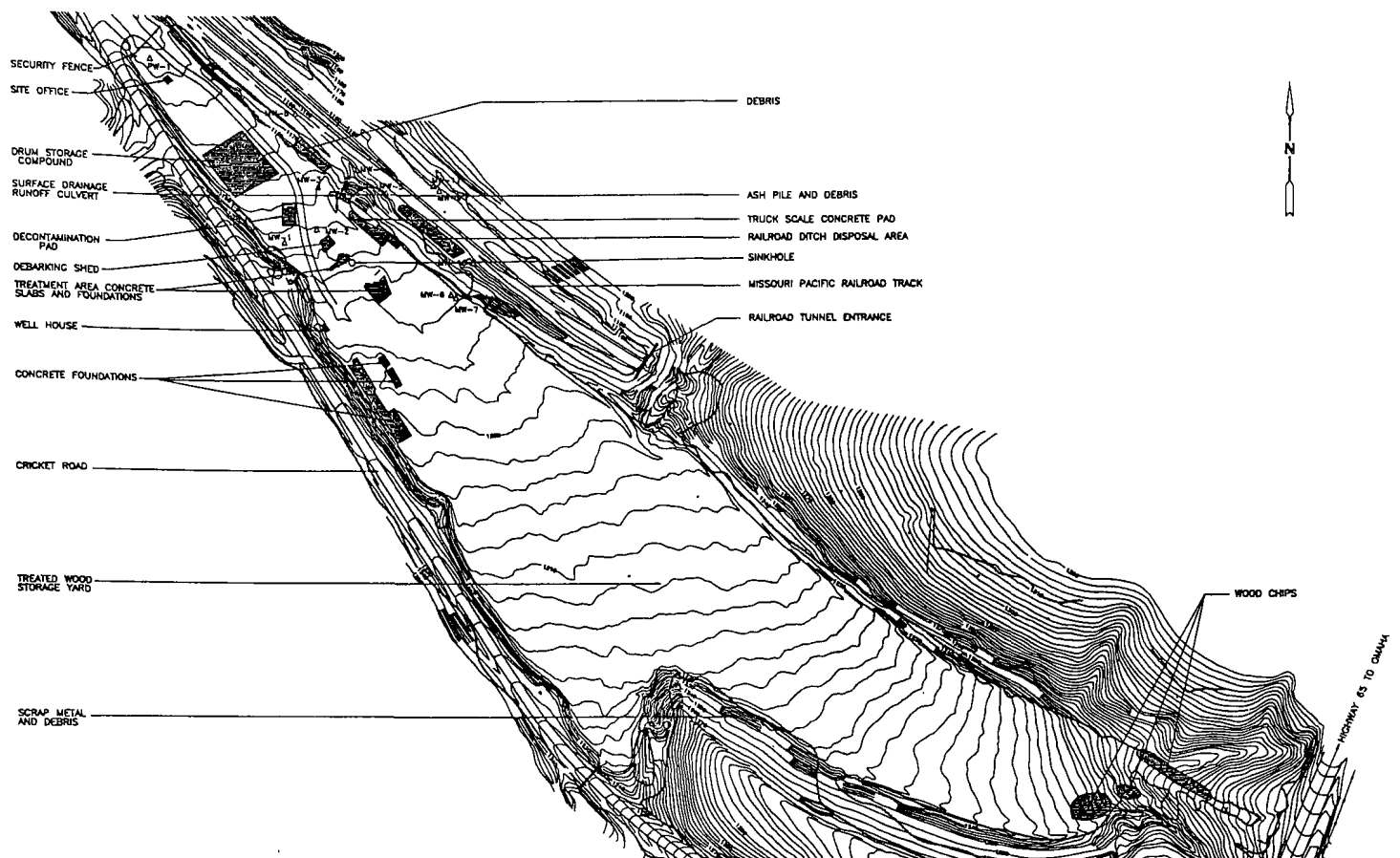
Figure 10
Case History D
Site Map

KEY:

▨ CLAY		SANDSTONE (SYLAMORE SS.)
▨ CLAY WITH CHERT	(RESIDUUM)	DOLOMITE (POWELL DOL.)
▤ LIMESTONE (ST. JOE FM.)		▽ G.W. LEVEL ON 5/4/89
		SCREENED OR MONITORED INTERVAL
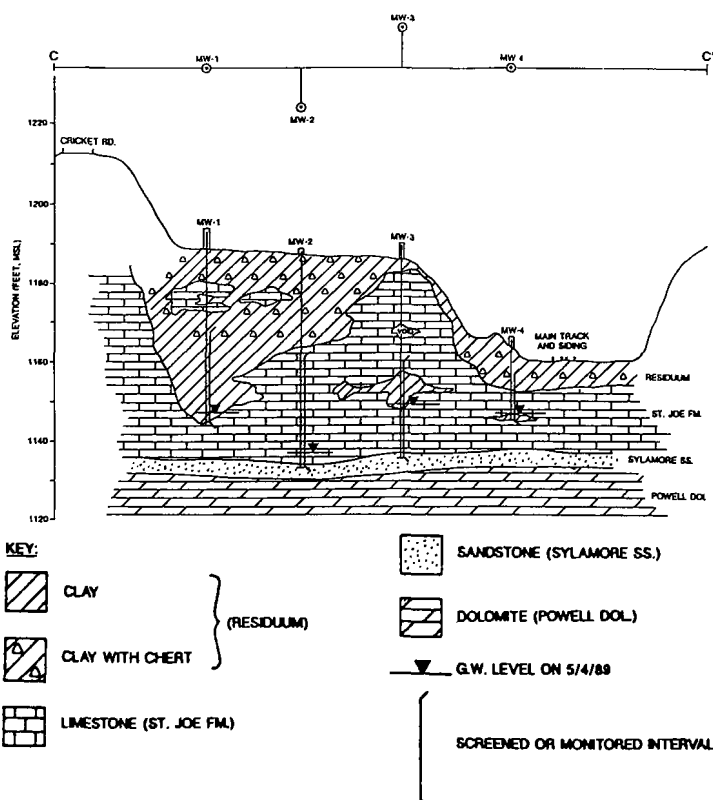
Figure 11
Case History D
Site Map

because the extent of contamination could not be defined. A spring approximately 500 feet from the site was contaminated with pentachlorophenol. Aside from this spring, no other contributions of contaminants to the surface water have been identified.

A clean closure of this site is not possible with current technologies. The remedial alternatives being considered focus on the sludges and soils present. The spring will be monitored to determine if natural attenuation is occurring. The decision regarding how to remediate the groundwater, if natural attenuation does not occur, has been delayed.

CONCLUSIONS

Knowing the physical properties and geological setting can provide indications of the migration of DNAPL in the subsurface. Due to the influence of apparently minor changes in stratigraphy on the flow pattern and the limitations of current investigatory techniques, defining the areas of residual saturation as well as the presence of DNAPL pools is difficult.

In the absence of a confining layer, or when migration of DNAPL is extensive, traditional remove-the-source remedial alternatives likely will not be feasible. Remediation of these sites will require an emphasis on containment to prevent further migration (if possible), minimization of the impact on human health and the environment and development of new technologies to truly remediate DNAPL sites.

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Remedial Actions for Superfund Sites
With PCB Contamination

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ABSTRACT

A summary of pertinent considerations in the development, evaluation and selection of remedial actions at Superfund sites with PCB contamination assists in promoting a consistent approach to addressing sites with similar characteristics. Starting point action levels of 1 ppm PCBs for residential sites and 10 to 25 ppm PCBs for industrial sites have been specified based on standard assumptions of direct contact risks. Within areas contaminated above these levels, high concentration material, identified as material with PCBs at 100 ppm PCBs or greater (residential) and 500 ppm PCB or greater (industrial), should be identified and treated consistent with Superfund expectations. Several innovative technologies are currently being evaluated for treatment of PCBs including dechlorination, solvent extraction, biotreatment and solidification. PCB-contaminated material that remains at the site at concentrations greater than the action level should be contained. The need for containment methods such as caps, liners and leachate collection systems will be determined based on the residual concentrations and site characteristics.

INTRODUCTION

PCBs were employed in the past primarily in capacitors and transformers. They also have been used in plasticizers, hydraulic and heat transfer fluids in heavy industrial use, lubricants and wax extenders. PCBs are no longer produced for industrial or commercial use in the United States. It was estimated in 1977 that, of the roughly 1.25 billion pounds of PCBs introduced into commerce in the United States since 1929, only 55 million pounds had been destroyed by incineration or by degradation in the environment.[5] The remaining PCBs were in landfills, in service or had been released to the environment. It is not surprising that they have become a major contaminant at many Superfund sites. The first PCB disposal regulations were promulgated in 1978.

Approximately 17% of the sites on the National Priorities List involve PCB contamination.[1] The remedy selection process for PCB sites is complicated for a number of reasons. From a regulatory point of view, there are unusually high numbers of potentially applicable or relevant and appropriate requirements (ARARs) and pertinent "to-be-considered" guidelines for actions involving PCB wastes that must be complied with at Superfund sites as required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Contingency Plan (NCP).[2]

PCBs are difficult to address technically due to their persistence and the apparently high toxicity of some isomers. Moreover, a large number of process options are potentially effective for addressing PCBs and deserve consideration.

In an effort to increase the consistency of Superfund site actions, the program is developing general frameworks for remedy selection for particular chemicals and site types. The general guidelines summarized here should provide the information necessary to determine starting point action levels for PCBs, to assess primary remedy components (treatment, containment) consistent with program expectations and statutory mandates and to assemble several focused alternatives within this framework.

REGULATIONS

The primary regulation governing actions taken at Superfund sites is the NCP.[2] The NCP describes a remedy selection process that will achieve the statutory mandates of the CERCLA and defines program goals and expectations. The overall Superfund goal is to select remedial actions that are protective of human health and the environment, that maintain protection over time and that minimize untreated waste. In addition to the overall goal, the Agency expects to develop appropriate remedial alternatives that:

- Use treatment to address the principal threats at a site, wherever practicable
- Use engineering controls, such as containment, for waste that poses a relatively low, long-term threat or where treatment is impracticable
- Use a combination of treatment and containment to achieve protection of human health and the environment as appropriate
- Use institutional controls to supplement engineering controls for long-term management and to mitigate short-term impacts
- Consider the use of innovative technology when such technology offers the potential for comparable or superior treatment, performance or implementability, fewer or lesser adverse impacts than other available approaches, or lower costs for similar levels of performance than more demonstrated technologies
- Return usable groundwaters to their beneficial uses wherever practicable, within a timeframe that is reasonable, given the particular circumstances of the site

The mandates of CERCLA also require that remedial actions comply with ARARs of other laws and regulations, be cost-effective and utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable.

ARARs for PCBs are relatively complex because PCBs are addressed by both the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA) and, in some cases, State regulations. Although the basic Superfund approach to addressing PCB-contaminated sites is consistent with other laws and regulations, this consistency must be documented in the feasibility study and Record Of Decision (ROD).

TSCA requires that material contaminated with PCBs at concentrations of 50 ppm or greater be disposed of in an incinerator or by an

alternate method that achieves a level of performance equivalent to incineration. Liquids at concentrations more than 50 ppm but less than 500 ppm and soils contaminated above 50 ppm may also be disposed of in a chemical waste landfill. TSCA outlines several requirements for chemical waste landfills that must be complied with unless it can be demonstrated that operation of the landfill will not present an unreasonable risk of injury to health or the environment. In these circumstances, a waiver of certain requirements may be approved by the Regional Administrator. Municipal sludges and dredged material can be disposed by a method approved by the Regional Administrator. Although TSCA requirements do not apply to PCBs at concentrations less than 50 ppm, TSCA also includes an antidilution provision under which the U.S. EPA can require disposal of PCBs based on the original concentration of the material spilled. This provision was created to ensure that PCBs would not be diluted as a means of relieving TSCA disposal requirements. It has been determined that the TSCA antidilution provisions are only applicable to CERCLA response actions that occur once a remedial action is initiated.[4] In selecting response action strategies and cleanup levels under CERCLA, the U.S. EPA should evaluate the form and concentration of the PCB contamination "as found" at the site and dispose of it in accordance with the requirements of 40 CFR 761.60(a)(2)-(5). Also under TSCA, the PCB Spill Policy was developed. This policy defines the level of cleanup required for recent, small volume PCB spills for different land use scenarios.

RCRA requirements apply to PCBs when liquid waste that is defined as hazardous under RCRA contains PCBs at concentrations greater than 50 ppm or nonliquid hazardous waste contains total halogenated organic compounds at concentrations greater than 1000 ppm. The land disposal restrictions require that when this material is placed on the land, it must be incinerated unless a treatability variance is obtained. Treatability variances are generally warranted for soil and debris wastes at Superfund sites. Superfund guidance on treatability variances for soil and debris indicates that for PCB concentrations greater than 100 ppm, treatment should achieve 90 to 99% reduction of PCBs.

Other requirements that derive from the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA) and their implementing regulations may apply or be relevant and appropriate when the site involves surface or groundwater contamination.

PRELIMINARY REMEDIATION GOALS

The first step in defining the problem that must be addressed is determining the action level, the concentration of PCBs over which some action, either treatment or containment, must be taken. Action levels should be evaluated for each medium that is contaminated. Media considered may include soils, groundwater and sediment.

For soils, the concentration of concern for PCBs will depend primarily on the type of exposure that will occur based on the land use—current and future residential or industrial. Based on direct contact exposure (including ingestion, inhalation and dermal contact) assumptions,[6] starting point concentrations have been set at 1 ppm PCBs for residential settings and 10 to 25 ppm PCBs for industrial settings. The 1 ppm starting point for sites in residential areas reflects a protective, quantifiable concentration. (Also, because of the persistence and pervasiveness of PCBs, PCBs will be present in background samples at many sites.) For sites in industrial areas, cleanup levels generally should be established within the range of 10 to 25 ppm. The appropriate concentration within the range will depend on site-specific factors that affect the exposure assumptions. For example, at sites where exposures will be very limited or where soil is already covered with concrete, PCB concentrations near the high end of the 10-to-25 ppm range may be protective of human health and the environment.

If groundwater that is or may be used for drinking water has been contaminated by PCBs, response actions that return the groundwater to drinkable levels should be considered. The Safe Drinking Water Act (SDWA) provides the basis for determining cleanup levels for the drinking water exposure pathway. Nonzero maximum contaminant level goals (MCLGs) or maximum contaminant levels (MCLs) should be attained in groundwater that is current or potential drinking water. State

drinking water standards may also be potential ARARs. Proposed nonzero MCLGs and proposed MCLs may be considered for contaminated groundwater. The proposed MCL for PCBs is .5 ppb. Since PCBs are relatively immobile in most soil types, their presence in the groundwater may have been facilitated by solvents (e.g., chlorobenzene diluents, mineral oil, etc.) or by movement on colloidal particles. Consequently, once PCBs reach an aquifer, they are difficult to completely remove using traditional groundwater extraction techniques. In some cases, an ARAR waiver for the groundwater may be supported based on the technical impracticability of reducing PCB concentration to health-based levels in the groundwater. Access restrictions to prevent the use of contaminated groundwater and containment measures to prevent contamination of clean groundwater should be considered in these cases.

The cleanup level established for PCB-contaminated sediment may be based on direct-contact threats (if the surface water is used for swimming) or on exposure assumptions specific to the site (e.g., drinking water supplies). More often the impact of PCBs on aquatic life and consumers of aquatic life will determine the cleanup level. Interim sediment quality criteria (SQC) have been developed for several nonionic organic chemicals, including PCBs, and may be considered in establishing remediation goals for PCB-contaminated sediments.[3] The method used to estimate these values is termed the equilibrium partitioning approach. It is based on the assumptions that: (1) the biologically available dissolved concentration of a chemical in interstitial water is controlled by partitioning between sediment and water phases that can be estimated based on organic carbon partition coefficients; (2) the toxicity of a chemical to, and bioaccumulation by, benthic organisms is correlated with the bioavailable concentration of the chemical in pore water; and (3) the ambient aquatic life water quality criteria (WQC) concentrations are appropriate for the protection of benthic communities and their uses.

Table 1 presents the sediment quality criteria and derived PCB-sediment concentrations based on the SQC for freshwater and saltwater environments and two organic carbon (OC) concentrations. These criteria are to be considered in establishing remediation goals for contaminated sediments.

Table 1
Sediment Cleanup Levels for Consideration

	Aquatic Environment	
	Freshwater	Saltwater
WQC	0.014 ppb	0.024 ppb
Sediment Quality Criteria (ug/g organic carbon)	19	33
OC = 10% (ug/g of sediment)	1.9	3.3

DEVELOPING REMEDIAL ALTERNATIVES

The potential response options at any site range from cleaning up the site to levels that would allow it to be used without restrictions to closing the site with full containment of the wastes. Figure 1 illustrates the process for developing alternatives for a PCB-contaminated site.

It is the expectation of the Superfund program that the primary alternatives for a site will involve treatment of the principal threats and containment of the remaining low-level material. As indicated above, for sites in residential areas, principal threats will generally include soils contaminated at concentrations greater than 100 ppm PCBs. For sites in industrial areas, principal threats will include soils contaminated at concentrations greater than or equal to 500 ppm PCBs.

Liquid and highly concentrated PCBs constituting the principal threats at the site should be addressed through treatment. Treatment options that are currently available or are being tested include incineration, solvent washing, chemical dechlorination, biological treatment and solidification. Compliance with TSCA ARARs requires that PCBs at greater than 50 ppm be incinerated, treated by an equivalent method or disposed in a chemical waste landfill. Equivalence to incineration

is demonstrated when treatment residues contain less than 2 ppm PCBs. If treatment is not equivalent to incineration, compliance with TSCA ARARs must be achieved by implementing long-term management controls consistent with the chemical waste landfill requirements. (Liquid PCBs at concentrations greater than 500 ppm may not be landfilled under TSCA regulations.)

Long-term management controls should generally be implemented for treatment residuals and other low-level contaminated materials

Key

Residential

Industrial

XXX Containment

Action Area Boundary

What is the action area assuming unlimited exposure?

1 ppm PCB or greater

10 – 25 ppm PCB or greater

What are principal threats to be treated?
(PCBs at 500 ppm or greater, or more than 2 orders of magnitude above the action level.)
Treat principal threats at least to levels that are to be contained (90% reduction)

1–100 ppm   1–100 ppm
100 ppm or greater
1–100 ppm

10 - 500 ppm
500 ppm or greater   10 – 500 ppm

Exceptions:
• Large municipal landfills
• Inaccessible contamination

10 ppm or greater

How should material remaining at the site be contained?

Exceptions:
• Small volumes
• Sensitive exposures
• Unreliable containment

Contain residues and remaining material (See Table 3)

Partially Treat

Treat to levels requiring fewer long-term management controls (See Table 3)

Fully Treat

Treat to levels for which no long-term management controls (including access restrictions) are necessary

1-100 ppm   10-500ppm

1-10 ppm   10–50 ppm

1 ppm   10 ppm

* These numbers are guidance only and should not be treated as regulations.

Figure 1
Key Steps in the Development of Remedial Alternatives
for PCB-Contaminated Superfund Sites

remaining at the site. Example scenarios for the use of long-term management controls appropriate for particular PCB concentrations are shown in Table 2. The substantive requirements of a chemical waste landfill specified in TSCA regulations are indicated, along with the justification that should be provided when a specific requirement is waived under TSCA. (Under CERCLA, on-site actions must meet substantive, but not procedural, requirements of other laws.) TSCA requires that nonliquid PCBs that are not incinerated or treated by an equivalent method be disposed in a chemical waste landfill; it may be appropriate to waive certain landfill requirements where treatment has reduced the threat posed by the material remaining at the site, as indicated in Table 2.

Treatment of low-threat material may be warranted at sites involving relatively small volumes of contaminated material, sensitive environments (e.g., wetlands) and floodplains or other conditions that make containment unreliable. Since concentrations remaining will be low in these cases, long-term management controls may be reduced. Containment of principal threats may be warranted at sites involving very large volumes of contaminated material for which treatment may not be practicable, PCBs mixed with other contaminants that make treatment impracticable and PCB wastes that are inaccessible (e.g., buried in a landfill).

SELECTION OF REMEDY

The analysis of remedial alternatives for PCB-contaminated Superfund sites is developed on the basis of the following criteria:

- Overall protection of human health and the environment
- Compliance with ARARs or justification of a waiver
- Long-term effectiveness and permanence
- Reduction of toxicity
- Mobility
- Reduction of volume through treatment
- Short-term effectiveness
- Implementability
- Cost
- State acceptance
- Community acceptance

Primary tradeoffs for PCB-contaminated sites will derive from the type of treatment selected for the principal threats and the determination of what material can be reliably contained. Alternatives that require minimal long-term management will often provide less short-term effectiveness and implementability because large volumes of contaminated material must be excavated and treated. They generally will be more costly but will provide high long-term effectiveness and per-

Table 2
Selection of Long-Term Management Controls
To Be Considered for PCB-Contaminated Sites

PCB CONCENTRATION (ppm)	APPROXIMATE DEPTH TO GROUND WATER	ACCESS	RCRA COROLLARY	Cover System	Leachate Collection	Leak Detection	Bottom Liner	Ground Water Monitoring	Surface Water Monitoring	Surface Water Management	Bottom Liner	Depth to Ground Water	Ground Water Monitoring	Leachate Collection	Surface Water Monitoring	Fence	POTENTIAL BASIS FOR TSCA WAIVER (761.75 (c) (4)) OF INDICATED CHEMICAL WASTE LANDFILL REQUIREMENT(S)
≤1	All Depths	• Nonrestricted Access	Clean Closure														No waivers required; clean closure
1-10	All Depths	• Nonrestricted Access	Hybrid Closure	2							X	3	X	X	X	X	Low PCB concentration / Design and installation of a protective cover system / Evaluation of PCB migration to GW and SW
10-25	All Depths	• Limited Access · Deed Notice	Hybrid Closure	2							X	3	X	X	X	X	Low PCB concentration / Design and installation of a protective cover system / Evaluation of PCB migration to GW and SW
25-100	All Depths	• Restricted Access · Fence · Deed Notice	Landfill Closure	X				X		4	X	3		X	X		Relatively low PCB concentration / Implementation of a GW monitoring program / Evaluation of PCB migration to GW and SW / Design and installation of a protective cover system
100-500	3-50 Feet	• Restricted Access · Fence · Deed Notice	Landfill Closure	X				X	X	4	X	X		X			Implementation of GW monitoring program / Design and installation of a protective cover system / Evaluation of PCB migration to GW and SW
	> 50 Feet	• Restricted Access · Fence · Deed Notice	Landfill Closure	X				5	X	4	X		X	X			Design and installation of a protective cover system / Demonstrate sufficient depth to GW to protect human health and the environment / Evaluation of PCB migration to GW and SW
> 500	3-50 Feet	• Restricted Access · Fence · Deed Notice	Landfill Closure Minimum Technology	X	X	X	X	X	X	4		X					Demonstrate other long-term management controls to provide adequate protection of GW
	> 50 Feet	• Restricted Access · Fence · Deed Notice	Landfill Closure Minimum Technology	X	X	X	X	X	X	4	X		X				Demonstrate sufficient depth to GW and long-term management controls to protect human health and the environment / Implementation of GW monitoring program / Evaluation of PCB migration to GW and SW

GW = ground water; SW = surface water

[1] Cover system may range from 12" soil cap for low concentrations to a full RCRA cap for concentrations exceeding 500 ppm.

[2] The need for a cover system will depend on the land use (i.e., residential or industrial).

[3] 40 CFR 761.75(b)(3) requires that landfills be located at least 50 feet above the high-water table.

[4] In accordance with 40 CFR 761.75(b)(4) if the site is located below the 100-year floodwater elevation, diversion dikes shall be constructed around the perimeter of the landfill site with a minimum height equal to 2 feet above the 100-year floodwater elevation. Flood protection for landfills above the 100-year floodwater elevation is not applicable to closed landfill units.

[5] When the site is located in a permeable formation, incorporation of this long-term management control should be evaluated.

manence and achieve significant reductions in toxicity and volume through treatment.

. Alternatives that involve containment of large portions of the contaminated site generally will have lower long-term effectiveness and permanence and achieve less toxicity or volume reduction through treatment. However, they generally will be less costly, more easily implemented and have higher short-term effectiveness.

A ROD for a PCB-contaminated Superfund site should include the following components under the Description of Alternatives section:

- Remediation goals defined in the FS for each alternative; i.e., concentrations above which PCB, contaminated material will be addressed and concentration above which material will be treated.
- Treatment levels to which the selected action is projected to reduce PCB concentrations before redepositing residuals. The consistency of these levels with TSCA requirements and other ARARs should be indicated.
- Long-term management controls that will be implemented to contain or limit access to PCBs remaining on-site. The consistency with RCRA closure and TSCA chemical waste landfill requirements (and

justification for appropriate TSCA waivers should be indicated).

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Aquifer Testing is Essential During Remedial Investigations

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ABSTRACT

Characterizing the hydrogeology of a Superfund site is a critical part of the remedial investigation and remedial design processes. During remedial investigations (RIs), it is essential to collect accurate hydrogeologic data for subsequent use in a feasibility study and engineering design(s) so that implementation of remediation is not delayed and remediation costs can be determined accurately. The determination of aquifer coefficients has proven to be a critical factor in the Remedial Investigation/Feasibility Study (RI/FS) process at sites where groundwater pumping may be selected as a remedial technology. Aquifer tests and slug tests are two methods which can be used to determine the aquifer coefficients.

Aquifer tests seldom are conducted during the remedial investigation due to the problems associated with the disposal of the contaminated groundwater. Slug tests usually are conducted as a substitute for aquifer tests but, in many cases, appear to provide inaccurate estimates of the aquifer coefficients.

A case history which compares the results of slug and aquifer tests illustrates that the slug test underestimated the hydraulic conductivity of the aquifer by a factor of two. As a result, the remedial pump-and-treat system was inadequately designed due to the unexpectedly rapid movement of groundwater contaminants. Additional remedial investigations were required to redefine the groundwater plume before the final pump-and-treat system could be designed.

INTRODUCTION

Characterizing the hydrogeology of a Superfund site is a critical part of the remedial investigation (RI) and remedial design processes. During remedial investigations, it is essential to collect accurate hydrogeologic data for subsequent use in a feasibility study and engineering design(s) so that implementation of remediation is not delayed and costs can be accurately determined. Several methods may be employed to obtain the hydrogeologic data for a particular site, including a literature search, subsurface soil borings, geophysical studies, groundwater sampling and aquifer testing. These methods are utilized collectively throughout the remedial investigation process and generally provide the only information to support the remedial alternative selection process, risk assessment and groundwater modeling.

A thorough literature search is important and should be conducted to identify any previous investigations within the study area. Borings may be necessary to determine not only hydrogeologic properties, but also geotechnical properties. Geophysical studies may be useful for determining the subsurface structure and stratigraphy and also may provide information regarding groundwater flow and chemical quality. The installation of monitoring wells and subsequent groundwater sampling will provide data regarding the extent of any groundwater contamina-tion. Aquifer testing provides the most accurate site-specific method of determining aquifer coefficients of hydraulic conductivity (K), transmissivity (T), storage (S) and rates of groundwater flow which are calculated from these coefficients. As remedial alternatives are being evaluated throughout the remedial investigation process, additional information may need to be collected.

Of all the methods that may be used to determine the aquifer coefficients at a site, aquifer testing is the most accurate and reliable method if the following conditions apply: (1) groundwater contamination is apparent; (2) soil borings indicate the presence of medium- or coarse-grained materials; and, (3) groundwater pumping is likely to be selected as a part of the remedial alternative. Aquifer tests usually are not conducted during the remedial investigation process because of the problems associated with the disposal of large volumes of contaminated groundwater.

Slug tests often are conducted as a substitute for aquifer tests even in hydrogeologic environments where they should not be used. Slug tests are similar to aquifer tests in that the coefficient of hydraulic conductivity and transmissivity can be calculated, but slug tests are more appropriately used to determine the hydraulic conductivity of fine-grained materials.[5] Therefore, when slug tests are substituted for aquifer tests, inaccurate estimates of the aquifer coefficients often are obtained.

The case history presented later in this paper will illustrate the importance of conducting aquifer tests. This case history demonstrates how slug test data inaccurately estimated hydraulic conductivity; as a result, the remedial pumping and monitoring systems were inadequately designed for the site.

Aquifer Tests

The constant rate pumping test is the most widely used aquifer test. A well is pumped at a constant rate while drawdown is measured in the pumping well and in several nearby observation wells at specific time intervals. Theoretically, only one fully penetrating observation well (in addition to the pumping well) is necessary, but several wells are recommended so that the average values of K, T and S can be calculated and aquifer heterogeneity can be accounted for. Aquifer tests can also be used to determine vertical hydraulic conductivity and leakage between layers of multiaquifer systems.

The drawdown or recovery data are plotted versus time on logarithmic paper, and the curves generated are matched against type curves for interpretation and evaluation of the aquifer coefficients. Type curves are available for confined, unconfined and leaky artesian groundwater systems.[2,6] In addition, the distances of observation wells from the pumping well may be plotted against the drawdown to determine aquifer coefficients over a large area and the effective capture zone developed.

If groundwater pumping is a potential alternative in the list of remedial alternatives, a properly designed aquifer test will provide more information than simply the average K, T and/or S of an aquifer. Information regarding the specific capacity of wells, well efficiencies, well interference and potential boundary effects also is obtained during an aquifer test. This additional information is sometimes critical to the remedial design and may play an important role in determining the number and location of recovery and monitoring wells.

Slug Tests

Slug tests also are conducted to determine the K of an aquifer.[1-3] Slug tests are an accurate method for determining the K of low-conductivity, water-bearing units.[5] The value of K is determined from the rate of rise, or fall, of the water level in a well after a known volume, or "slug," is removed from or injected into the well.

The water level in the well is measured initially and then at specific time intervals after the slug has been removed until the water level returns to equilibrium. These data are then plotted on a semilogarithmic scale and matched to type curves to obtain values of hydraulic conductivity.[3] Although similar to the methods used during pump test analysis, the data actually represent a relatively short period of time and a very small portion of the aquifer. In addition, slug test analyses require assumptions which oversimplify actual conditions.

Slug tests usually are conducted in existing monitoring wells which

are installed with a gravel pack. Consequently, a slug test conducted in a monitoring well will provide information regarding the hydraulic conductivity of the gravel pack and not the aquifer material. Most monitoring wells are inadequately developed for slug testing purposes and, for this reason, may underestimate hydraulic conductivity.

CASE HISTORY

The following case history illustrates how data obtained from slug tests underestimated the hydraulic conductivity of the site conditions; as a result, the remedial pumping and monitoring networks were inadequately designed for the site.

The geology of the case site is glacial in origin with recent influences from fluvial activities. There are two water-bearing units beneath the site (shallow and deep aquifers) which are comprised of fine-to-medium sands and gravels. The two aquifers are separated by a lacustrine deposit of fine sands, silts and clays. The site boundary and the hydrogeologic cross section are shown in Figures 1 and 2, respectively. Groundwater contamination is restricted to the shallow aquifer in which groundwater travels in a north/northwesterly direction. Groundwater in the deep aquifer is present under confined conditions, and the flow direction is to the south/southwest. The confining layer between the two aquifers appears to have successfully prevented contamination in the shallow aquifer from migrating to the deep aquifer.

The RI provided a large amount of information regarding past studies,
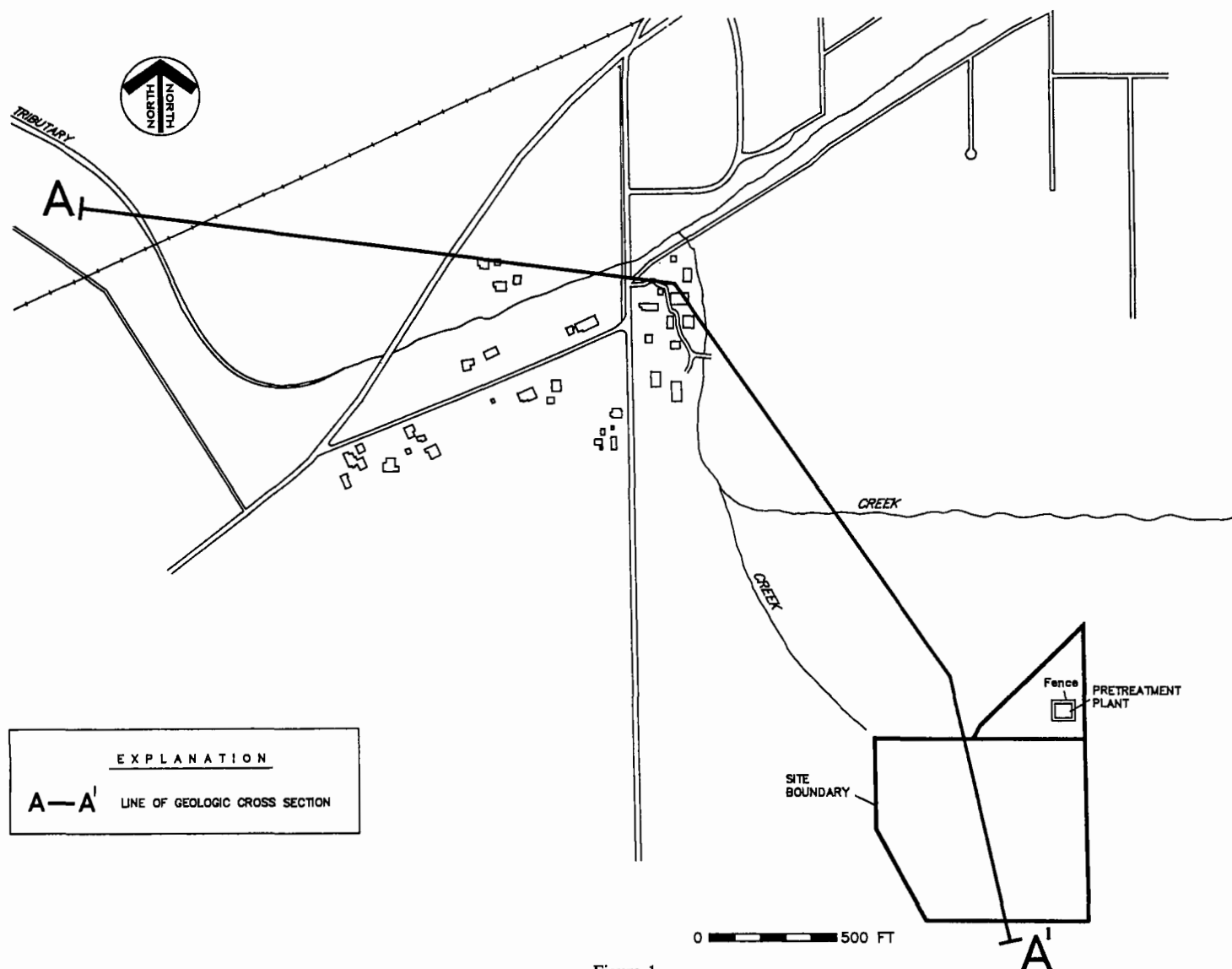
Figure 1
Site Boundaries

EXPLANATION

A — A' LINE OF GEOLOGIC CROSS SECTION
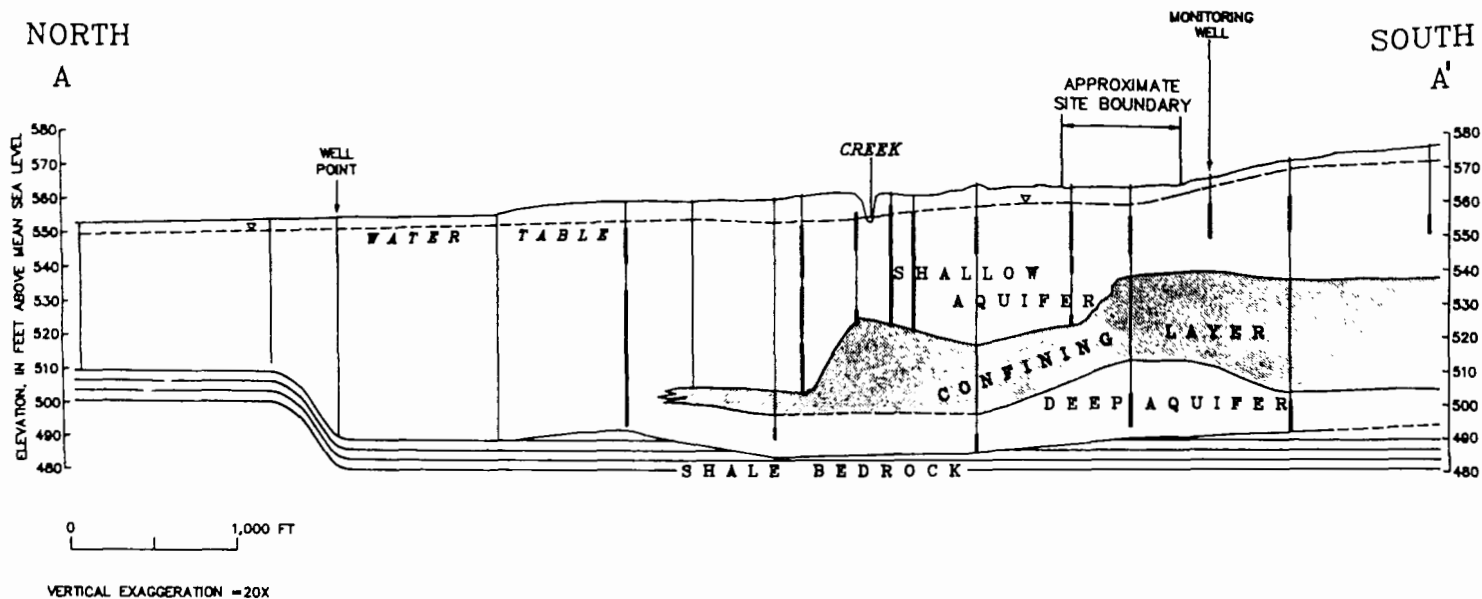
Figure 2
Hydrogeologic Cross-section
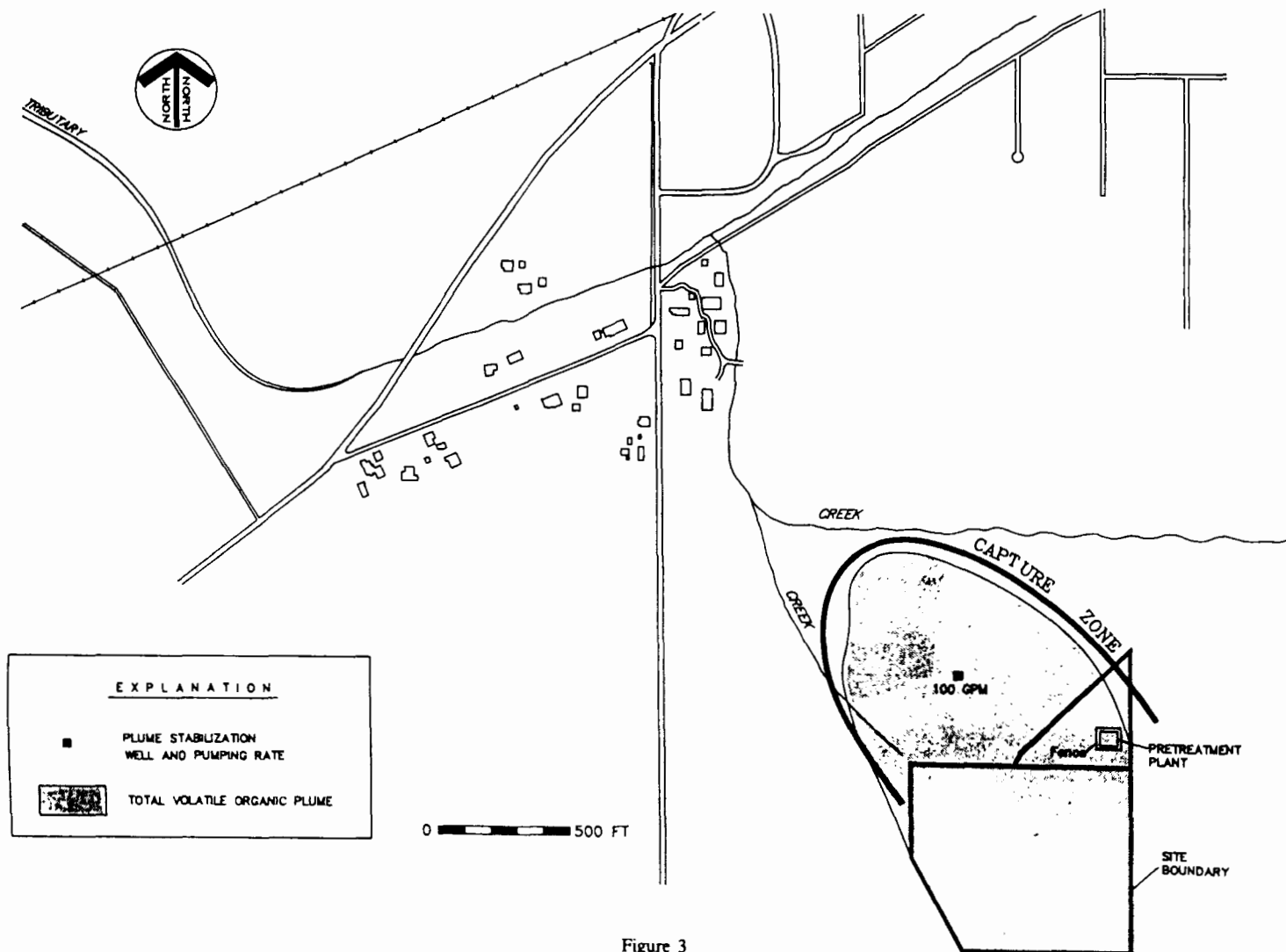
Figure 3
Extent of Total Volatile Organic Plume as Defined
During the RI, 1985, and Effective Capture Zone
of the Plume Stabilization Well

soil contamination, groundwater contamination, biota studies and surfacewater quality. Approximately 38 monitoring wells were installed, three rounds of groundwater samples were collected and numerous analyses were performed on the soils. Slug tests were conducted to determine the aquifer coefficients. The slug tests were performed by lowering a slug of known volume into the water and measuring the rise of the water level in the well until it returned to the initial level. Similar measurements were taken when the slug of water was removed from the well. The procedure was repeated twice, resulting in four measurements made in the same well.

The slug test data were evaluated using methods in Bouwer and Rice[1] and Hvorslev.[3] The Bouwer and Rice procedure was selected because it makes allowances for field situations where the aquifer is not under artesian conditions and the wells do not fully penetrate the aquifer, but the analysis does assume a homogeneous, isotropic aquifer. The Hvorslev method is simpler to use, but is based on more assumptions and was originally designed for zones of low permeability.

The calculated hydraulic conductivities for the shallow aquifer were 28 feet per day (ft/day) using the Bouwer and Rice method and 78 ft/day using the Hvorslev method. By applying Darcy's law and using average values of K from both the Hvorslev and Bouwer and Rice methods, an average hydraulic gradient across the site and an estimated effective porosity of 0.25, the groundwater velocity was calculated to be between 103 and 289 feet per year.

At the completion of the RI/FS, the groundwater plume was defined to extend approximately 600 feet from the site boundaries, as illustrated in Figure 3. The plume was defined by the total volatile organic compound (TVOC) concentrations detected during three separate groundwater monitoring programs. Based upon the TVOC concentrations detected and the hydraulic conductivity of the shallow aquifer, the RI/FS concluded that remediation of the groundwater contamination would be effectively accomplished through a groundwater pump-and-treat system. The pump-and-treat system was initiated by installing a plume stabilization well to stop further migration of the groundwater plume while the final remediation system was being designed.

The plume stabilization well was designed to pump at a rate of 100 gallons per minute (gpm) which would generate a capture zone that would cover the area of groundwater contamination defined in the RI/FS (Figure 3). A temporary treatment unit was constructed so that an aquifer test could be conducted on the plume stabilization well and the design of the remedial pumping program could be finalized. Once the aquifer test was concluded, it was determined that the K of the shallow aquifer was 122 ft/day, twice the average K calculated from the Bouwer and Rice and Hvorslev methods, and that groundwater contaminants were traveling twice as fast as originally expected.

A comparison of the hydraulic conductivities calculated from the slug and aquifer tests is presented in Table 1. This finding, and calculations of contaminant travel times, indicated that the area of contamination was larger than predicted in the RI report, and that two well clusters theoretically beyond the extent of contamination had failed to detect this additional migration of the plume. Another extraction well was immediately installed downgradient of the original plume stabilization well in an attempt to capture the groundwater plume. Additional monitoring wells and well points were installed to redefine the plume.

The well point program included driving temporary stainless-steel well points to a predetermined depth and collecting discrete groundwater samples. The water samples were then analyzed for VOCs by

an analytical laboratory, and rapid turnaround of the results was requested so that decisions could be made regarding the location of the next well point. The initial program, which was designed to install 10 well points, began in January 1990. By June 1990, 31 well points, five soil borings and 16 piezometers were installed.

The well point program indicated the following: (1) groundwater contamination extended approximately 3500 feet beyond what was originally determined during the RI; (2) the direction of groundwater flow changed from north/northwest to a more westerly direction; (3) the change in flow direction appeared to be the result of a change in aquifer materials and consequently a change in the hydraulic conductivity; (4) the confining layer, which separated the shallow and deep aquifers, pinched out and the two aquifers became one hydrogeologic unit; and (5) the remedial extraction and monitoring well networks designed immediately after the RI was completed were in need of significant modifications. In order to capture the contaminant plume, additional extraction wells were required. The extent of groundwater contamination defined during the well point program, June 1990, and a remedial pumping array which will effect capture of the plume and prevent further migration of contaminants are shown in Figure 4.

If an aquifer test had been conducted at this site during the RI process, much of this additional investigative work and cost may have been avoided. Although aquifer tests are not foolproof, if designed and orchestrated properly, they provide important information that is necessary for a remedial pump-and-treat design.

An Alternate Approach

If, during the course of the RI/FS process, it becomes apparent that a remedial pump-and-treat system will be incorporated into the remedial design, aquifer tests can be conducted even if the groundwater is contaminated. An aquifer test array of pumping and monitoring wells often can be installed off the site where groundwater is uncontaminated. This off-site test obviates the need for treatment, and water from the pumping well can be discharged into the surfacewater drainage system. Sometimes it is possible to discharge directly to a publicly owned treatment works (POTW) if pretreatment standards can be met and the contaminants will not cause upset or pass through the plant untreated.

If access to an area upgradient or sidegradient of the site is difficult to obtain, or if the hydrogeology upgradient or sidegradient is drastically different and will not be representative or if a POTW is unavailable, a temporary and/or portable treatment unit can then be utilized to treat the water prior to discharge. Portable air strippers and granular activated carbon (GAC) units are readily available from many manufacturers. Given the amount and quality of data generated during an aquifer test, the extra cost (even if treatment is required) outweighs the costs of additional post RI/FS studies and the costs of overdesigning a treatment plant which often will be incurred because of a lack of data.

CONCLUSIONS

Based on our experience outlined in this paper, we have drawn the following conclusions:

- Accurately defining the hydrogeology of a site is an essential aspect of the RI, especially in cases where a pump-and-treat system may be chosen as part of the remedial alternative or where contaminant migration in the groundwater is an important issue.
- Aquifer tests provide a means by which aquifer coefficients of hydraulic conductivity (K), transmissivity (T) and storage(s) can be accurately determined. If designed properly, they can be used to determine the average aquifer coefficients over a relatively large portion of the aquifer and can determine well interference effects, boundary conditions and expected well efficiencies.
- Slug tests provide an accurate means by which the aquifer coefficients of K and T can be determined in zones of low permeability. However, slug tests should not be substituted for aquifer tests in a permeable aquifer and should not be done in monitoring wells that have been gravel packed.
- At sites were groundwater is contaminated, aquifer tests often can be done upgradient or sidegradient where groundwater is uncon-

Table 1
Comparison of Hydraulic Conductivities Determined
by Slug Tests and Aquifer tests

	Bouwer & Rice[1]	Hvorslev[3]	Aquifer Tests
Minimum	12	12	90
Maximum	61	252	126
Mean	28	78	122

Values are in ft/day
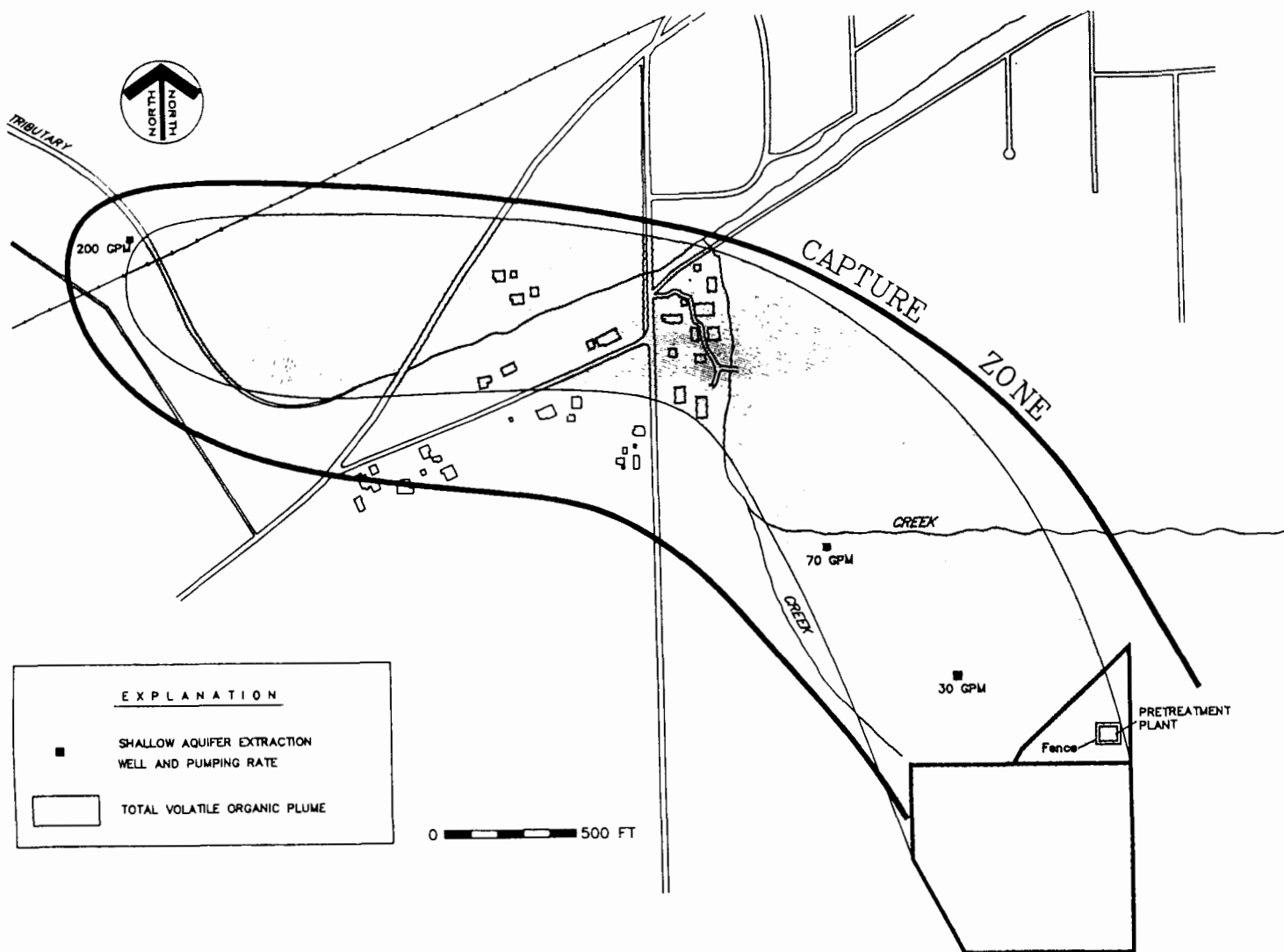
Figure 4
Extent of Total Volatile Organic Plume
as Defined in June 1990 and Effective Capture Zone
of the Revised Plume Stabilization System

taminated. If it is not possible to install a well(s) upgradient or sidegradient, contaminated groundwater produced during the aquifer test can be treated through a temporary treatment unit prior to disposal.

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Sampling Structures at Superfund Sites: A Case Study from the Sand Creek Industrial Site, Commerce City, Colorado

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ABSTRACT

As is common for RODs on Superfund sites that include buildings and other structures, the remedy identified for the facilities on the Sand Creek Superfund site is demolition and off-site disposal. However, both the new federal restrictions on land disposal and the impending expiration of the variance allowing disposal of certain wastes from Superfund cleanup sites made it necessary to determine if demolition material from the site would be acceptable at land disposal facilities and whether or not treatment of some or all of the material would be necessary.

The structures investigation described below was undertaken by Brown and Caldwell Consultants as a subcontractor to URS Consultants as part of the Remedial Design (RD) phase of an Alternative Remedial Contracting Strategy (ARCS) contract with Region VIII of the U.S. EPA. The field work consisted of sampling and dimensional measurement of the structures. The sampling strategy was developed, in part, based on the data requirements of landfill operators and transporters as well as the requirements for determining if separate handling procedures or actual treatment would be required for portions of the demolition debris. The sampling strategy for the site structures, a summary of analytical results and conclusions about the utility of the sampling strategy for the RD phase are presented in this paper. At this time, the remedial design itself has not been finalized.

SITE HISTORY AND DESCRIPTION

The Sand Creek Industrial site is located in Commerce City, Colorado, a suburb north of Denver. The site was proposed for the NPL in December 1982 and placed on the list in September 1983. The site contains four potential source areas that have been designated as Operable Units (OUs): (1) the Colorado Organic Chemical Co. (COC) property (OU1), (2) the L.C. Corporation acid pits (OU2), (3) the 48th and Holly landfill (OU3), and (4) the area-wide groundwater contamination associated with the Sand Creek Industrial site area (OU4).

This paper focuses on the RD investigation conducted by Brown and Caldwell Consultants at the Colorado Organic Chemical Co. (COC) property (OU1) during December 1989. The property was used to manufacture pesticides from 1960 to about 1984. Two major fires are known to have occurred in manufacturing buildings at COC, one in 1968 and one in 1977. The site is located in an industrial/warehouse area with an active warehouse directly adjacent to COC on the north and a concrete batch plant to the west. The former site of the tank farms for the Oriental Refinery is to the south and east of the COC property.[1]

Sixteen structures, exclusive of standing tanks, were present on the site during the investigation, including: two, single-room, metal buildings and two cinderblock buildings, each with a concrete slab floor; one multi-room office/process building built of a variety of materials with both concrete and dirt floors; four open concrete slabs; one con-

crete pit; two metal tank bottoms; and four locked wooden railroad cars composed of wood and metal (Fig. 1). The standing, intact tanks were excluded from the sampling program because they were to be investigated by another U.S. EPA contractor. However, they were part of the inventory of structural material on the site.

What little is known about the specific chemical processes and uses that occurred in each structure was obtained from a single interview with the owner of the facility.[2] Reportedly, DDT, aldrin, dieldrin and other products were formulated on-site (Metal Building on Figure 1). Solvents were used in the formulation process and parathion and penta were stored in tanks on-site. A diazinon-formulating operation was constructed but never used (Quonset Hut and Addition). The upper floor of the Office/Process complex has been and continued to be used as an office during the time of the field investigation. The lower portion of the building was used as a laboratory and now is used for storage. Methylene chloride was used in the production of DDVP (Vapona) in the northernmost of the two metal structure portions of this complex. In addition to the pesticide manufacturing, metal products, including pipe, were formed, welded and stored on-site (Hains Engineering and Quonset Hut). Nothing is reported about the structures in the portion of the site west of the buildings except that they are located in an area where 2,4-D was formulated.

The RI/FS conducted on this property identified chemicals of concern in the soil (Table 1), but no previous sampling of the structures themselves had been done.[1]

Table 1
Sand Creek
Chemicals of Concern in the Soils Identified in the RI/FS

Volatiles	Pesticides and Herbicides
Chloroform	4,4'-DDT
Methylene chloride	Chlordane
Tetrachloroethene (PCE)	Dieldrin
Trichloroethene (TCE)	Heptachlor
	2, 4-D

Metals
Arsenic
Chromium

DEVELOPMENT OF INVESTIGATION STRATEGY FOR STRUCTURES

The basic principle used in designing this structures investigation was "work backwards;" that process is one in which one determines data

needs of the steps in the process leading to the ultimate destination of the material and gathers data to assist in the design of the activities associated with the process. The selected remedy for structures within OU1 of the COC site is demolition and off-site disposal.[3] The objectives of the structures sampling and material inventory were:

- Determine if chemical concentrations or material characteristics identified in samples taken from building material exceed limits that would exclude placement of the material in a Subtitle D landfill
- Determine if "hot spots" exist in the building material that would indicate that some material requires treatment prior to disposal
- Provide volume estimates of total demolition debris, debris by material category and volume of material in "hot spots" so that costs of demolition or other disposal or treatment options can be properly estimated
- Provide analytical data on chemical concentrations, RCRA characteristics and the presence or absence of asbestos so that demolition bid documents can be prepared that reflect actual conditions
- Provide sufficient analytical information so that hazardous waste transportation manifests can be prepared
- Provide analytical information that can be used by landfill operators as part of their process of determining if demolition debris can be accepted by their facilities

We reviewed U.S. EPA/Department of Transportation (DOT) manifest requirements and interviewed operators of several Subtitle C landfill facilities to determine requirements for analytical data on manifests and submissions with the profile sheets that accompany waste to land disposal sites. The consensus was that "representative" analytical data from each structure should be submitted with the manifests and that a representative sample from each structure should accompany any delivery of material to their facility. There was no requirement for a representative sample from each truckload of material from the landfill operators. Interestingly, no landfill operator was willing to define the term representative. However, the manifesting requirements of truck transport of potentially hazardous waste are such that some segregation of material by building or type of debris in the loading of transport trucks may be required. It should be noted that this work was done prior to the promulgation of the third-third portion of the land ban. Some differences in landfill practices are emerging that should be taken into account on other projects.

It also was not clear that the sampling should identify any "hot spots" that could potentially contain high concentrations of chemicals or exceed RCRA thresholds for corrosivity, ignitibility, reactivity or toxicity so that consideration could be given to segregating this material and either treating it or disposing of it separately from other debris from the site. This separation obviously could save money in the ultimate disposal of material from this facility.

We set the Data Quality Objectives (DQOs) as follows:

- *DQO I. Confirmation of Selected Demolition and Disposal Remedy.* Perform limited "hot spots" sampling to determine if areas exist with concentrations of Halogenated Organic Compound (HOCs) greater than 1000 ppm that will prevent disposal of all or part of the demolition debris in a Subtitle C landfill.
- *DQO II. Prepare Demolition Bid Package.* Conduct limited sampling to assess general level of contamination in each structure; identify classes of building material and take material measurements to support estimates of material volume.
- *DQO III. Demolition Health and Safety Plan.* Perform limited waste characterization and contaminant screening to determine classes of contaminants present in each structure in sufficient detail to recommend levels of respiratory and dermal protection required for demolition crews.
- *DQO IV. Prepare Documentation for Transport of Demolition Debris that Can Be Landfilled.* Provide analytical information that identifies the types of contaminants present and that demonstrates that no areas sampled showed HOC concentrations greater than 1000 ppm.
- *DQO V. Provide Landfill Operators with Waste Characterization Sufficient for Acceptance of Demolition Debris from Site.* Provide analytical data from pre-demolition sampling conducted during the RD phase

SAMPLING AND MATERIALS MEASUREMENT PLAN

A sampling and measurement plan was prepared based on the DQOs and observed conditions at the site. The first round of sampling originally was intended to identify areas that should be further sampled. However, budgetary and time constraints precluded further sampling. The plan can be summarized as follows:

Chemicals/Characteristics of Concern

Sampling was planned to: identify the chemicals of concern found in the soil during the RI (Table 1); determine the RCRA waste characteristics of corrosiveness, reactivity, ignitability and toxicity; determine if certain suspect materials contained asbestos; and determine if mercury was present in the buildings, which would account for its presence in the soil in certain locations close to buildings. Because of the history of fire in a facility that manufactured 2,4-D, sampling to identify the possible presence of dioxin contamination in several of the buildings also was planned. Table 2 summarizes the analytic methods specified for the samples taken for this investigation.

Table 2
Sand Creek
Analytical Procedures Used for Structures Samples

1.	RCRA Waste Characterization	
	a. Corrosivity.	U.S. EPA Method #9040. Reported as pH. Threshold is less than 12.5
	b. Ignitability.	SWA846. U.S. EPA Method #846 Reference flash point is 75 °F.
	c. Reactivity.	U.S. EPA draft. Positive or negative. Including cyanide and sulfides.
	d. EP toxicity.	Inorganics. U.S. EPA Method 6010. (Includes arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver). Range of method detection limits is 0.1 to 0.6 mg/L. Organics. U.S. EPA Method #8080. (Includes lindane, endrin, methoxychlor, toxophene, chlordane, dieldrin and heptachlor). Ranges of method limits is 0.05 ug/L to 1 ug/L.
2.	Halogenated Organic Compounds (HOCs).	U.S. EPA Method #9020. The detection limit is 20 mg/L.
3.	Dioxin.	U.S. EPA Method #8280. Tetra-octa chlorinated dioxins and furans. Method detection limit is 0.1-1 ug/L.
4.	Mercury.	U.S. EPA Method #7470. Method detection limit is 0.5 mg/L.
5.	Asbestos.	U.S. EPA Method #600/M4-82-020 for bulk samples. Polarized light method. Analysis is for five asbestos types: amosite, chrysotile, crocidolite, actinolite/tremolite and anthophyllite. The detection limit is 1%.

Note: these analytical procedures were used for all building media sampled. The specified method detection limits or equivalent are included. Wipe samples were reported in milligrams. No corrosivity, ignitability or reactivity tests were performed on wipe samples.

Sampling Methods

Three sampling methods were employed. Wipe samples using Whitman 541 filter paper in 15 cm circles soaked in either hexane or acetic acid were taken of 1 m² of metal and block surfaces.[4] Composite grab samples of up to four subsamples were taken of fiber and wood wall materials, soil in interior dirt floors and suspected asbestiform materials, soil in interior dirt floors and suspected asbestiform material. Composite samples of three subsamples of concrete slabs were assembled by using a hand-held drill with a wide bit to pulverize the material at several locations on each slab sampled. The holes were drilled to a depth of approximately 4 m each.

Sample Locations

General sampling locations were specified in the sampling plan with the actual locations to be chosen in the field based on observation of potential "hot spots." Prior to sampling each structure, a "hot spot" survey was done. The following visually observable characteristics were considered sufficient to label an area a potential "hot spot":

- Staining
- Corrosion or crumbling
- Standing liquid or sludge
- Spilled powder or liquid material
- Stored bags, bottles or drums
- Evidence of fire or explosion
- Pipes, tanks or other closed vessels

All the concrete samples were to be composites from potentially hot areas. Dioxin samples were to be taken from the areas that had visible marks of burning. Wipe samples were to be taken from both inside and outside walls for each structure. Field notes were kept of all identified "hot spots."

Health and Safety Procedures

All building work, whether initial survey, sampling or measuring, was done with teams consisting of a minimum of two people. Prior to the start of the field work, a building hazard survey was conducted to determine if any dangerous structural conditions existed or if any spaces were present that might contain chemical or explosion hazards or that would meet the definition of confined space. None was observed.

With one exception, all sampling was done in Level C respiratory protection. The operator of the drill used for concrete sampling wore a Self Contained Breathing Apparatus (SCBA) (Level B) because of the large amount of possibly-contaminated dust generated in the process. Dermal protection during all field operations was achieved with Saranex-coated Tyvek suits taped at all openings, vinyl undergloves, nitrile overgloves and rubber boot covers. During wipe sampling, surgical overgloves replaced the nitrile overgloves.

MATERIALS ESTIMATES

In addition to collecting samples, the field crew measured the structures in the field, including the standing tanks, to estimate the amount of demolition debris that would be generated. No drawings were available for any of the structures on the site. In the case of buildings, measurement proceeded from the exterior to the interior. A building footprint sketch was made on a grid pad, with a reference direction noted. The exterior dimensions (length, width and height) were measured using handheld tape measures and a measuring rod. Building materials were noted on the sketch. If more than one building material was present on the exterior, the dimensions of each material were measured and noted. Windows and doors were noted on the sketch and measured. Once the exterior procedures were completed, the building was entered and the thickness of the exterior walls was measured or estimated. All internal walls were measured for height, width and thickness. Different building materials were measured separately so that volume calculations by material could be made. The slab width was measured and the size of the foundation was estimated if direct measurements were not possible. Pipes, tanks, other machinery and dry, stored material were measured. Nonbuilding structures such as slabs, tanks, etc. also were measured.

RESULTS

Sixty-five samples were taken in and around structures on the site and from the warehouse building north of the site, and 55 samples were taken from 40 locations in or on structures on the COC site. An additional two samples to be analyzed for dioxin were taken from the active warehouse on the north boundary, which had suffered damage from past fires. Additionally, seven QA/QC samples and one health and safety monitoring air sample were obtained.

The analytic results are summarized below.

Dioxin (TCDD)

Six wipe samples (including two from the off-site warehouse and one blank) were taken from blackened areas in four buildings and analyzed for TCDD. No dioxin was detected above 0.400 pg/cm^2. These results are below the 1 ppb standard for land disposal of treated dioxin waste.

Asbestos

Material that was suspected to contain asbestos was observed in only two buildings, in boiler insulation and in floor tile. The boiler insulation was determined to be 45% asbestos; neither the floor tile nor its adhesive contained asbestiform material.

Halogenated Organic Compounds (HOCs)

Total HOCs in the composite concrete samples ranged from 980 mg/kg to 30 mg/kg. All samples were composites from stained areas. Total HOC concentration was 800 mg/kg in a composite weathered sludge sample from the open tank bottoms. Total HOCs were identified in fiber, wood and soil samples within structures in ranges from 9000 mg/kg to 100 mg/kg. The highest concentrations came from a sample from the railroad cars on-site where unidentified dry chemicals and other materials were stored. Total HOCs in wipe samples were identified in ranges from 0.44 mg/m^2 to 0.012 mg/m^2, with the highest concentration on the inside of a former mixing vessel and the lowest on a wall location inside a process building.

Corrosivity, Ignitability and Reactivity

Of these RCRA waste characteristics, only the test for corrosivity yielded results above thresholds. Most of the concrete samples showed pHs between 12.5 and 12.7. Although the samples were composites from stained areas, it is possible that the naturally basic nature of concrete caused the high pH readings.

Metals

Arsenic, barium, chromium and mercury were identified in composite concrete samples below RCRA maximum concentrations. Two samples contained arsenic at 5.6 mg/L and 7.9 mg/L, levels that exceed the RCRA maximum concentration of 5.0 mg/L for this contaminant. Arsenic, barium, cadmium, chromium, lead and silver from wipe samples taken on building walls were identified at concentrations ranging from 0.0046 to 2.2 mg/m^2. These levels are extremely low and likely to indicate that nothing is present on the walls in concentrations that exceed thresholds. On soil sample taken from inside a structure contained mercury at 1.4 mg/kg, a level that may indicate a concentration that exceeds the RCRA maximum concentration limits for this constituent.

Pesticides

Dieldrin, endrin and/or lindane were identified in every concrete sample in concentrations ranging from 38 to 0.034 ug/L. Lindane and endrin exceeded the RCRA maximum concentrations in every instance where they were identified. A single soil sample from within a structure identified BHC isomers including lindane at 51.4 ug/L. Wipe samples indicated the presence of low levels of p,p'-DDE and DDT, dieldrin, lindane, endosulfan and toxaphene throughout the site at concentrations at or below 3.2 ug/m^2. A single wipe sample identified toxaphene at 740 ug/m^2 on the outside of a process mixing vessel.

Materials Measurement

Material in structures was estimated for six categories: concrete/concrete block; wood/fiber; sheet metal; structural metal, pipes and metal doors; metal in outside tanks; and concrete in outside tanks. Total material in the structures as they stood was estimated to be 1214 yd^3. To account for voids between pieces of rubble, this volume of standing material was increased by a factor of 1.5 to arrive at an estimate for demolition debris of 1821 yd^3. An approximate estimate of the potential landfill volume was made to account for some recompacting of material during disposal. The demolition debris volume was multiplied by 0.80 for estimated landfill volume of 1457 yd^3.

CONCLUSIONS

As a result of our work, the following conclusions were drawn:

1. The sampling techniques used in this investigation yielded results that contributed required information to the RD phase. Specifically, the composite sampling of concrete, weathered sludge on open tank bottoms, wood/fiberboard wall material and soil within structures identified the presence of "hot spots" within these materials in concentrations high enough to indicate the presence of RCRA wastes. The wipe sampling technique, while it did not yield information as to concentration in a form that is convertible to RCRA thresholds, did show relative values that indicate the presence of contaminants associated with a process vessel.

2. Volume estimates of structural material were easily made. Field notes contain sufficient information to estimate the volume of potential "hot spot" material.

3. Asbestos was identified as present in only one location on the site. Thus, the substance will not present a major problem or cost in the demolition process.

4. Sufficient analytic data were gathered to prepare transportation manifests.

5. Assuming that "hot spot" areas are demolished and separated from cleaner material, the results of this study have identified actual "hot spots" through the inventory and sampling process. Further sampling may be required of each unit of drummed or separately handled "hot spot" material.

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Detoxification of Released Vapors/Particulates by Entrapment in Chemically Active Foam

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ABSTRACT

In the wake of the Bhopal disaster, there has been increasing public and governmental concern over the possibility of toxic gas and vapor releases from chemical plants. Title III of SARA, specifically addresses emergency preparedness for such releases. Industry is under intense pressure to provide additional safeguards to prevent gas clouds from threatening populated areas.

Many ways to prevent releases are already in use by industry, ranging from safety-conscious plant design, through safety alarms and interlocks, to backup devices such as scrubbers and flares. However, once a gas or vapor leak occurs, the options for its control are few.

This paper describes the use of foam scrubbing, a novel option for controlling emergency releases of airborne toxics. In this approach, foam is generated with conventional equipment, actually using the contaminated air to form the foam. The foaming solution contains neutralizing agents and may require a special surfactant system for compatibility with these agents and with the contaminants. With the airborne gases, vapors and particulate materials encapsulated in the foam, a large, interior, liquid surface area is available for their sorption. Neutralizing agents present in the bubble walls then react with the entrapped toxic gas or vapor to render it innocuous. The self-collapsing foam yields a processable liquid that may be reusable.

This proposed technology has potential applications for emergency control. Among these are fixed installations in plants, portable field units for use by emergency response teams and mobile units for treating materials handling releases at Superfund sites.

INTRODUCTION

Foam scrubbing can be used as a technique for mitigating emergency releases of gases, vapors, mists, aerosols or particulates by containing and scrubbing the released substances. Foam has the advantages of high surface area and positive control of vapors (through encapsulation). It also can be quickly generated whenever and wherever needed. A reagent can be added to the foaming solution to react with the absorbed gas or vapor.

This paper summarizes the information that is currently available on this subject and describes work currently underway by the U.S. Environmental Protection Agency (EPA). Judging from the literature, industrial experience and experimental results available to date, the potential usefulness of foam in mitigating accidental chemical releases is indeed promising.

Figures 1, 2 and 3 illustrate several possible applications of foam scrubbing to the control of emergency releases:

- For an indoor plant with an existing ventilation system, a foam generator can be installed in the ventilation system near its exhaust point, as shown in Figure 1. Any accidental release of a gas (i.e.,

pressure relief, rupture disk and vessel failure) within the plant could be treated by simply turning on the foam generator or through automatic alarm activation triggered by high contaminant concentration.

- Rapid, high pressure gas releases into the open atmosphere are the most difficult to detoxify. For an outdoor facility with potential leakage points such as flanges, loading connections, etc. that may permit formation of a vapor cloud, a foam generator can collect the released gases under suction, as shown in Figure 2. The generator can be either a portable or a fixed installation (depending on facility size). The gases can be collected using a suction fan and flexible ducts. Emergency response teams would require a portable version.

- A foam generator may be placed at the discharge of a pressure safety valve (PSV), as shown in Figure 3, so that any escaping gas would generate foam using its own pressure. Calculations have shown that some gases may not be directly treatable at high concentration, since the heat required to neutralize high concentrations may destroy the foam. In such cases, dilution air must be drawn into the foam in order to reduce the concentration of the toxic gas.

EXISTING VENTILATION SYSTEM   FOAM GENERATOR

ENCLOSED PROCESSING FACILITY
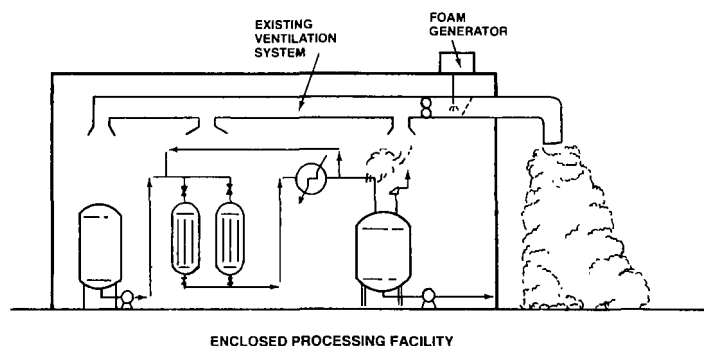
Figure 1
Schematic of an Application of Foam to Mitigate Vapor Release
at an Indoor Chemical Processing Facility

Handling the foam once it has served its purpose — capture, neutralization and collapse—depends in part on the needs of the specific plant. In some instances, if the collapsed liquid is neutral and innocuous, it can be allowed to drain naturally (like fire fighting foam). Alternatively, the liquid could drain into a catch basin for collection, treatment and environmentally-acceptable disposal or potential reuse.

Use of foam for emergency control is attractive because, unlike conventional equipment such as a scrubber, foam need not involve a large

fixed installation. The foam generator and liquid reservoir are relatively small; they can remain on standby until needed. At that time, foam generation can be triggered either by emergency personnel or by an automatic system. The foam mass itself intrinsically provides the residence time needed for control. In conventional equipment, residence time can be extended only by increasing the size of the unit.
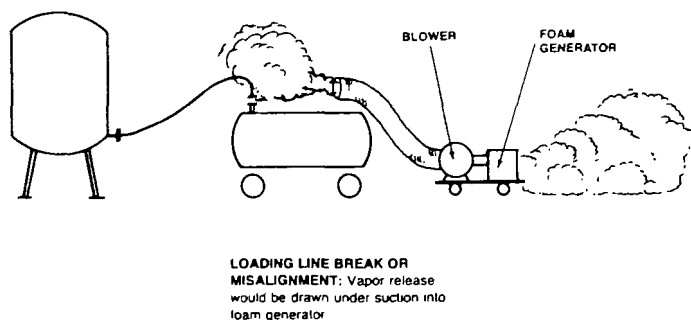
Figure 2
Schematic of an Application of Foam to Mitigate Vapor Release
from Miscellaneous Sources
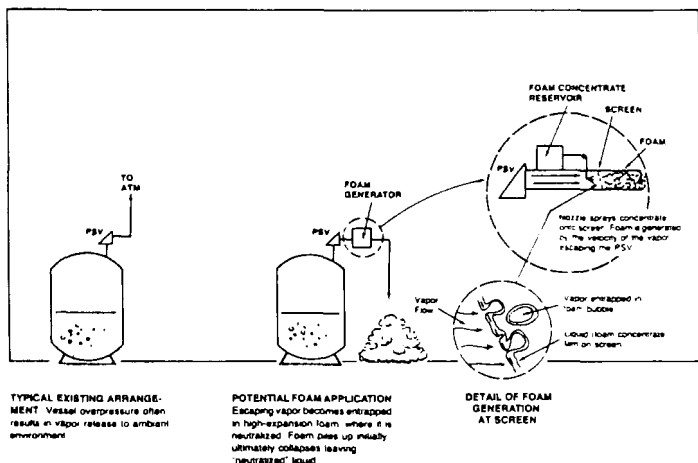
Figure 3
Schematic of an Application of Foam to Mitigate
Vapor Release from Pressure Safety Valves (PSVs)

Potential applications of foam scrubbing for emergency control are many: the chemical industry (ammonia, hydrogen chloride, phosgene, sulfuric acid, formaldehyde and other substances), municipalities (chlorine tanks at water chlorination facilities) and emergency responders (chemical spills, tank truck accidents, etc.).

Foam scrubbing could be used at Superfund sites during excavation to safeguard workers and surrounding communities from the hazards of buried tanks or drums of volatile toxic materials. Nitrogen tetroxide facilities (U.S. Air Force) have been considered candidates for emergency foam scrubbing systems.

FOAM BASICS

Foams have very large surface areas, typically in the range of 1000 to more than 2500 m^2/m^3,[1] which appears very attractive for absorption. Partially offsetting this benefit, however, is the fact that the surfactant present in the bubble walls may retard the mass transfer of contaminants.[2] Most researchers have found some inhibition of absorption, although others have found an improvement.

Foams can be generated over a range of expansion ratios. The expansion ratio is the volume of foam generated per volume of liquid in the foam (foam concentrate).[3] For high expansion foam, the expansion ratio ranges from 200:1 to approximately 1000:1.[4] In practical terms, the expansion ratio is approximately equal to the volume of gas that

is treated per volume of liquid.

Commercial equipment used in foam generation generally consists of a screen or perforated plate against which the foam solution is sprayed. Air is either blown or aspirated through it to form the foam. A second type of device is the flooded plate generator in which the air is bubbled through a plate flooded with foam solution. Based on results to date, it is believed that existing types of foam generators can be used for foam scrubbing purposes.

SUMMARY OF PREVIOUS WORK

Collection of Gases

Researchers have studied the absorption in foam of numerous gases, including carbon dioxide, hydrogen sulfide, formaldehyde, acetaldehyde and mercaptans. Research has generally shown success in the removal of contaminants by foam. Also, tests in which reagents were incorporated into the foaming solution generally were able to both produce stable foams and to neutralize the absorbed gas.

Table 1 provides an overview of studies of absorption of gases into foams. These studies have included compounds that are of concern from an environmental emergency viewpoint, such as hydrogen sulfide, nitrous oxides, ammonia and formaldehyde.

Collection of Particulates

Table 2 presents an overview of studies of collection of particulates and aerosols into foam. Results, again, are generally positive, although complications due to factors such as particle agglomeration were encountered.

These results (e.g., Damle, Ref.[11]) show that collection efficiency increases for longer residence times and for smaller bubble sizes. For a bubble size of 0.8 mm, the particle removal over a residence time of 90 seconds ranged from 80% to nearly 100%.

Comparison with Alternative Techniques

A variety of techniques are currently available to prevent, control or mitigate accidental releases of hazardous air toxics. Preventive techniques include, for example, alarms and interlocks that facilitate corrective action before a release occurs. Control measures such as scrubbers, flares and other devices capture and destroy escaping contaminants before release. Finally, if a release does occur, mitigative measures such as water curtains can be used to reduce off-site impact.

Foam scrubbing falls into the categories of both control and mitigation. A foam generator can be used, like a scrubber, to protect against releases from process equipment or buildings. It also can be used to draw in a gas cloud from, for example, a leaking pipeline or vessel. (Strategic positioning of a unit where it might be needed must be considered.)

In the first case, the advantages of the foam generator are:

- Equipment is relatively small and can remain on standby until needed
- Large volumes of gas can be controlled with relatively small amounts of liquid
- Residence time can be provided within the foam mass, rather than a large, permanent vessel
- The foam generator can be readily sized for a large emergency flow [i.e., up to 30,000 cfm (850 m^3/min) per unit]

Techniques currently used for mitigation of vapor clouds include water sprays and water, steam and air curtains. Where liquid is also present, techniques include dilution, neutralization, temporary covering, freezing and ignition.[15,16]

The water, steam and air curtain techniques are primarily used to disperse the released gases. They have reduced concentrations by a factor of from 1.5 to 4, depending on wind speed.[12] Some scrubbing is also provided by water curtains, but only when very large water volumes are used. In tests with hydrofluoric acid, up to 50% of the acid was scrubbed.[17] The main disadvantages of these techniques are their relatively low efficiencies and the high levels of plant utilities required.

Based on the foam scrubbing efficiencies measured by previous researchers, this technique may, in many cases, provide better mitigation than the currently available alternative techniques.

Table 1
Summary of Previous Research on Gas Scrubbing Using Foam

Study	Gaseous Contaminant Type	Concentration	Surfactant Type	Amount	Reagent	Bubble size	Expansion Ratio	Results
Metzner, 1956 [5]	CO_2[1]	Saturated[1]	Detergent: Nacconal and Glim	Varied: 0 to 0.33%	None	1-5 mm	Varied: 1.03 to 1.6	Mass transfer found comparable to conventional packed column.
Jackson, 1963(2) [6]	Varied: NH_3 N_2O_3 SO_2 CO_2	Varied	NR[3]	NR	Varied: NaCl H_2SO_4 NH_3	NR	NR	Absorption rate coefficients from 7 to 260 times higher than conventional equipment.
Biswas, 1981 [7]	CO_2	0.4-0.5 vol.%	NR	NR	NaOH	NR	Varied:[4] 20 to 35	Mass transfer agreed with polyhedral model.
Shah, 1984 [1]	CO_2	10 vol%	HDTMAB Triton X-100	0.5 wt% 1 vol%	NaOH $Na_2CO_3/NaHCO_3$	2.2 to 5.4 mm	Varied: 20 to 500	Mass transfer higher than packed beds for slow reaction; lower for fast reaction.
Brander, 1984 [8]	H_2S HCHO CH_3CHO CH_3CH_2CHO	Varied: 0.017 to 0.36 vol%	Varied	Varied	$CuSO_4$ $Na_2S_2O_5$	NR	4-6	Very good removal in 1.75 to HCHO: 80% to >99%, CH_3CHO: 74% to >99% H_2S: >90%.
Gillberg, 1980(2) [9]	a. Nitrous gases	NR	NR	NR	Urea NaOH	NR	NR	High efficiency.
	b. Mercaptans H_2S	NR	NR	NR	Cu(II) Salts or pH>10.7	NR	NR	Effectively removed.
Ohkawa, 1987 [10]	O_2	NR	NR	NR	None	3.5mm avg	NR	Mass transfer coefficients ranged from 9×10^{-5} to 2×10^{-4} m/sec.

Notes: [1] The surfactant solution was saturated with CO_2 before foaming. The authors measured rate of _desorption_ of CO_2 into foam.
[2] Review of other research work.
[3] NR   Not reported
[4] Calculated as inverse of volume fraction liquid (for newly generated foam).

EXPERIMENTAL WORK UNDER THE U.S. EPA PROGRAM

The U.S. EPA is sponsoring an ongoing laboratory-scale testing program. This section describes the testing process as well as its results to date.

Test Setup

The test setup consists of a foam generator, a foam containment chamber and a sampling arrangement. Figure 4 illustrates the apparatus.

The foam generator is a modified 2-in. diameter air-aspirating unit of commercial design. The air intake is sealed and connected to gas cylinders. Nitrogen is used for these tests, and certified gas mixtures purchased from Matheson are used for test runs.

Premixed foam solution is supplied from a small vessel, pressurized by nitrogen to 25 to 50 psi. The nominal flow of foam solution is 0.22 gpm. The test gas flow is adjusted to vary the expansion ratio.

The containment chamber is a square, clear, rigid plastic box 2 ft x 2 ft x 1.5 ft, equal to 6 cu ft (170 L) in volume. At 300:1 expansion, the box will fill in 40 seconds. The box has a hinged top closure so that it can essentially be sealed once it is filled with foam. Top, side and bottom sampling ports are provided.

The chamber is mounted on a digital scale which records the weight of its contents. Drainage liquid, produced as the foam collapses, is collected in a graduated cylinder below the box. A thermocouple is inserted well within the box to monitor the temperature of the foam mass (i.e., for heat of reaction). The entire box is mounted in a laboratory fume hood.

Procedures

Run preparations include premixing the foam solution at 6% concentration. For these tests, MSA "P" Foam[R] was used. This is an anionic surfactant type for salt water containing alkyl lauryl sulfates, alcohols and long chain amides. When a reagent is added, it is mixed with the prepared foam solution. The vessel is then pressurized with nitrogen.

Figure 4
Schematic of Test Setup

Study	Particulate/Aerosol Type	Size	Surfactant Type	Amount	Bubble size	Results
Bransky & Diwoky, 1940 [1]	H_2SO_4 fog	NR [2]	NR	NR	NR	>90% in > 10 sec.
Yano et al, 1955 [1]	Ammonium chloride Cigarette smoke H_2SO_4 mist	~0.1um	NR	NR	2-7 mm	~100% in 90 sec.
Pozin et al, 1954-1956 [1]	Dust	2-30 um	NR	0-0.1 %	NR	"Good" for >5 um size. Surfactant improved efficiency.
Jackson, 1963 [1]	NR	NR	NA	0 %	NR	Confirmed above findings.
Taheri, 1968 [1]	NR	< 3 um	NR	0-NR	NR	50% for 3 um, 10% for < 1 um, Surfactant decreased efficiency.
Silverman, 1962 [1]	Uranine	0.072 um 0.02 um	NR	NR	~1 cm	95% in 160 sec.
Browning & Ackley, 1962 [1]	Iodine	0.0065 um 0.0014 um	NR	NR	NR	95% in less time than above.
Surati, 1975 [1] Limaye, 1976	Polystyrene latex	0.18 um 0.8 um	varied	NR	NR	> 90% in 3-4 sec. Surfactant type showed little effect.
Kaldor, 1976 [12]	Fly ash	1.3 um avg	Note (3)	0.3 g/l	3 mm Avg.	High efficiency on >2 um particles [6]. Aggregation suspected.
Ctvrtnicek, 1976 [13]	Dioctyphthalate Polypropylene glycol	0.18-1.0 um	Tergitol TMN Aerosol OT Sterox	2%	0.8 mm 3.9 mm	Dioctyl phthlate:~95% in 80 sec, polypropylene glycol: ~75% in 80 sec.
Ctvrtnicek, 1977 [4]	Fly ash	0.056-1.0 um	Tergitol	0.25 wt%	3 mm est	50% to 75% in 20 sec, better efficiency for the smallest particles.
Ramsey, 1977 [14]	Fe_2O_3	0.2-10 um	Tergitol	NR	1.0 mm	95% in 2 minutes.
Damle, 1980 [11]	Wax Methylene blue	0.1-5.0 um	HDTMAB [5] Sodium Oleate Triton	0.5 wt % 0.5 wt % 1.0 vol %	Varied: 0.8mm to 5.3 mm	<0.4 um: 70% in 90 sec. 0.56-1.0 um: 90% for wax. >2 um: 100%, 0.8 mm bubbles.

Notes: [1] As reported by Damle, 1980 [11]
[2] NR   Not reported
[3] Ethylhexadecyldimethylammonium bromide
[4] 500 cfm pilot scrubber
[5] Hexadecyltrimethylammonium bromide
[6] For particle size range of 0.3 to 10.0 um.

For each run, foam is blown, using certified test gas, to fill the test chamber. The chamber lid is open approximately 6 in. during filling and is then closed. Fill time is monitored and recorded for correlation with the estimated expansion time.

Bubble sizes are measured as an average, based on the number of bubble intersections in a 6-in. linear path at the surface of the box. Actual sizes of individual bubbles can vary up to a factor of two in either direction (half or twice the average).

After a specified time (5 min for most tests), the residual foam is collapsed by injecting a small amount of fine silica through an access port (with the chamber lid still closed), and a gas sample is drawn from the center of the chamber. A sample of the liquid drainage is taken at the same time. Liquid and gas samples are then analyzed for the test contaminant.

Analytical

To date, testing has been carried out using ammonia and chlorine as the test gases. The ammonia concentration in the gas phase is determined by titration of the extracted sample. In this procedure a gas sample, drawn from the chamber with a calibrated syringe, is injected through a bubbler into a fixed volume of 0.01 normal certified HCl solution to extract the NH^3 The solution is back-titrated with 0.1008 normal certified NaOH to neutralize the excess HCl and determine the NH^3 content. The free ammonia in the liquid phase is measured by direct titration of samples drawn from the drainage sump. Total liquid-phase ammonia is determined by the Kjeldahl method.

To determine chlorine in the gas phase, gas samples are extracted using potassium iodide solutions and subsequent titration with thiosulfate. For the liquid, samples are treated with KI and then back-titrated with thiosulfate. For tests where chloride is present, a silver nitrate titration is used.

Results

In test runs using a standard foam solution (i.e. not acid-modified) and ammonia concentrations of 1% and 5% by volume, an average of 60 to 65% of the ammonia was collected by the liquid. In most cases, the material balance agreed to within ± 10%. Table 3 presents the data for runs with standard foam solution, using ammonia at a starting concentration of 1%.

Table 3
Capture of 1% Ammonia by Unmodified Foam[1]

Exansion	Bubble size (in)	Final NH₃ (2) Liquid (%)	Gas (%)
147	.20	65.5	32.8
147	.22	65.5	32.2
145	.25	65.3	32.6
258	.22	65.5	35.6
258	.25	65.0	35.1
390	.28	65.1	35.3
395	.30	64.2	34.0
500	.30	61.0	31.0
518	.27	61.3	31.4
512	.35	61.2	31.4

[1] MSA "P" Foam[R], 6% concentration.
[2] Percent of original ammonia. Ammonia added to nominal 1% concentration (actual 0.95%).

It should be noted that even the 30 to 35% of the ammonia that was found in the gas phase at the end of the runs is "controlled" (in the sense that it is entrapped within the bubbles). In a spill scenario, this ammonia would eventually be released, but at a much slower rate than the initial spill. Thus, downwind concentrations would be lessened not only by the amount reacted/absorbed in the liquid, but also by the effects of the time delay caused by ammonia entrapment in the foam.

Subsequent runs were made in which sulfuric acid was added to the premixed solution before blowing the foam. As shown in Figure 5, the capture of ammonia in the liquid phase was much improved by this modification. No ammonia was detected in the gas phase at the end of the run when the stoichiometric amount of sulfuric acid was used.

TEST CONDITIONS

Test gas:	1% ammonia in nitrogen
Neutralizing reagent:	Sulfuric acid
Expansion ratio:	150:1 to 500:1
Bubble size:	0.25-in. avg.
Residence time:	5 min.
Temperatures:	Ambient and 150°F

RESULTS
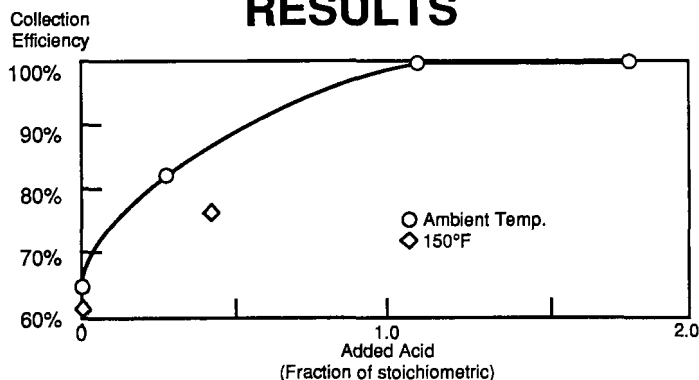
Figure 5
Capture of 1% Ammonia by Acid-modified Foam

Figure 6 shows similar data for the capture of 5% ammonia. Several runs were made in which the temperature of the blowing gas was raised to 150°F using a Calrod[R] sheathed heater with a downstream thermocouple for temperature control. These data are also shown.

A potential concern with foam is that the addition of acids and bases can cause a temperature rise that would lead to premature foam collapse. To this end, the temperature within the box was measured before and after it was filled with foam. Figure 7 shows that up to a 12°F

temperature increase occurred when treating 5% ammonia with acid-modified foam. Despite this temperature increase, the foam collapse rate was not excessive.

TEST CONDITIONS

Test gas:	5% ammonia in nitrogen
Neutralizing reagent:	Sulfuric acid
Expansion ratio:	150:1 to 500:1
Bubble size:	0.25-in avg.
Residence time:	5 min
Temperatures:	Ambient and 150°F
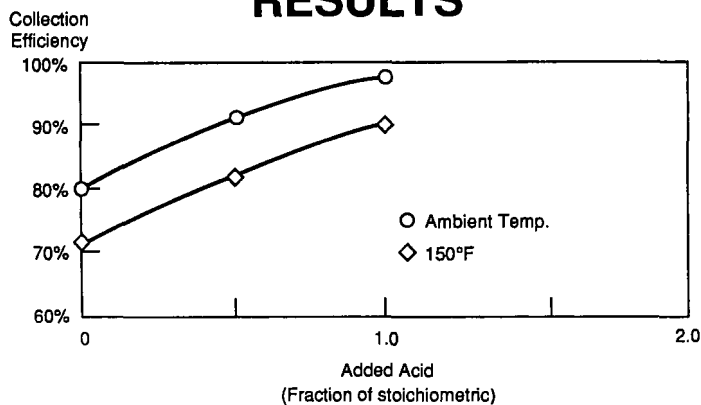
RESULTS

Figure 6
Capture of 5% Ammonia by Acid-modified Foam

GAS-PHASE TEMPERATURE RISE
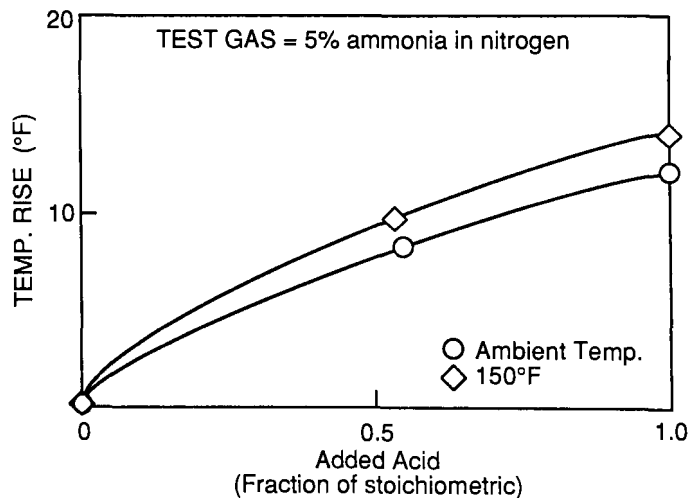
Figure 7
Temperature Rise Resulting from Capture of Ammonia by Acid-modified Foam

A limited set of runs was carried out using chlorine in nitrogen as the test chemical. In this case, aqueous ammonia was added to consume the products of chlorine decomposition. Although not studied in detail, these products may include hypochlorite and chloramines, probably leading to a final product that is primarily ammonium chloride. Table 4 shows that up to 99% of the chlorine was collected in the liquid phase under the highest stiochiometry used.

Table 4
Collection of Chlorine by Aqueous Form

TEST CONDITIONS

Test Gas:	1% chlorine in nitrogen
Neutralizing reagent:	Ammonia
Expansion ratio:	250:1
Bubble size:	0.20-in average
Residence time:	8 min
Temperature:	Ambient
Foam type:	MSA "P" Foam², 6% concentration

RESULTS

Additive NH₃	Chlorine (% of original)	
% stoichiometric	Gas	Liquid
0	35.0	63.5
150	5.0	94.2
150*	Not detected	99.0

*Plus a copper salt to catalyze conversion of hypochlorite to HCl.

Current test work includes higher concentrations of ammonia (10% and 20%) and chlorine (5% and 10%). Although no quantitative data are yet available, preliminary runs have established that foam can be successfully generated at both the higher ammonia concentrations and the higher sulfuric acid concentrations needed to neutralize it.

Future runs will test phosgene and HF (initially at low concentrations) and will experiment with shorter time intervals.

CONCLUSIONS AND RECOMMENDATIONS

The results of the ongoing U.S. EPA experimentation with foam scrubbing are encouraging, as are the findings of previous researchers. A need still exists, however, for additional testing (with more compounds under varying conditions) and for trial operation on a larger scale to bring the foam concept to an industrial reality.

This project tentatively plans to carry out larger scale tests in a wind tunnel and/or at a host site. This testing will help to prove the process under realistic scenarios.

The accumulated test data indicate that foam technology can be a valuable addition to the range of available techniques for the control of hazardous emissions.

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Integrated Zero-Emission Groundwater and Soil Remediation Facility at Lockheed, Burbank

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INTRODUCTION

The Lockheed Aeronautical Systems Company (LASC) has over 200 acres of aircraft manufacturing facilities located in Burbank, California. Among the famous aircraft that have been assembled at this facility are the P-38 Lightning, the F-104 Starfighter, the U-2 and the L-1011.

In late 1987, solvent-contaminated soil and groundwater were identified near Building 175. As a result, the Los Angeles Regional Water Quality Control Board (RWQCB) issued a Cleanup and Abatement order requiring soil and groundwater remediation to commence by Aug. 1, 1988 and Oct. 15, 1988 respectively.

LASC selected AWD Technologies, Inc. (AWD) to design, install and operate a treatment facility to meet the requirements of the RWQCB. AWD is a corporation created by The Dow Chemical Company, Guy F. Atkinson Company and Woodward-Clyde Consultants. AWD provides a comprehensive range of services for remediation of contaminated soil and groundwater and can draw upon the specialized resources and expertise of its founding companies.

TECHNOLOGIES INVOLVED

Two technologies were integrated in an innovative way. The two technologies were AquaDetox, a low-pressure steam stripping technology developed by Dow Chemical to extract volatile organic compounds (VOCs) from the groundwater, and Soil Vapor Extraction (SVE) treatment of the VOCs in the vadose zone. The following paragraphs describe the unique features of these technologies. Their integration into a zero emission treatment facility is described in a subsequent section.

AquaDetox

There has been an effort over the past several years to improve the efficiency of air stripping in removing contaminants from groundwater. This work has led to the development of the AquaDetox technology, which surpasses more conventional approaches to air stripping in terms of reduction efficiency. In most cases, AquaDetox can reduce contaminants in groundwater to below Maximum Contaminant Levels (MCLs) without liquid-phase carbon bed treatment. Moderate vacuum and deep vacuum AquaDetox steam stripping go even further, allowing the near total recovery of contaminants for possible recycling.

AquaDetox technology can be used to remove a wide variety of volatile compounds and many compounds that are normally considered "non-strippable" (i.e., those with boiling points in excess of 400°). The application of AquaDetox for the removal of compounds with boiling points greater than 400°F and the use of vacuum are patented by The Dow Chemical Company.

Stripping is commonly defined as a process to remove dissolved, volatile compounds from water. A carrier gas, such as air or steam, is passed through the contaminated water, with the volatile components being transferred from the water into the gas phase. While the physical principles involved are straightforward, the practice of stripping has undergone considerable development since the early 1970s.

Dow's effort has focused on:

- Development of the proper technical relationships that provide a clear understanding of the stripping process
- Application of these relationships, along with the correct hardware, to attain higher levels of contaminant removal than previously possible
- Development of the proper scale-up parameters to go from pilot units handling less than 1 gpm to production units handling greater than 3000 gpm
- Development of the conditions under which compounds with very high boiling points (e.g., 400°F) can be stripped from water
- Compilation of a vapor-liquid equilibrium data base with special emphasis on U.S. EPA priority pollutants

The effort necessary to address these criteria has been carried out by the Separations Section of the Applied Science and Technology Department of Dow. The research and development has been under the direction of Dr. Lanny Robbins. By the early 1980s, the result of this effort was the AquaDetox process, an innovative technology for the high efficiency stripping of organic contaminants from water.

AquaDetox can effectively strip more than 90 of the 110 volatile compounds listed in CFR 40, July 1, 1986, by the EPA (Table 1). The ability of AquaDetox to efficiently attain low levels of contamination in the effluent represents a major breakthrough. Conventional strippers will normally achieve only 95 to 98% removal of the contamination, whereas AquaDetox can achieve up to 99.99% removal.

Another major concern raised regarding conventional stripping systems is that they simply transfer contaminants from the water to the air. The contaminated air usually is treated over carbon beds, but still releases sometimes significant amounts of contaminants into the atmosphere. The AquaDetox steam stripper (moderate or deep vacuum) condenses the contaminated steam to form a multiphase liquid from which the liquid phase contaminants can be decanted for possible recycling. Only a small stream of non-condensable gases is emitted following carbon treatment.

There are three versions of the basis AquaDetox technology:

- Air Stripping AquaDetox
- Moderate Vacuum AquaDetox (requires steam)
- Deep Vacuum AquaDetox (does not require steam)

Typical schematic flow diagrams for each type of AquaDetox technology are included in the paper by Street, Robbins and Clark.[1]

Soil Vapor Extraction

Soil vapor extraction (SVE) is a technology commonly applied for

Table 1
Strippable U.S. EPA-Designated
Priority Pollutants

Volatiles

acrolein	2-chloronaphthalene
acrylonitrile	4-chlorophenyl phenyl ether
benzene	chrysene
bromoform	1,2-dichlorobenzene
carbon tetrachloride	1,3-dichlorobenzene
chlorobenzene	1,4-dichlorobenzene
chlorodibromomethane	* 3,3'-dichlorobenzidine
chloroethane	di-n-butyl phthalate
2-chloroethylvinyl ether	2,4-dinitrotoluene
chloroform	2,6-dinitrotoluene
dichlorobromomethane	di-n-octyl phthalate
1,1-dichloroethane	* 1,2-diphenylhydrazine (as azobenzene)
1,2-dichloroethane	fluroanthene
1,1-dichloroethylene	fluorene
1,2-dichloropropane	hexachlorobenzene
1,3-dichloropropylene	hexachlorobutadiene
ethylbenzene	hexachlorocyclopentadiene
methyl bromide	* hexachloroethane
methyl chloride	* indeno(1,2,3-cd)pyrene
methylene chloride	isophorone
1,1,2,2-tetrachloroethane	napthalene
tetrachloroethylene	nitrobenzene
toluene	* N-nitrosodimethylamine
1,2-trans-dichloroethylene	* N-nitrosodi-n-propylamine
1,1,1-trichloroethane	* N-nitrosodiphenylamine
1,1,2-trichloroethane	phenanthrene
trichloroethylene	pyrene
vinyl chloride	1,2,4-trichlorobenzene

Acid Compounds

	Pesticides
2-chlorophenol	aldrin
2,4-dichlorophenol	* alpha-BHC
2,4-dimethylphenol	* beta-BHC
* p-chloro-m-cresol	* delta-BHC
pentachlorophenol	chlordane
2,4,6-trichlorophenol	4,4'-DDT
	4,4'-DDE
Base/Neutral	4,4'-DDD
acenaphthene	dieldrin
acenaphthylene	* alpha-endosulfan
anthracene	* beta-endosulfan
benzidine	endosulfan sulfate
benzo(a)anthracene	* endrin aldehyde
benzo(a)pyrene	heptachlor
3,4-benzofluoranthene	heptachlor epoxide
benzo(ghi)perylene	* PCB-1242
benzo(k)fluoranthene	* PCB-1254
bis (2-chloroethoxy) methane	* PCB-1221
bis (2-chloroethyl) ether	* PCB-1232
bis (2-chloroisopropyl) ether	* PCB-1248
bis (2-ethylhexyl) phthalate	* PCB-1260
* 4-bromophenyl phenyl ether	* PCB-1016
butylbenzyl phthalate	toxaphene

*Needs further pilot study to determine treatability

the in situ removal of VOCs from soil. A vacuum is applied to vadose zone extraction wells to induce air flows within the soil toward the wells. The air acts as a stripping medium which volatilizes the VOCs in the soil. Soil-gas from the extraction wells typically is treated in activated carbon beds before release to the atmosphere. Alternatively, the treated soil-gas is reinjected in the soil to control the direction of air flow in the soil.

LOCKHEED PROJECT

On Feb. 1, 1988, LASC awarded AWD a contract for pilot testing, design and installation of an integrated 1200-gpm groundwater treatment plant and 300-scfm SVE system. Fast-track project techniques were used and seven and half months later all systems of the $4 million project were operational.

Under AWD management, process engineering and design were performed by Dow Chemical engineers, the SVE conceptual design and permit acquisition were performed by Woodward-Clyde Consultants and construction was performed by a division of Guy F. Atkinson.

Integrated System

The integrated system consists of two basic processes: an AquaDetox vacuum stripping tower using low pressure steam and a soil-gas vapor extraction/reinjection process. The system removes VOCs from the groundwater and soil with no gaseous emissions to the atmosphere. Figure 1 shows a schematic flow diagram of the integrated system.

Integrating the two technologies creates a unique system. While the AquaDetox system extracts and treats contaminated groundwater, an array of SVE wells removes contaminated soil-gas from the vadose zone. The soil-gas is treated in activated carbon beds and then reinjected into the ground to sweep through the soil and remove additional contamination. The AquaDetox and SVE systems share a 3-bed granulated activated carbon (GAC) unit. When one of the GAC beds is regenerated, the steam and organic vapors are condensed in the secondary condenser of the AquaDetox system. Condensed organics are pumped to a storage tank for recycle; water condensate is pumped to the recycle tank for further treatment by the AquaDetox process; and non-condensables are transferred to the active GAC bed.

Groundwater Treatment Facility

The groundwater treatment technology at the Lockheed site is the Moderate Vacuum Steam Stripper (MVSS) AquaDetox system. Process flow diagrams are shown in Figures 2 and 3.

Contaminated groundwater is fed from extraction wells to a cross exchanger, where it is heated by the treated water. The heated water then enters the top of the stripping column (9 ft in diameter x 60 ft tall) and flows down the column, contacting the rising vapor flow generated by the introduction of steam to the bottom of the column. Under a pressure of 100 mm Hg absolute, the contaminants are stripped from the liquid into the vapor stream, which exits from the top of the column. The treated water leaves the bottom of the column. The treated water passes through the heat exchanger, where it is cooled and the contaminated feedwater is heated. The water exiting the treatment facility is thereby controlled to 9 to 10° F higher than the incoming groundwater.

The overhead vapors flow to a water-cooled condenser, where the water vapor is condensed and recycled back to the contaminated feedwater. The water for cooling the condenser is provided by diverting a portion of the cool feed stream through the condenser and back to the main feed stream.

Total condensation of the overhead vapors is not possible due to non-condensable gases from vacuum leaks and dissolved gas contained in the contaminated groundwater. These non-condensable vapors, carrying some water, inert gases and VOCs, enter a vacuum pump where they are compressed to atmospheric pressure. Cooling this compressed vapor stream results in condensation of water and VOCs.

The water phase is recycled to the contaminated feedwater and the organic solvent phase is withdrawn for reclamation by a contract recycler. The coolant for this secondary condenser is supplied from the feedwater as is done for the first condensing unit.

The vent stream from the secondary condenser contains the non-condensable VOCs and an equilibrium quantity of VOCs. This stream is passed through vapor-phase GAC prior to discharge into the reinjection wells of the SVE system.

Soil Vapor Extraction (SVE) System

Soil vapor extraction (SVE) is being used at the Lockheed site to remediate contaminated soil because of the relatively volatile character of the reported contaminants, the depth to groundwater in the range of approximately 140 to 150 feet and the predominantly coarse-grained nature of subsurface soils.

Figure 4 shows the locations of the extraction and reinjection wells. The design of the SVE system focused on the distribution of the wells to produce an effective and non-disruptive pneumatic flow regime. The effectiveness of the SVE depends on establishing radially inward flow (toward an extraction well) throughout the areas of probable soil contamination. The term non-disruptive pneumatic flow regime refers to injection well placement such that: (1) fugitive atmospheric emissions are not created and (2) soil-gas within the areas of probable soil contamination is not displaced from the zone of extraction well influence.

Extraction wells connected to a common header feed up to 300 cfm of contaminated soil-gas to the system for processing and decontamination via carbon adsorption. Liquids collected in the SVE scrubber sump are pumped to the water recycle tank for processing through the

Figure 1
Zero Air Emissions AquaDetox/VES
Integrated System

Figure 2
Lockheed Aqua Detox Flow Diagram

Figure 3
Lockheed VES Flow Diagram

AquaDetox tower. Vapors are exhausted to the GAC beds for hydrocarbon removal prior to reinjection.

Three GAC beds remove chlorinated hydrocarbons from SVE system extraction well soil-gas and from the vent gases from the AquaDetox system. The GAC beds are operated alternately, with two beds on-line in series while the remaining unit is being regenerated. Once each 8 hours, the regenerated off-line bed is placed in service and spent carbon bed is removed from service and regenerated. Steam is used to strip chlorinated hydrocarbons from the GAC units. The vapors from this regeneration process are condensed and processed in the AquaDetox separator.

Treated soil-gas is reinjected into the ground at depths ranging from 50 to 150 feet through the vadose zone. The soil-gas then sweeps horizontally through the contaminated soil, picking up additional hydrocarbons and is once again collected in the soil-gas extraction well system, where hydrocarbons are again removed.

SYSTEM OPERATION

The groundwater treatment plant operates at an average flow rate of 1000 gpm and the SVE operates at 170 cfm. The contaminants removed are listed in Table 2. Initially, total VOC concentrations were 12,000 mg/L in the groundwater and 6,000 mg/L in the soil-gas. After the integrated system had been operating several months, these concentrations decreased to 5,000 mg/L and 450 ppm, respectively. At these levels, the AquaDetox/SVE facility removes more than 70 pounds per day of PCE/TCE from the groundwater and 40 pounds per day from the soil-gas.

Table 2 lists the major contaminants in the groundwater feed to the treatment plant. Effluent analyses show that all contaminants were removed to below the analytical detection level (1 mg/L for most contaminants). These data equate to a removal efficiency greater than of 99.99%. The soil-gas treatment by two of three 3,500 pound carbon beds removes VOCs to below 2 ppm before the air is reinjected in the ground. These data equate to a removal efficiency of greater than 99%.

While the treatment plant has operated consistently at average design flow rates (95% availability factor) and has produced water effluents at non-detectable VOC concentrations, it has not been devoid of typical startup problems and one operational problem. Typical startup problems were failures of instrumentation and control software bugs, which have been resolved. A more persistent problem, however, has been caused by the high alkalinity of the groundwater and resulting calcium carbonate scaling in parts of the treatment plant.

The solubility of the calcium carbonate in the groundwater is reduced in two ways as the water is processed through the AquaDetox system. First, the water is heated. Second, carbon dioxide is removed during the stripping process in the column, thereby increasing the pH. Consequently, scaling occurs due to carbonate deposition. The principle disadvantage of scaling is the reduction in the heat transfer efficiency of the cross exchanger, resulting in greater steam consumption. Currently, an anti-scalant is injected in the feed water, but it cannot totally halt the scaling due to the subsequent removal of carbon dioxide and concomitant pH increase. Periodically, the heat exchanger is acid-treated to maintain its heat transfer properties.

A design project is under way to resolve the scaling problem. A sulfuric acid injection system will be installed to control pH and eliminate scaling. The costs associated with the addition of sulfuric acid will be more than offset by: (1) eliminating anti-scalant injection; (2) eliminating phosphoric acid used to clean the heat exchanger periodically; and (3) lowering average steam consumption by improving heat exchanger efficiency. Less than 20% of the steam consumption in the AquaDetox facility is needed to strip contaminants; the other 80% is needed to raise the incoming water to its boiling point of 120°F at 100 mm Hg. The cross exchanger helps reduce this steam requirement by using heat from the effluent water. This is a highly energy-efficient and cost-
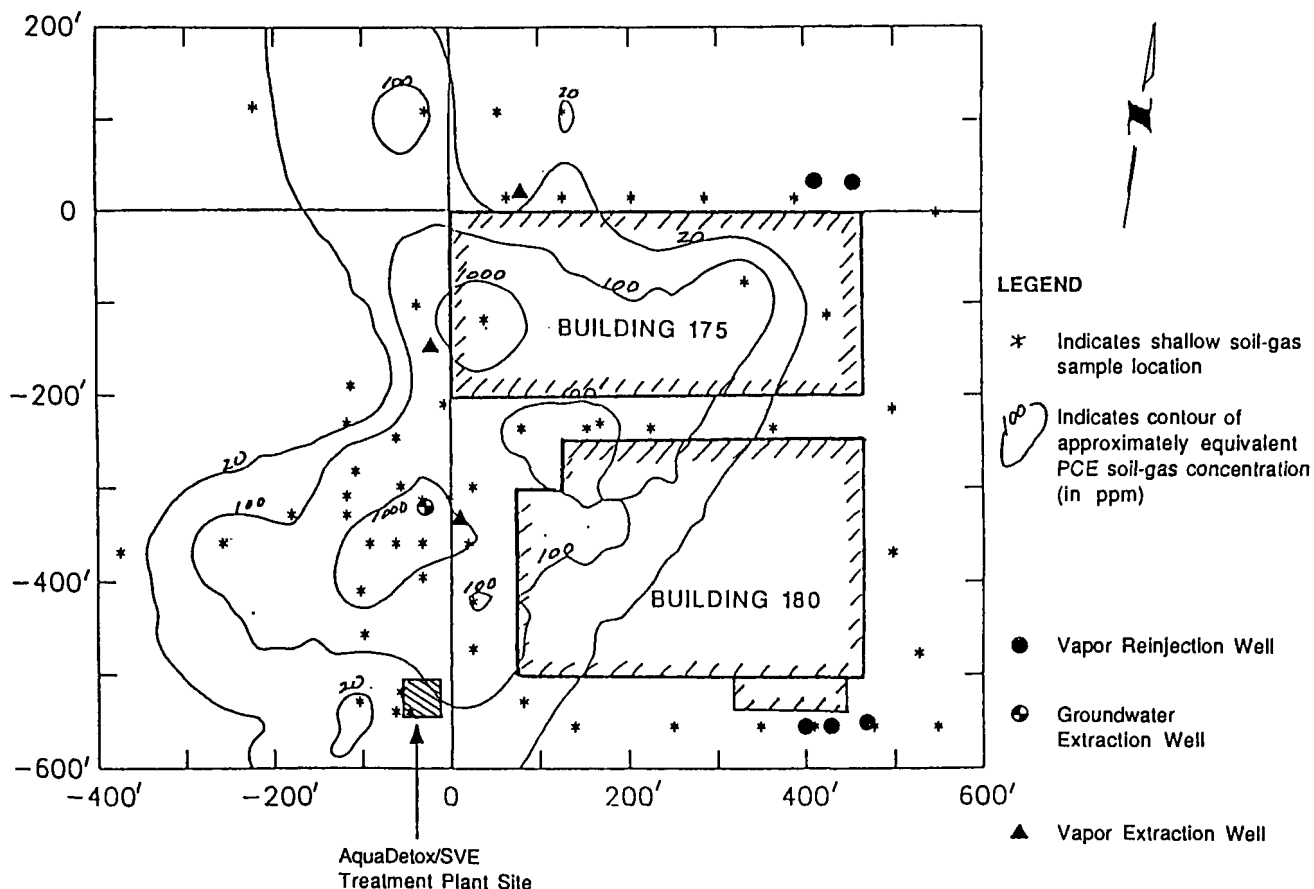
Figure 4
PCE and Soil-Gas Concentrations

effective approach and future systems will have even larger cross ex-
changers.

OPERATING COSTS

Annual operating costs for the AquaDetox/SVE plant are shown below.

Labor

One person was assigned full-time for the maintenance and opera-
tion of the facility, but after the first six months of operation his time
was reduced to three days per week. It is expected that after another
year of operation, no more than one day per week will be needed. Cur-
rent labor costs are approximately $8,000 per month.

Steam

Steam, which is provided by an existing Lockheed boiler, is costed
at $5.70 per 1,000 pounds. At a 1000 gpm flow rate, the steam con-
sumption is 3,500 lb/hr before calcium carbonate scaling shows its ef-
fect on the cross exchanger efficiency. An additional 340 lb/hr of steam
(equivalent continuous average) is used to regenerate the carbon beds.
This results in a total monthly steam consumption of 3,840 lb/hr at a
cost of $14,700.

Chemicals

Significant amounts of anti-scale and scale-removing chemicals are
currently being consumed, with limited success. A more appropriate
solution of sulfuric acid injection is currently being implemented and
will result in a monthly cost of $1,800.

Power

The power requirement to operate the treatment plant is 88 kW. At
a cost of $0.70 per kWh, this represents a monthly cost of $4,200. This
does not include the power consumption for the groundwater extrac-
tion well.

Table 2
Integrated System at Lockheed-Burbank
Design Criteria and Performance Results

AQUADETOX

Design Contaminants	Design Feed Water Concentration (ppb)	Actual (11/88) Influent Concentration (ppb)	Design Effluent Concentration (ppb)	Actual Effluent Concentration (ppb)
Trichloroethylene	3300.0	2200	4.5	<1
Toluene	180.0	<100	9.5	<1
Tetrachloroethylene	7650.0	11000	3.5	<1
Trans-1,2,dichloroethylene	19.5	<100	15.0	<1
Chloroform	30.0	<100	N/A	<1
1,1-dichloroethane	18.0	<100	5.5	<1
1,2-dichloroethane	4.5	<100	0.8	<1
Carbon tetrachloride	7.5	<100	N/A	<1
Benzene	30.0	<100	0.65	<1
1,1,2-trichloroethane	34.5	<100	N/A	<1
Ethylbenzene	255.0	<100	N/A	<1

SVE

Contaminants	Actual (9/89) Extraction Gas (ppb)	Actual (9/89) Reinjection Gas (ppb)
Total Hydrocarbons	450,000	2,000
Tetrachloroethylene	420,000	365
Trichloroethylene	8,000	60

AQUADETOX/SVE OPERATING COSTS
LOCKHEED-BURBANK

		ANNUAL $	COST PER 1000 GALLONS (1)
Labor:	$8,000/month	$96,000	0.18
Steam:	3,840 lb/h x 8,760 h x 0.92 x $5.70/1000 lb	176,400	0.34
Chemicals:	$1,800/month	21,600	0.04
Power:	88 kW x 8760 h x 0.92 x 0.07 $/kWh	50,400	0.10
Supplies:	$5,000/month	60,000	0.11
		404,400	0.77

(1) Total gallons per year = 1000 gpm x 60 min/h x 8760 h/yr = 525 x 10⁶ gal/yr

Supplies

Miscellaneous supplies such as oil, replacement gauges, pump seals, spare parts, etc. cost about $5,000 per month.

Based on the above data, we calculate monthly operating costs average $33,700 or $.77 per 1000 gallons. Further reductions (particularly labor) are anticipated with time, and further savings in steam costs can be accomplished by installing larger cross exchangers.

REFERENCES

1. Street, G., Robbins, L. and Clark, J., "AquaDetox Stripping System for Groundwater Remediation," paper presented at HazMat Central 1989, Chicago, IL.

Remedial Action Program for the Weldon Spring Quarry

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ABSTRACT

The U.S. Department of Energy (DOE) is responsible for conducting remedial actions at the Weldon Spring site, located approximately 30 mi southwest of St. Louis, Missouri. Because the site is listed on the NPL, these remedial actions are being carried out consistent with CERCLA. The site is adjacent to the U.S. Army Weldon Spring Training Area, which is also listed on the NPL.

The Weldon Spring site consists of two distinct geographical areas: (1) the chemical plant/raffinate pits (CPRP) area and (2) the quarry. These areas are approximately 4 mi apart.

The quarry was created by the U.S. Army during World War II as a source of foundation material for the construction of the Weldon Spring Ordnance Works (WSOW). After the war, the WSOW was demolished and the site was used by the Atomic Energy Commission to construct a uranium feed materials plant. Chemical and radioactive wastes for both the WSOW and uranium processing operations were dumped in the quarry. Approximately 95,000 yd³ of chemically and radioactively contaminated bulk waste and 3,000,000 gal of contaminated water, requiring remediation, are presently located in the quarry. The program to remediate the quarry, with the focus on the waste removal, is the subject of this paper.

The quarry is being remediated as two separate operable units. This strategy is necessitated by the fact that the heterogeneity of the quarry waste is such that it cannot be adequately characterized in place. Therefore, the basic strategy is to dewater the quarry and remove the solid waste using an observational approach. The waste will be transported to a temporary storage area located at the CPRP site, where it will be sorted and characterized prior to ultimate treatment and disposal. Waste removal and storage constitute the first operable unit. The second operable unit consists of remediating residual contamination in the quarry and remediating groundwater and vicinity properties.

Details of the remedial action program for the first operable unit are presented in this paper. The discussion includes methods to remove and treat the water, removal of the waste using an observational approach, protection of worker and public health and safety, and operation of the temporary storage area where the wastes will be segregated, characterized and stabilized.

INTRODUCTION

Between 1941 and 1967, the federal government manufactured trinitrotoluene (TNT) and dinitrotoluene (DNT) explosives and processed uranium and thorium ores at a facility located near Weldon Spring, Missouri. A limestone quarry was excavated nearby to provide construction material for the facility. This quarry was subsequently used as a disposal site for residues of explosives manufacturing and ore processing. Contaminated building rubble and equipment were also disposed in the quarry as a result of facility decontamination and demolition activities.

The processing facilities and the quarry have been placed on the NPL. The U.S. Department of Energy (DOE) is remediating the facilities and the quarry under the requirements of CERCLA. DOE contracted with MK-Ferguson Company as the Project Management Contractor (PMC), with Jacobs Engineering Group as the major preselected subcontractor. The PMC is responsible for environmental safety and health, site characterization, engineering, site remediation and waste management activities. Argonne National Laboratory is under a separate DOE contract to prepare environmental documents required by NEPA and CERCLA.

The quarry is being remediated as two separate operable units. The objectives of this paper are to: (1) describe the site operating history, (2) identify the potential hazards posed by the quarry to human health and the environment and (3) discuss the quarry remedial action program with emphasis on bulk waste removal.

WELDON SPRING SITE DESCRIPTION

The Weldon Spring Site (WSS) is located in heavily forested, rolling terrain approximately 30 mi southwest of St. Louis, Missouri. The site consists of two areas: (1) the chemical plant, and (2) the quarry which lies approximately 4 mi south of the chemical plant.

The U.S. EPA listed the quarry on the NPL in July 1987. This listing was expanded to include the chemical plant area in March 1989. At that time, the expanded listing was designated as the "Weldon Spring Quarry, Weldon Spring Chemical Plant and Weldon Spring Raffinate Pits (DOE/U.S. Army)." The quarry and chemical plant/raffinate pit (CPRP) areas are under the control of the U.S. Department of Energy. The CPRP area, covering approximately 220 ac, is immediately west of the U.S. Army Reserve and National Guard Training Area, which is also listed on the NPL, is the responsibility of the Department of the Army. Figure 1 presents a map of the WSS and vicinity.

The quarry is surrounded by the Weldon Spring Wildlife Area. The Howell Island Wildlife Area is immediately west of the quarry across the Missouri River. These areas are managed by the Missouri Department of Conservation and are open to the public on a year-round basis for recreational purposes. While the quarry area is heavily wooded, agricultural crops are grown on alluvial terrain to the south.
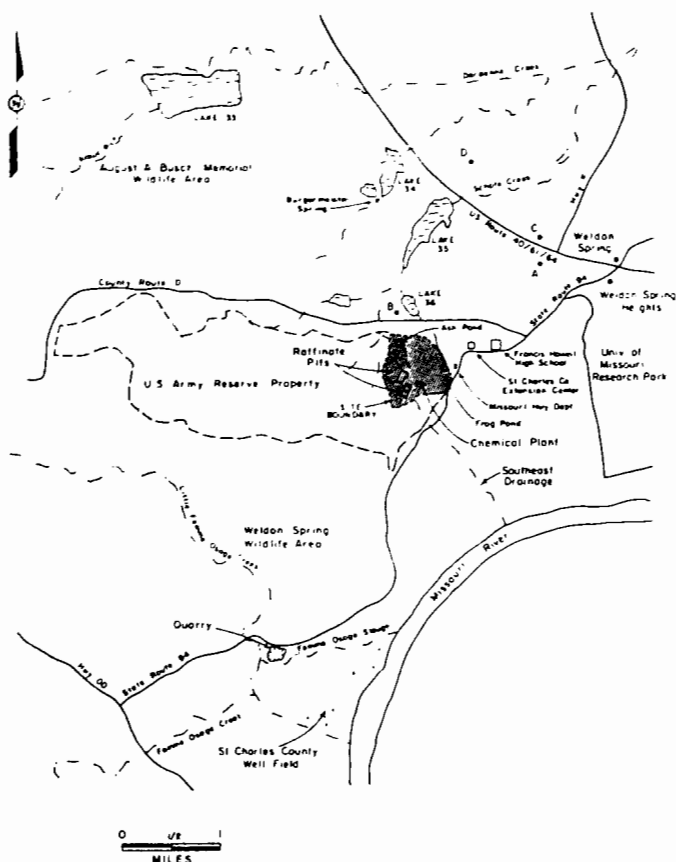
Figure 1
Weldon Spring Site and Vicinity

The quarry was excavated in a limestone bluff above the Missouri River floodplain. The limestone formation contains cracks and fissures and the waste is in hydraulic communication with the local groundwater. The quarry is approximately 1,100 ft long and 450 ft wide, covering approximately 9 ac. Approximately 95,000 yd³ of radioactively and chemically contaminated waste have been placed in the quarry.[6]

The Missouri River is located approximately 1 mi to the southeast of the quarry. The Femme Osage Slough is located between the quarry and the river, approximately 0.15 mi south of the quarry. In addition, an alluvial well field, which supplies drinking water to more than 60,000 residents, is located 0.5 to 1 mi southeast and downgradient of the quarry. DOE has installed 26 groundwater monitoring wells on the north and south sides of the slough. Data from these wells show that groundwater between the quarry and the slough is contaminated with chemical and radioactive constituents leaking from the quarry. However, the slough appears to act as a hydrologic barrier to contaminant migration as no contamination has been detected in the monitoring or drinking water wells south of the slough.

The area of the quarry is sparsely populated, but sensitive human receptors in the vicinity must be considered. The quarry is adjacent to State Route 94, a well-traveled, north-south highway through the area. In addition, the surrounding wildlife area receives several thousand recreational visitors each year. A permanently occupied residence is located approximately 1 mi to the southwest of the quarry. Also, Francis Howell High School, located on Route 94 approximately 4.5 mi northeast of the quarry, serves approximately 2,300 students and faculty.

SITE HISTORY

In 1941, the U.S. Army acquired approximately 17,000 ac in St. Charles County, Missouri, for construction of the Weldon

Spring Ordnance Works. The quarry was excavated to provide building material for the ordnance works complex. The ordnance works produced TNT and DNT explosives between 1941 and 1944. Briefly reopened during 1945 and 1946, the ordnance works were subsequently closed and declared surplus by the Army in 1946. The excavated quarry was used by the Army during the 1940s for disposal of chemically contaminated materials.[4]

The Atomic Energy Commission (AEC) acquired a portion of the ordnance works property in 1955 to construct and operate a uranium feed material plant. The quarry was transferred to the AEC in 1960. The feed material plant was used to process uranium and thorium ore concentrates. The AEC used the quarry to dispose of radioactively contaminated material.[2] These materials included drummed and uncontained uranium and thorium residues, contaminated building rubble, process equipment and nitroaromatic residues from cleanup of the old ordnance works. The Army reacquired the chemical plant site in 1967 for conversion to a herbicide production facility. Although herbicide was never produced, the Army did partially decontaminate some of the buildings. Some rubble and process equipment were placed in the quarry. Since that time, the chemical plant and the quarry have been unused.[4] Throughout the period of waste disposal, a variety of waste was disposed in the quarry, including structural steel, drums of solid and liquid radioactive and chemical waste, process equipment, concrete, soil, etc.

QUARRY REMEDIATION PROGRAM

Protection of human health and the environment is the primary objective of the project. The proximity of the quarry to the county well field and the knowledge that the quarry is leaking provides a sense of urgency to the accomplishment of this objective. However, the situation is complicated by the fact that the heterogeneity of the quarry bulk waste precludes adequately characterizing the waste in place. Therefore, the Weldon Spring Site Remedial Action Project (WSSRAP) is carrying out a strategy to remediate the quarry as two separate operable units (SOUs); removal and temporary storage of the bulk waste and subsequent remediation of the residual contamination.

The first SOU, removal of the bulk waste, is actually an interim remedial action. Limited characterization data, coupled with historical information, were used to prepare bulk waste remedial investigation and base line risk evaluation reports. The preferred alternative presented in the feasibility study calls for expedited excavation of the waste and truck transport on a dedicated haul road to the chemical plant site for placement and characterization at a temporary storage facility.

Once the bulk waste is removed, the quarry floor and walls, groundwater and vicinity soils will be characterized to determine the nature and extent of contamination. This characterization program will be adequate to support the CERCLA decision-making process for final cleanup of the quarry and associated vicinity properties, which constitutes the second operable unit.

BULK WASTE REMOVAL

There are four basic components to bulk waste removal at the Weldon Spring Quarry:

- Quarry dewatering
- Bulk waste excavation
- Waste transportation
- Temporary waste storage

Quarry Dewatering

Approximately 6 mo prior to the initiation of excavation, dewatering will begin by treating the water in the quarry pond and discharging the effluent to the Missouri River under an NPDES permit. Figure 2 provides a layout of the quarry water treatment plant facilities.

The pond, which contains approximately 3 million gallons of

Figure 2
Quarry Water Treatment Plant Area

will begin flowing into the pond. The rate of inflow is expected to be approximately 3 gpm, based on pumping studies by Richardson.[3] Groundwater levels in the vicinity of the quarry will be monitored during pumping to verify gradient reversal. This water probably will be contaminated due to contact with the quarry bulk waste and contaminated soils in the vicinity of the quarry. In addition, storm water run off within the quarry will also be directed to the pond. The water treatment plant will also treat these sources of water. The plant will operate approximately 6 mo prior to bulk waste excavation in an effort to dewater the bulk waste as much as possible.

Bulk Waste Excavation

The physical characteristics of the bulk waste are not completely known. Therefore, the waste will be excavated using an observational method, which will provide a structured approach for managing uncertainty. This approach is based on available

Table 1
Selected Constituents in the Quarry Pond Water

Constituent	Average Concentration ($\mu g/l$)
Aluminum	45
Arsenic	75
Barium	110
Boron	540
Calcium	86,000
Chromium	13
Iron	68
Lithium	25
Magnesium	22,000
Manganese	70
Mercury	4
Molybdenum	350
Phosphorus (as P_2O_5)	500
Potassium	15,000
Silicon (as SiO_2)	16,000
Sodium	22,000
Strontium	470
Zinc	68
Chloride	44,000
Fluoride	1,000
Nitrate (as N)	3,700
Sulfate	200,000
Bicarbonate	210,000
Cyanide	3
Toluene	5
Bis(2-ethylhexyl) phthalate	2
Di-n-butyl phthalate	3
Diethyl phthalate	2
2-Amino-4,6-dinitrotoluene	26

Constituent	Average Concentration ($\mu g/l$)
2,4,6-Trinitrotoluene	9
4-Amino-2,6-dinitrotoluene	15
2,4-Dinitrotoluene	10
2,4-Diamino-6-nitrotoluene	6
2,6-Diamino-4-nitrotoluene	3
6-Amino-hexanoic acid	254
Uranium-238	170 pCi/l
Thorium-232	16 pCi/l
Thorium-230	540 pCi/l
Radium-226	63 pCi/l

Adapted from DOE/OR/21548-039

water, is at the elevation of the water table. Table 1 gives a list of primary contaminants in the water.

The pond water will be pumped to a double-lined equalization basin and hence to the treatment plant. The plant is designed for a nominal treatment rate of 80 gpm. The plant is designed to treat the water to drinking water standards, where applicable. The plant is designed to treat uranium to a level of 30 picocuries per liter (pCi/L). The NPDES permit established a uranium effluent concentration not to exceed 100 pCi/L.[5]

The treatment process includes the following steps or stages:

- Lime addition to remove manganese and uranium
- Clarification/granular media filtration to remove suspended solids
- Activated alumina adsorption to remove arsenic and uranium
- Ion exchange to remove uranium
- Granular activated carbon to remove 2,4-DNT

Waste sludge from the process will be filter pressed to remove excess water and containerized for storage until a final disposal solution can be achieved.

The treated water will be discharged to one of two effluent ponds. The two ponds will allow for verification testing of the water prior to batch release. When one pond is filled to capacity, the treated water will be directed to the second pond. Each pond will have a capacity for approximately 10 days to allow for analytical testing of the effluent. If the effluent meets the discharge limitations, it will be released via a buried pipeline to the Missouri River.[5]

As the pond is drawn down, it is anticipated that groundwater

data and assumptions of field conditions. Reasonable deviations from the basic plan and mechanisms to identify their occurrence are defined. Plans are then developed to address adverse impacts as a result of the deviation. For example, the initial design will assume that waste will be adequately dewatered so that an excavation can be performed safely relative to the environment, operating personnel and equipment. Possible deviations to the plan that could be addressed by the observational method include:

- Additional dewatering requirements
- Greater concentrations of radon or chemical contamination than estimated
- Higher level of protection required for personnel
- Greater time required to perform the work
- Increased cost and schedule due to the inability to adequately dewater the material
- Stability of quarry walls
- Pockets of high concentrations of nitroaromatics

Present estimates place the maximum depth of the waste material at 40 ft.[1] Current conceptual plans call for the excavated waste to be cast directly behind the excavator where room will be available for gross sorting and loading onto trucks to be hauled away. Front-end loaders would be used for sorting and truck loading. A hydraulic crane could be used to remove, sort, stack and load heavy structural shapes. A bulldozer will work in the quarry floor at the face of the waste pile to push the waste to the back hoe. This method assumes the waste will be adequately dewatered. Trenches will be cut in the quarry floor to facilitate dewatering. Dewatering wells could be installed in the waste to enhance dewatering if necessary.

Emissions of airborne radon and radon daughter products may increase as the waste is dewatered and distributed. Ambient radon monitoring will be conducted within the quarry and at the rim for comparison with the annual environmental standard of 3 pCi/L. This level will be used as a guideline to define acceptable hourly average concentrations to protect the public and remedial action workers. If radon concentrations exceed acceptable levels, engineering controls will be implemented to mitigate emissions. In addition, current plans call for workers in the quarry to be outfitted in Level B protective gear with supplied air respirators. As required, equipment cabs will be enclosed and supplied with positive pressure air.[1]

Should engineering controls be required to reduce emissions, the following may be implemented:

- Application of water to reduce dust and radon
- Reduction of the exposed working face
- Cover exposed face with flexible membrane sheeting
- Application of mechanical ventilators
- Cessation of work until airborne concentrations stabilize

Waste Transportation

The quarry waste will be hauled to a temporary storage area located approximately 4 mi to the northeast at the chemical plant site. The haul will be accomplished on a dedicated road constructed for this purpose. Over-the-road 10 to 15 yard trucks will be used for the haul. The trucks will comply with U.S. Department of Transportation requirements for hauling hazardous and low-level radioactive waste.

During waste transportation activities, the following actions will be taken to promote safety and prevent the spread of contamination:

- The trucks will be decontaminated and scanned prior to leaving the quarry.
- The truck cargo boxes will be designed to meet the DOT definition of a strong, tight container, including leak-proof bottoms and secure covers.
- Truck speeds will be limited.
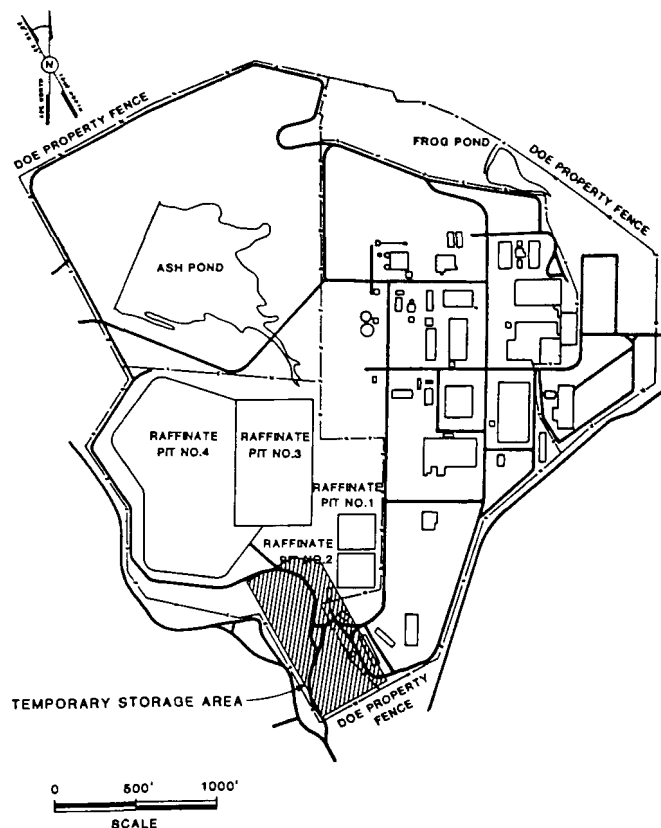
Figure 3
Temporary Storage Area Location

- Loads will be inspected to ensure that they are properly secured.
- Waste-tracking paperwork will accompany each load.
- Trucks will be radio-equipped for communication with other drivers and bulk waste supervisory personnel.
- Grade separation may be constructed at the quarry exit to allow passage of the haul road under Highway 94.
- The haul road will be regularly maintained and repaired.
- Water or chemical palliatives will be applied to the road surface to mitigate fugitive dust emissions.

Temporary Waste Storage Area

The temporary storage area (TSA) will be located in the southwest corner of the chemical plant site, immediately south of the four raffinate pits. The location of the TSA is shown in Figure 3. As the quarry bulk waste has not been adequately characterized to define the exact nature of contamination, the TSA will be designed and constructed consistent with RCRA requirements for a waste pile. A conceptual layout for the TSA is given in Figure 4.

The TSA, covering approximately 13 ac, will be designed to store approximately 140,000 yd³ of excavated material. The design volume will accommodate variations in the quantities of contaminated materials due to swelling of excavated material and will provide some allowance for over-excavation that may occur.

The TSA receiving/sorting area will be a reinforced concrete pad suitable for handling trucks and front-end loaders. The storage area will have separate sub-areas for materials based on their physical or chemical characteristics. A structure could be made available as a dust control contingency measure under the observational approach.

The storage area pad will consist of asphalt concrete surfacing underlain by a compacted aggregate base course over a layer of recompacted in-place clay having a maximum permeability of 1×10^{-7} cm/sec. The design life of the drainage facilities and pavements will be for 10 yr of operation. During this period these

LEGEND:
- Ⓐ — ROCK & CONCRETE
- Ⓑ — FINE GRAINED SOIL
- Ⓒ — SLUDGE
- Ⓓ — NITROAROMATIC CONTAMINATED SOIL
- Ⓔ — STRUCTURAL
- Ⓕ — DRUMS
- Ⓖ — EQUIPMENT
- Ⓗ — CLEARING & GRUBBING
- ⊐⊏⊐ EXCAVATION
- ⊐⊏⊐ EMBANKMENT
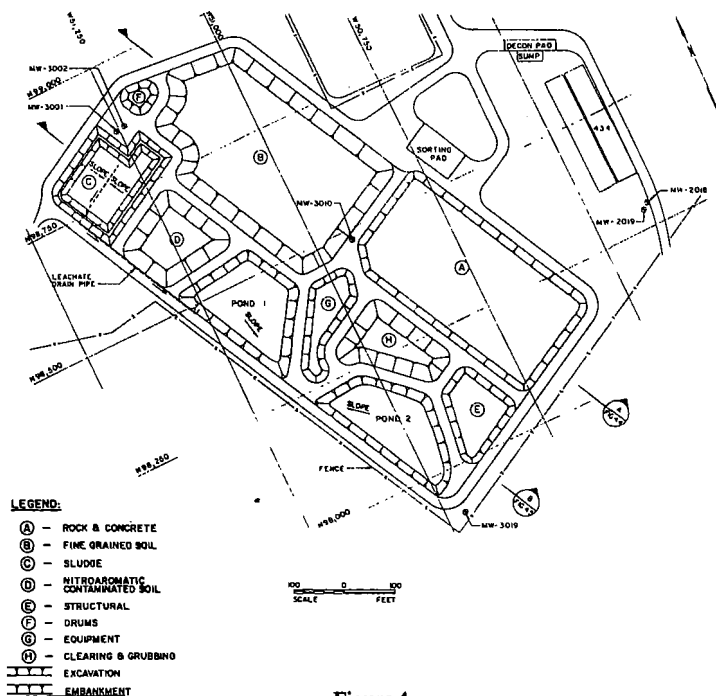
Figure 4
Temporary Storage Area Layout

facilities will be maintained in order to protect the environment.

All stormwater run-off and leachate from the TSA will drain by ditches and swales to collection ponds within the TSA. The storm water run-off and drainage system will be designed for a 25-yr, 24-hr storm (approximately 5.67 in. of precipitation). The design will also include a double liner and a leachate collection system. The retention basins will be lined with compacted clay and flexible membrane. Surface water run-on will be controlled by the use of diversion ditches to prevent contamination of clean surface water.

Bulk waste piles will be constructed with stable sideslopes. The top of fine-grained soil waste piles will be sloped to facilitate drainage. Dust suppression measures will be administered to control wind erosion in the nitroaromatically contaminated soil and fine-grained soil storage areas. Periodic spraying with water and binder agents will be used to control dust while the waste pile is being constructed. When a section of pile is completed, more permanent dust and radon control measures such as a flexible membrane liner, crusting agents, geotextile membrane and/or soil cover will be used.

Management of the TSA will include regular inspection of facilities, repair or reinforcement of engineering controls where required, monitoring for radon gas and removal of contaminated water from retention basins to the wastewater treatment facility. All storm water run-off and leachate collected from the TSA in the retention basins will be pumped to a newly-constructed wastewater treatment facility at the chemical plant site.

CONCLUSION

Environmental monitoring in the vicinity of the Weldon Spring Quarry indicates the quarry is leaking and that contaminants are migrating toward a county well field which provides potable water for over 60,000 people. In response to this potential health threat, the U.S. Department of Energy has determined that expedited response is necessary to remove the bulk waste from the quarry, which is the source of chemical and radiological contamination. This action is being carried out as a separate operable unit under CERCLA. The RI/FS process for this action has been completed and the Record of Decision is being negotiated with U.S. EPA Region VII. The proposed action involves:

- Treating contaminated surface and groundwater within the quarry
- Removing the bulk waste
- Transporting the bulk waste to the chemical plant site
- Segregating the waste by physical and contaminant characteristics
- Characterizing the waste to meet the requirements of CERCLA and associated ARARs
- Storing the waste in a secure and stable manner until the final remedial action is accomplished

ACKNOWLEDGEMENT

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A Remediation Program That Is Working

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ABSTRACT

A remediation program has been operating for approximately 20 months at an east-central Florida site contaminated with VOCs. The program consists of a groundwater recovery air strip-recharge system treating between 180 and 256 gpm. A two-dimensional groundwater flow and solute transport model was developed to project drawdowns and the movement of major contaminants. The placement of recovery wells and recharge trenches were subsequently based on the modeling effort. Ten recovery wells were installed to various depths in and around the contaminant plume for the purpose of capturing and retarding the off-site migration of 1,1-dichloroethene (DCE) and other VOCs. The recharge trenches were placed in the most heavily contaminated portion of the plume and along the north, east and southern sides of the plume, effectively recharging the aquifer on the lateral edges of the plume and blocking its downgradient movement.

Three types of data collected verify the effectiveness of the remediation program: (1) significant declines in concentration of various contaminants in monitoring wells placed at four depths throughout the plume; (2) declines in air-stripper influent concentration of DCE, 1,1-dichloroethane (DCA) and 1,1,1-trichloroethane (TCA); and (3) potentiometric surface data showing the drawdown of the water table at or near steady-state operation of the remediation system, indicates capture of the plume. The simulations largely agree with field data but differ because of the two-dimensional nature of the model.

Success of the program is attributed to the ability of transport modeling to optimize the recovery system, an extremely efficient air stripper (CarbonAir Services, Inc.), fully-screened recovery wells and an efficient and continuous maintenance effort.

INTRODUCTION

The purpose of this paper is to present evidence that an operating recovery program for a VOC-contamination problem is effectively removing contaminants and remediating the surficial aquifer. The site is located in east-central Florida near Melbourne adjacent to the Indian River (Intracoastal Waterway) and is the site of an electronics manufacturing firm specializing in high speed printers. The site is located within an industrial park and is largely covered by buildings, asphalt parking lots and concrete surfaces. Groundwater contamination is believed to have occurred as a consequence of discharge of waste VOC into a former holding tank. The site is underlain by coastal deposits of the Anastasia Formation consisting of sands, silts and clays.

Contamination assessment at the site began in 1986. After approval of a Remedial Action Program by the Florida Department of Environmental Regulation (FDER), startup of the air stripper began in October 1988. The contamination assessment revealed that contamination consisted primarily of six VOCs in the surficial aquifer which exceeded the FDER's Maximum Contaminant Levels (MCL) for drinking water. These contaminants included 1,1,1-trichloroethane (TCA), 1,2-dichloroethane (DCA), trichloroethene (TCE), 1,1-dichloroethene (DCE), tetrachloro-ethene (PCE) and vinyl chloride (VC). Two of these, DCE and TCA, have been found at high concentrations within the aquifer.

Seven other VOCs were found in the surficial aquifer but were not in concentrations above any standard or proposed standard. One of these, 1,1-dichloroethane (DCA), was found in significant concentrations within the aquifer.

Of all the contaminants, DCE has the most widespread distribution, and the remediation program was designed to recover contaminated groundwater underlying the maximum areal extent of the DCE plume (Fig. 1). The recovery effort was based on the conservative assumption that if all the DCE was captured, then all other contaminants would be captured as well.
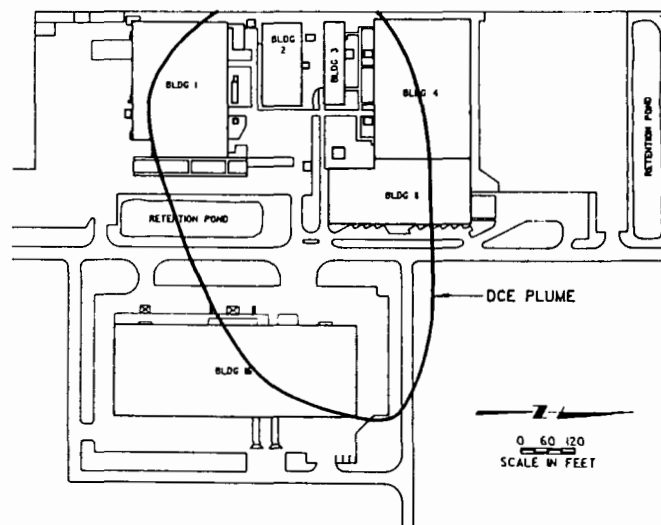
Figure 1
Location of DCE Plume at the Site Based on the Contaminant Assessment

The remediation program was designed as a pump-and-treat system followed by recharge of the treated water back into the groundwater system through a series of trenches. Four trenches were originally constructed. Three supplemental recharge trenches were added in 1989

and early 1990 (Fig. 2). The trench locations were designed with a two-fold purpose: (1) to add water back into the cone of depression generated by the recovery system in order to flush out contaminants and (2) limit the lateral and downgradient migration of the plume.

GROUNDWATER FLOW MODEL

The U.S. Geological Survey Computer Model of "Two-Dimensional Solute Transport and Dispersion in Groundwater" was used to simulate groundwater flow, DCE movement and the action of both the recovery wells and the trenches. The original model was modified to simulate equilibrium controlled sorption-desorption for a linear isotherm. Adsorption of contaminants onto organic carbon in aquifer materials has a profound influence on contaminants as they flow through the aquifer. The rate at which contaminants migrate is heavily influenced by partitioning onto the organic matter which, in turn, is also dependent on both soil and contaminant properties. Modeling of DCE transport assumed retardation by organic material and a DCE velocity of less than that of groundwater.

GROUNDWATER RECOVERY WELLS

Based on the modeling, ten recovery wells were sited in the DCE plume. The recovery wells are 4 inches in diameter. The construction details of the wells are given in Table 1. The wells are screened from five feet below land surface to the bottom of the well. The depths of the recovery wells were adjusted based on the depth of the contamination determined from the monitoring well program. The wells were all equipped cost-effectively with 0.02-inch slotted polyvinyl chloride (PVC) screens. Each well was equipped with a stainless steel Grundfos 1.5 hp submersible well pump (Model SPO4-14).

The pumps were set within the screens at depths at which the maximum contamination occurred within the aquifer, again, based on the monitoring program. The pumps have an operating flow range of 11 to 28 gpm which can be adjusted by a valve on the discharge side of the well. Three of the wells are pumped at 20 gpm and 7 are pumped at a rate of 28 gpm for a total capacity of 256 gpm. Each well is equipped with a paddle wheel flow meter with a totalizer. All of the wells are manifolded together and pumped to the air stripper. Each recovery well is equipped with a water level control probe which will shut down an individual pump should the drawdown in the well fall below the operating level for the pump.

groundwater. JMM's computer modeling indicates that 95% of the originally dissolved DCE will be removed from groundwater during the 4-year remediation period dictated by the FDER.

RECHARGE TRENCHES

The water discharged from the air stripper flows into a distribution box and then flows by gravity to seven trenches located in and around the plume. The total length of the trenches for recharging the treated water to the ground is 2,300 feet. Four of the trenches were constructed to a depth of 5 feet, then lined with filter fabric. Slotted PVC (.040 inch) screen 4-inches in diameter was laid horizontally the length of the trench and the trench was backfilled with 30 inches of limestone gravel (0.75-inch). Two layers of 30 pound roof felt were placed over the filter fabric. The trenches were then backfilled to grade with fill and covered with either concrete or asphalt.

Three of the trenches were constructed to a depth of 16 feet and a width of 13.5 inches using a new technology which will be the subject of a separate paper. The trenches were constructed using a specialized leaky pipe and pipe-laying equipment. Using this equipment, 500 feet of trench could be excavated and the recharge pipe laid in just one hour. These trenches were cut deeper than the previous trenches to penetrate low permeability hardpan layers. The recharge pipe, which is five inches in diameter is installed at the bottom of the trench. The pipe is perforated with up to 32 openings per linear foot and is covered with a geotextile sock to keep sand from infiltrating into the pipe (Fig. 3). A vertical riser pipe connects the perforated pipe to the gravity distribution system.

GROUNDWATER MONITORING PROGRAM

Over the course of the project, 23 monitoring wells have been constructed. Their locations are shown in Figure 2 with respect to the DCE plume. These wells are 2-inch diameter PVC wells and are constructed to various depths into the aquifer (Table 2). The wells range in depth from 15 feet to 140 feet below land surface (bls) and have slotted PVC screens 5 to 10 feet in length.

Groundwater samples have been collected from these wells from two to five times depending on the well since July 1986. Groundwater samples were collected and analyzed before and after startup of the recovery well system and air stripper in order to determine the efficiency of the clean-up operation (Table 3).

Table 1
Recovery Well Design/Pumping Rate

Well Number	Total Well Depth (feet)	Screen Length (feet)	Pump Setting Below Ground Surface (feet)	Pump Flow Rate (gpm)
1	60	55	25	28
2	60	55	25	20
3	140	135	60	28
4	140	135	60	28
5	140	135	40	28
6	94	89	40	28
7	140	135	40	20
8	145	140	40	20
9	60	55	25	28
10	100	95	40	28

AIR STRIPPER

The design capacity of the air stripper is 270 gpm. The air stripper has a total packed column height of 17 feet with a total column height of 40 feet. The stripper column diameter is 4 feet. The design loading rate is 21.5 gpm/ft^2. The column is packed with 3.5 inch Tripac balls of polypropylene. The tower has a demister section located in the narrow column at the top of the tower.

The stripper blower is all aluminum construction with a 15 hp spark-proof Class B motor and will deliver 7,200 cfm air. The air blower is sized to provide an air:water ratio up to 200:1. The air stripper is designed to be 99.9% efficient in removing VOCs from the influent

Figure 2
Location of Recharge Trenches, Recovery Wells,
Air Stripper and Monitoring Wells Across the Site
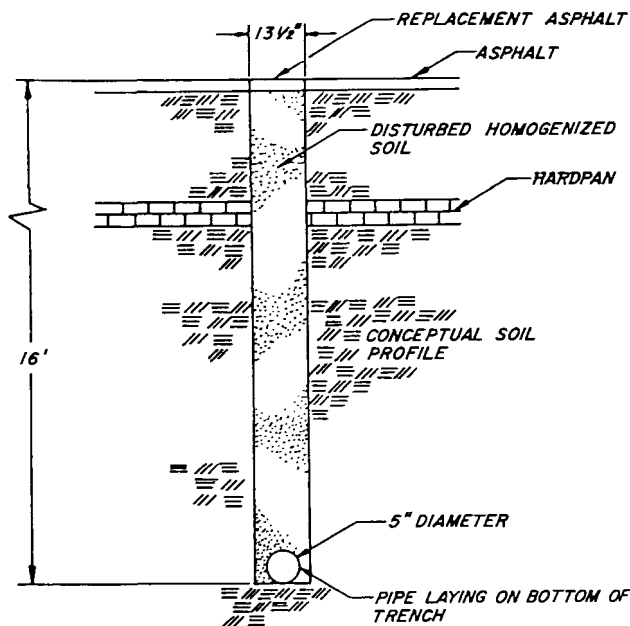
Figure 3
Cross Section of Supplemental Recharge Trench

Table 2
Monitor Well Construction Details [a]

Well Number	Depth of Well (feet)	Cased Depth (feet)
SL-1	40	35
SL-2	40	35
SL-3	40	35
SL-4	40	35
SL-5	40	35
SL-6	40	35
SL-7	40	35
SL-8	40	35
SL-9	40	35
ML-1-15	15	10
ML-1-40	40	35
ML-1-60	60	55
ML-2-15	15	10
ML-2-40	40	35
ML-2-60	60	55
ML-3-15	15	10
ML-3-40	40	35
ML-3-60	60	55
M-1	140	130
M-2	60	50
M-3	40	30
M-4	100	90
M-5	40	30

[a] All wells are 2 inches in diameter and have screen with 0.020 inch slots.

Table 3
Summary of Volatile Organic Compound Analyses for Monitoring Wells
(All results in μg/L)

[a] ND: Not Detected
[b] ( ) Tentative Value

Well	1,1-Dichloroethene	1,1-Dichloroethane	1,1,1-Trichloroethane
SL-1			
July 1986	5.30	480	ND[a]
May 1988	410	880	ND
June 1990	120	170	3 0
SL-2			
July 1986	270	150	11
June 1990	5 0	4 0	ND

SL-3:			
July 1986	510	350	57
May 1988	250	130	ND
November 1989	100	55	ND
June 1990	51	26	ND
SL-4:			
July 1986	1100	670	15
June 1990	51	26	ND
SL-5:			
July 1986	190	150	10
May 1988	130	89	ND
November 1989	75	100	ND
June 1990	15	17	ND
SL-6:			
July 1986	0.1	0.2	0.1
July 1986 (dup.)	0.2	0.1	ND
June 1990	ND	ND	ND
June 1990 (dup.)	ND	ND	ND
SL-7:			
July 1986	300	150	2.6
May 1988	7800	ND	ND
November 1989	90	36	ND
June 1990	37	12	ND
SL-8:			
July 1986	8	23	ND
January 1989	11	18	ND
November 1989	3.5	4.9	ND
June 1990	5.0	9.0	ND
SL-9:			
July 1986	0.1	0.1	ND
June 1990	2.0	8.0	ND
MW-1:			
September 1987	2800	1100	380
May 1988	11000	1800	350
January 1989	1800	510	ND
November 1989	820	300	(0.7)[b]
June 1990	71	33	ND
MW-2:			
September 1987	13	ND	0.1
June 1990	9.0	33	ND
MW-3:			
September 1987	170	300	0.8
May 1988	340	450	ND
November 1989	65	190	ND
June 1990	16	64	ND
MW-4			
September 1987	ND	ND	ND
January 1989	ND	ND	ND
November 1989	ND	ND	ND
June 1990	ND	ND	ND
MW-5:			
September 1987	21	52	0.4
June 1990	120	45	ND
ML1-15:			
July 1986	12000	30000	14000
May 1988	360	23000	39000
November 1989	41	1400	1500
June 1990	19000	ND	32000
ML1-40:			
July 1986	6000	1500	17000
May 1988	32000	270	47000
May 1988	25000	310	52000
November 1989	1400	(39)	8020
June 1990	140	10	830
ML1-60:			
July 1986	240	1200	1800
May 1988	340	300	1600
November 1989	1.9	9.2	2.4
June 1990	ND	ND	ND
ML2-15:			
July 1986	2.6	9.4	2.0
June 1990	6.0	9.0	ND
ML2-40			
July 1986	26000	2300	9000
June 1990	18	12	ND
ML2-60			
July 1986	460	1100	37
June 1990	71	16	6.0
ML3-15:			
July 1986 (dup.)	11	96	4.0
July 1986	4 6	23	ND
May 1988	2.1	6.1	ND
June 1990	ND	ND	ND
ML3-40			
July 1986	12000	6300	2700
May 1988	43000	6900	1800
November 1989	170	78	ND
June 1990	130	42	2 0
ML3-60			
July 1986	1900	2200	ND
May 1988	13000	4400	ND
November 1969	950	230	ND
June 1990	500	80	ND

A total of 41 different VOCs have been monitored during the last four years. VOCs have been detected 198 times in the 23 monitoring wells during that period. Of these, 188 of the detections are associated with primarily decreasing trends. Nineteen of the 23 wells showed decreasing trends for DCE and 21 of 23 wells showed decreasing trends for both DCA and TCA. All wells with VOC concentrations greater than 1,000 μg/L have shown declines except for ML1-15.

A number of wells showed increases in VOC contamination during the May 1988 sampling which was conducted prior to startup of the remediation program. This increased contamination level is believed to be due to expansion of the plume as a consequence of both continuing advection and easy vertical movement due to the fully-screened nature of the recovery wells which were penetrating a significant thickness of the aquifer. The original contamination assessment showed that contaminants are stratified in the aquifer with a tongue of contaminants moving down into the aquifer as they move downgradient (Fig. 4). Prior to startup of the recovery wells, contaminants were free to continue to move both laterally downgradient and, also, to move down into the aquifer through the screens of the recovery wells which in several cases penetrated almost the entire thickness of the aquifer. Because the contamination site is in a recharge area, the vertical gradient is downward in the aquifer.

During the course of monitoring, one well, ML1-15, has shown a significant increase in VOC concentration. This last increase occurred during the last sampling in June 1990. Significant increases occurred in ML-1-15 when compared with previous sampling results for DCE and TCA. This well has been sampled again to confirm the analyses but at this time the analyses have not been completed. An adjacent recovery well was off during the period of time immediately preceding sampling and this may have allowed high contaminant concentrations to flow toward this well.

AIR STRIPPER INFLUENT TRENDS

Influent concentrations, while fluctuating, have shown an overall decline through the nearly 2 years the system has been operating. Figure 5 is a plot of concentration plotted versus time for DCE. Plots for DCA and TCA show similar trends. The fluctuations most likely reflect the influence of recovery pumps which were operating the day sampling was performed. Pump plugging and routine maintenance requires pumps to be taken out-of-service on a routine basis.

Air stripper samples are grab samples and naturally will be affected by which pumps are operating on the day sampling is performed. The overall decline in influent concentrations is a reflection of the declining VOC concentrations in the groundwater at the site. Oddly, the influent has yielded DCE, DCA and TCA concentrations which are higher than would be expected from the monitoring well data. This result may be due to the location of the recovery wells in the most heavily contaminated portion of the plume and because the recovery wells have long screens and may be receiving water from zones of the aquifer which are more heavily contaminated than the monitored zones.
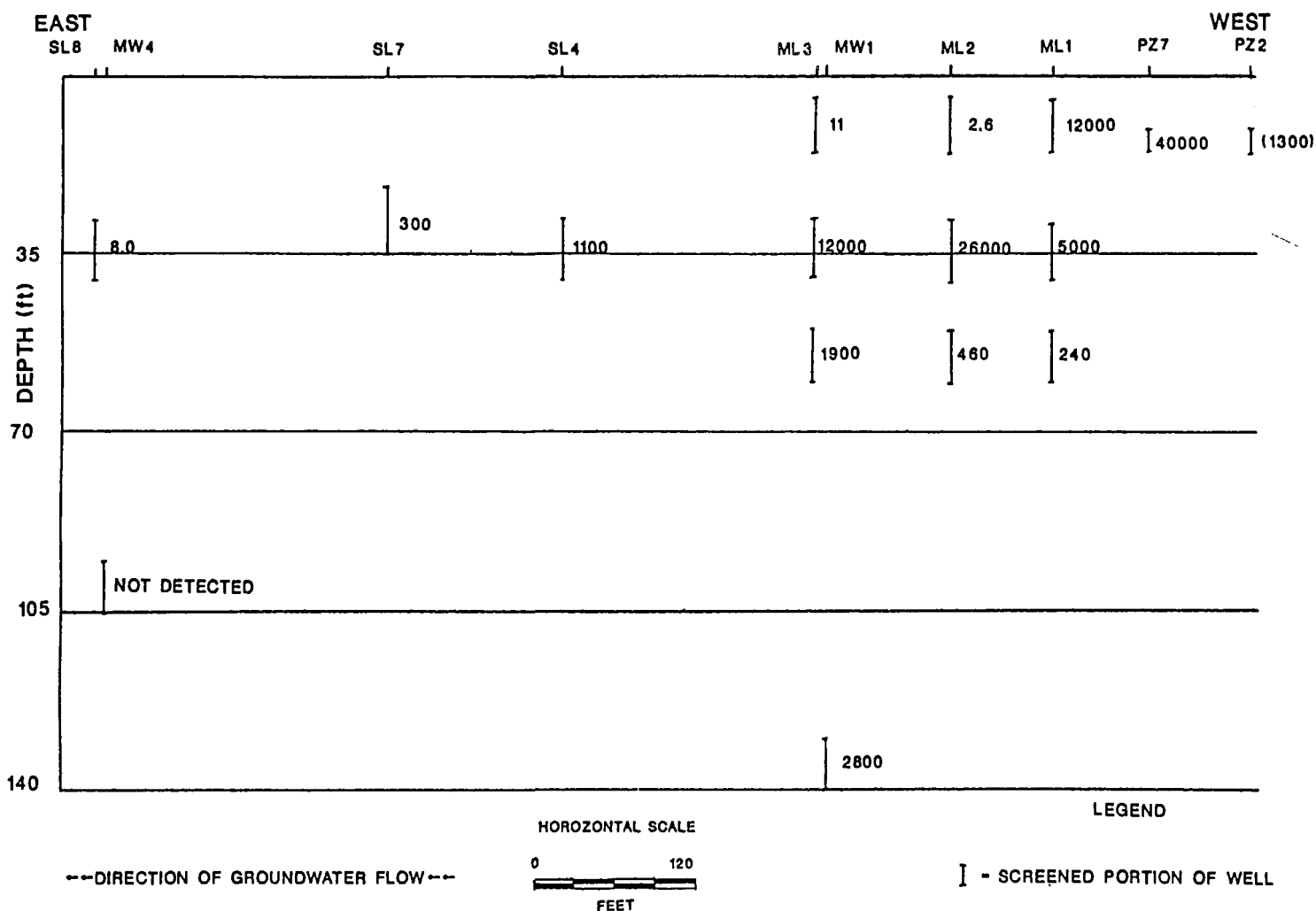
Figure 4
Cross Section of DCE Plume Showing Vertical Stratification
Concentration in mg/L
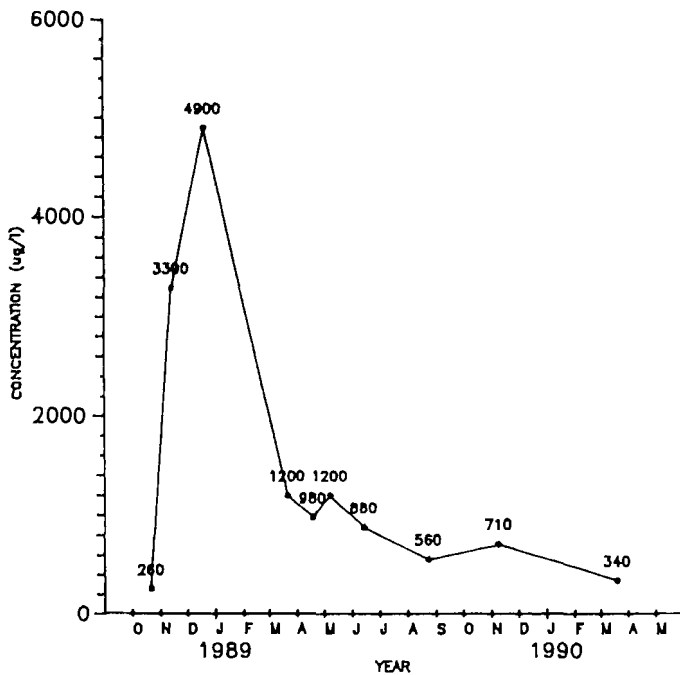
Figure 5
Decline with Time of DCE Concentration
in Air Stripper Influent

using the model and that the contamination is within a cone of depression generated by the recovery well system.

NOTE: CONTOURS IN FEET ABOVE NGVD.

Figure 6
Model Predicted Groundwater Levels Under
Steady State Conditions with Pumpage at 270 gpm

POTENTIOMETRIC SURFACE DEPRESSION

Examination of the potentiometric head surface in the 40 foot deep wells indicates that a cone of depression has been generated by the operation of the recovery well system. Potentiometric surface maps for the wells were constructed to show prepumping potentiometric surface levels (October 10, 1988) and potentiometric surface levels at three different times during pumping (November 15, 1988, January 13, 1989 and April 19, 1989). These data indicate that within one month after starting up the system in October 1988, a significant cone of depression was generated. For all sampling dates, the cone of depression captures the plume which extends eastward and downgradient to monitor well SL-8. The cone of depression is from 2 to 3 feet deep at its center and parallels the northeastern axis of the recovery well system. The cone of depression appears to expand and contract depending on rainfall and the number of recovery wells in operation. Figure 6 shows the model predicted groundwater levels simulating recovery well operation at 270 gpm. Figures 7 and 8 show potentiometric head contours generated for two different times, November 15, 1988 and April 19, 1989, respectively, when actual operation of the recovery system was at a pumping rate of 180 to 200 gpm.

The comparison shows general agreement, but with some differences as would be expected. For the most part, the field data show greater drawdowns than predicted, even though the recovery wells are pumping less than the model simulates. The water levels portrayed in the model results are higher than the water levels found in the 40 foot deep wells. The 11 and 12 foot contours on the field data maps are much broader than on the computer simulated maps. In addition, the model shows greater expression of the recharge occurring from the recharge trenches than is expressed in the 40 foot deep monitoring wells. The limitations of a two-dimensional model in simulating a three-dimensional problem are apparent.

The correspondence between the modeling and the field data show that the model was an extremely effective way of siting the most effective locations for the recovery wells and predicting drawdowns in order to limit the expansion of the plume. Because of the layering and vertical heterogeneity in the aquifer system, the monitoring well network will not agree perfectly with the computer modeling simulations. The field data, however, indicate that the remediation system is working as planned
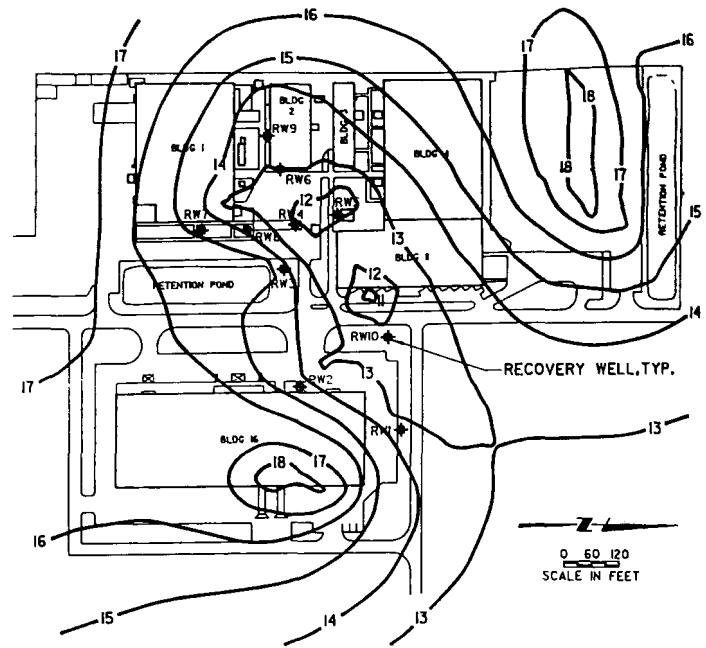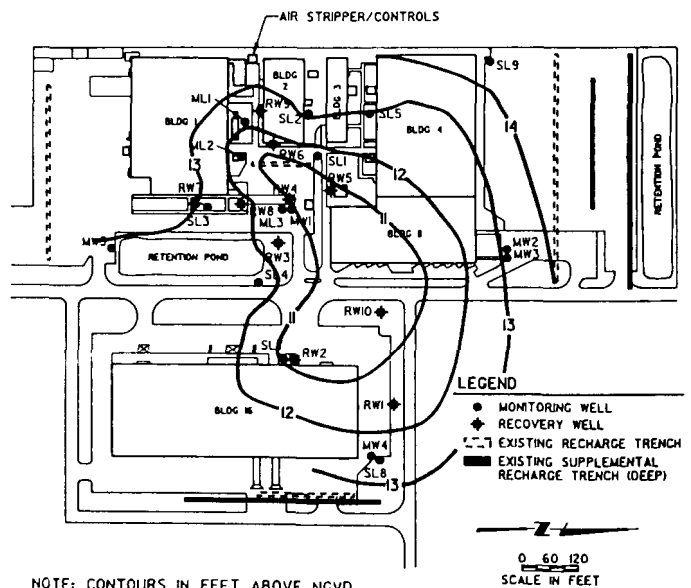
NOTE: CONTOURS IN FEET ABOVE NGVD.

Figure 7
Field Data Based Potentiometric Head Contours
for November 15, 1988

ELEMENTS OF SUCCESS

The success of the pump-and-treat program is attributed to four different elements. First, use of a groundwater flow and contaminant transport flow model to optimize the location of the recovery wells, predict plume capture and predict long-term recovery of the contaminants was an essential part of the design process for the remediation program.
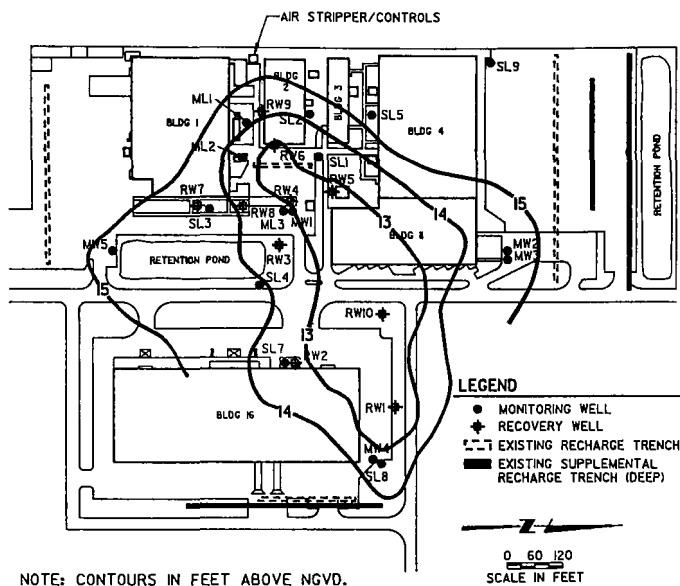
Figure 8
Field Data Based Potentiometric Head Contours
for April 19, 1988

Second, the highly efficient (99.9%) air stripper has been flawless in operation requiring only periodic cleaning. The effluent from the air stripper has always shown removal of all VOCs to below MCLs even though influent concentrations were higher than anticipated when the stripper was designed.

Third, the fully screened recovery wells are removing contaminants from the entire thickness of the contaminated aquifer rather than discrete intervals. The influent to the air stripper is showing that some horizons in the aquifer are more contaminated than the monitored horizons. These data suggest that flow of the contaminants towards the recovery wells is being controlled to some extent by vertical heterogeneities.

Fourth, operation of the system has shown a continuing need for maintenance. This task has been carried out effectively and responsibly by the owner of the property. The operation of the system requires daily monitoring to ensure that the system is running properly. Pumping rates on all wells and flowrates into metered trenches are recorded daily. A decrease in pumping rate for any of the ten recovery wells indicates a need for maintenance of the pump. Pumps are maintained both in situ and periodically by removal and replacement of the pump. The packing in the air stripper is cleaned frequently to maximize VOC degassing. Trench operation is observed periodically particularly during rainfall events which raise water levels around the trenches. Flow of recharge water into trenches must be monitored to prevent overflow.

How Clean is Clean? The Importance of Using Site-Specific Factors in Developing Cleanup Levels At Hazardous Waste Sites

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ABSTRACT

One of the principal objectives of remedial actions at hazardous waste sites is to ensure that residual concentrations of constituents present at the sites following such actions will not pose a threat to human health and the environment. The purpose of this work is to develop target chemical concentrations in soils and groundwater at several hazardous waste sites in the United States to guide the source control remedial design to be undertaken at these sites. Establishing the basis for determining cleanup standards, or "how clean is clean," prior to the commencement of the remedial design activities is necessary because waste and contaminated soil volumes dictate the remedial design and drive the costs of the remedy.

Resolution of the "how clean is clean" question is achieved by designating a threshold level of contamination such that environmental media (soil, river sediments, etc.) containing hazardous residuals at that level or greater would be subjected to excavation, while media containing lower levels would be left undisturbed. A method has been developed for the derivation of cleanup criteria using quantitative risk assessment techniques.

This paper emphasizes the estimation of target release rates by means of environmental fate and transport modeling and the importance of using site-specific factors in developing cleanup levels at hazardous waste sites. The study shows that generic standards need to be modified prior to their application to specific sites because of the conservative assumptions that are incorporated into generic standards. The cleanup levels selected were the most stringent ones produced by the different exposure scenarios. The controlling exposure scenario for a particular compound depended on the physico-chemical and toxicological properties of the compound.

INTRODUCTION

Cleanup standards are developed on a site-specific basis to identify when removal of wastes and affected soils is complete. Establishing the basis for determining cleanup standards, or "how clean is clean," prior to commencement of the remedial design activities is necessary because waste and contaminated soil volumes dictate the remedial design and drive the costs of the remedy.

Cleanup standards are best derived by definition of the potential risks to human health and the environment posed by waste constituents remaining at the site after remediation is complete. Potential risks are defined following standard risk assessment protocols that focus on evaluation of the potential fate of residual waste constituents and their effect on potential receptors (i.e., humans, river organisms, etc.). The residual chemical concentrations at the site should assure protection of groundwater, surface water and air and pose no direct human contact hazard.

In many cases where risk-based cleanup levels are derived, it may be necessary to consider multiple potential exposure pathways and migration pathways for each medium. For instance, where on-site soils are contaminated, evaluation of the following scenarios may be required:

- Protection of the casual trespasser or on-site worker, considering dermal contact, incidental soil ingestion and inhalation of volatile compounds and fugitive dust from contaminated soil
- Protection of a shallow aquifer underlying a site, considering the migration of contaminants from the unsaturated zone to the saturated zone
- Protection of a deep aquifer, considering migration of contaminants from the shallow aquifer to the deeper unit
- Protection of a surface water body adjacent to a site, considering both contaminated surface run-off and contaminated groundwater discharges that may enter the water body

In such cases where multiple scenarios are evaluated, the most restrictive soil concentration for each chemical of concern is selected as the proposed alternate cleanup level.

For sites where the derivation of health-based cleanup levels is proposed, it is essential that comprehensive site data be collected. Rigorous definition of site characteristics is required, including the nature and extent of contamination, the estimation of key hydrologic parameters (i.e., hydraulic conductivity and aquifer thickness) and the determination of soil properties.

In general, conservative worst-case exposure scenarios are used to develop health-based standards or criteria. Unfortunately, real life exposures may differ from those used to develop the risk-based numbers. Thus, a risk-based number may "over protect" the individuals being exposed. This problem can be avoided by developing situation-specific risk-based cleanup criteria or by developing a range of exposure scenarios that can be selectively applied to specific situations. The most conservative approach is to use reasonable worst-case exposure scenarios to protect the most sensitive individual likely to be exposed. This is the approach used in this paper.

The soil cleanup guidelines derived represent contaminant levels that pose an acceptable human health risk and are protective of the environment for both present and future uses of the sites. The soil cleanup levels selected were the most stringent ones produced by the different exposure scenarios.

PURPOSE OF THE RISK ASSESSMENT

The primary purpose of this paper is to demonstrate the importance of assessing the effect various simplifying factors have on the development of cleanup levels. Examples of methods used to develop cleanup levels (in soil or water) at hazardous waste sites are presented.

Soil cleanup guidelines are derived by determining the amount of chemicals that can remain in the soil environment and result in accept-

able risks to human health and the environment. Since risk is a function of toxicity times exposure, an acceptable soil cleanup guideline may be determined by setting an acceptable risk level (e.g., 10^{-6}), determining the extent of human exposure to soil (in mg of soil per day per kilogram of body weight) and then solving for the concentration of chemical that can remain in site soils. In this risk analysis, U.S. EPA cancer potency factors were used to get the acceptable chronic intake values for chemical carcinogens. Reference doses (RfDs) were used to set the acceptable dose for non-carcinogenic chemicals.

The chemicals evaluated include all the compounds that were detected in the waste units; were found in high concentrations; or are toxic, mobile and persistent in the soil or groundwater environment.

The human and environmental exposure scenarios developed below are used as the basis for establishing soil and water cleanup guidelines. Soil and water cleanup guidelines are based upon human exposure to site surface soil, site groundwater, river water and fish ingestion, as well as protection of river aquatic life.

Figure 1 illustrates the general approach for determining when cleanup is complete at the site. The main steps used to determine the cleanup criteria using U.S. EPA-recommended procedures[1] are shown in Figure 2. These steps are briefly outlined below for an example assessment.
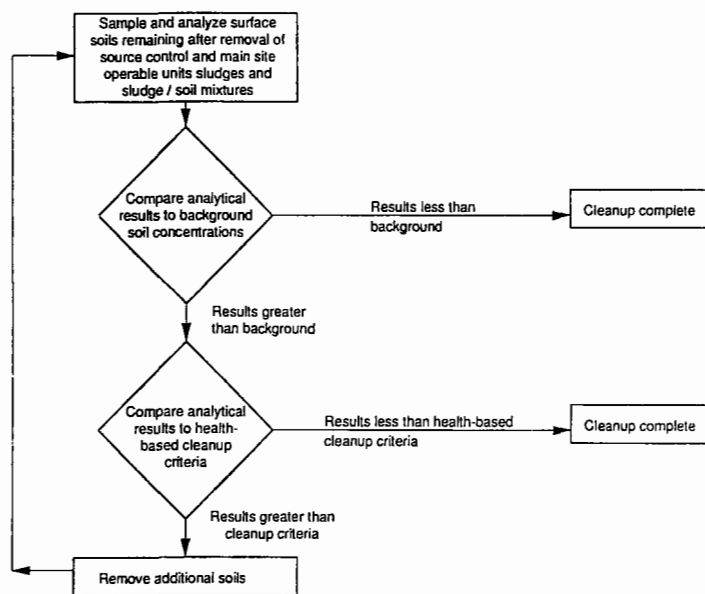
Figure 1
Cleanup Completion Decision Network

Step 1—Selection of Indicator Constituents

In accordance with U.S. EPA guidance[1], the indicator chemical list was developed on the basis of site concentration data, physical and chemical properties, fate and persistence information, toxicity and environmental mobility.

Generally, at sites where both carcinogens and non-carcinogens are involved, the carcinogens will drive the remedial design process because concentrations corresponding to the target risk range are usually lower than acceptable concentrations of non-carcinogens.

Step 2—Identification of Potential Exposure Pathways

The second step in determining target concentrations for management of the site remediation is identifying potential exposure pathways. A complete exposure pathway has four components: a source of chemical release, an environmental transport medium, a point where human receptors could be exposed and a likely exposure route. In this step, determination is made of the possible sources of chemical release, environmental transport media, human exposure points and exposure routes.
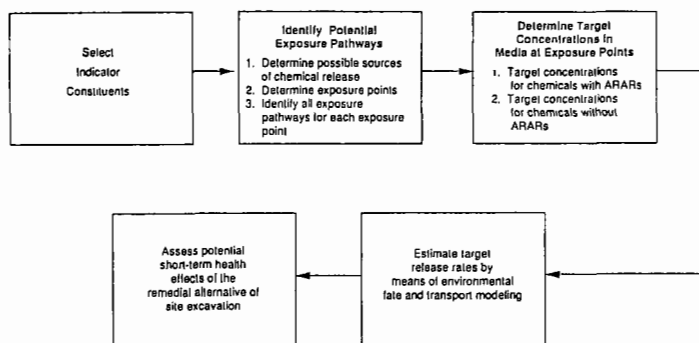
Figure 2
Development of Performance Goals and
Analysis of Risks for Site Excavation

Possibilities of chemical releases to air, surface water, groundwater and soil from the sources on the site after remediation is complete are considered for establishing cleanup levels. Potential exposure pathways and receptors for the site are illustrated in Figure 3. It is always necessary to simplify the total number of exposure pathways illustrated in Figure 3 to include only probable worst-case analyses.

The cleanup guidelines are based on acceptable human health and environmental risks. This risk assessment attempts to establish a soil cleanup level that, among others, protects:

- Human health from direct contact with site surface soil
- Human health from ingestion of affected groundwater
- Human health from ingestion of affected creek water and ingestion of affected fish tissue
- The aquatic life of the creek
- Workers on the site

Step 3—Determination of Target Concentrations in Media at Exposure Points

In this task, target concentrations for each indicator chemical at the points of human exposure are calculated on the basis of applicable or relevant and appropriate requirements (ARARs) or the target cancer risk range of 10^{-4} to 10^{-7}. For all the indicator chemicals that have applicable or relevant and appropriate ambient concentration requirements, those requirements are used as the basis for the target concentration range. Otherwise, target concentrations are based on the target carcinogenic risk range. Where more than one ARAR is available, the requirement most appropriate for site exposure conditions is used.

Step 4—Estimate Target Release Rates

In this step, target release rates at the identified sources of release, after remediation of the affected soils and groundwater, are calculated by means of environmental fate and transport models. The *Superfund Exposure Assessment Manual*[2] describes available models and their limitations that can be used to assess contaminant fate and transport in air, surface water and groundwater. The estimated target release rates will help determine the design criteria for the site remediation alternatives.

Step 5—Assess Potential Short-Term Health Effects

After the target release rates have been estimated, the potential short-term public health effects of the remediation processes are considered. For the remedial steps, fugitive dust generation by heavy equipment and other remedial activities, fume inhalation and other temporary sources of chemical release are assessed and the most appropriate management practices are determined during implementation of the remedial design.

Public health evaluation of short-term effects is similar to the evaluation for chronic health effects. Predicted short-term chemical concentrations are compared with the acceptable intake of chemicals for subchronic exposures (AIS) to assess health risk.

FATE AND TRANSPORT MODELING

This section defines the environmental and modeling parameters and methods used for modeling the potential exposure scenarios described earlier in Step 2. Conservative assumptions are used throughout the modeling process to represent the reasonable worst-case situations.

The modeling process used at ERM, Inc., is a step-wise, interactive process that proceeds below:

Define Objective Criteria

These criteria refer to the level of modeling detail required to meet the objectives of the study. This step is a very crucial part of the modeling and states the questions that modeling is to answer (i.e., "What is the allowable concentration of benzo(a)pyrene that can remain on the site soils such that the resulting concentrations at the exposure point will be less than the health standard?").

Develop Modeling Approach

In this step a model's ability to simulate site-specific transport and fate is evaluated. The evaluation is based on the site's and contaminant's physical, chemical and biological characteristics. Some of the important transformation/transport processes and key factors affecting them are shown in Table 1. The simplest mathematical model that can achieve the defined objectives is usually selected. To quantify the uncertainty associated with modeling, a sensitivity analysis is conducted. In some cases calibration and validation data are used to reduce the uncertainty inherent in the results.

Modeling Results Review

If the questions identified in the first modeling step are adequately answered by the modeling results, the modeling is complete. Otherwise, a model able to better simulate the complex environmental setting is selected and the modeling process returns to the second step. It should be noted that for one constituent, the use of a simple model may be adequate, while for a second constituent a more complex model may be required. The step-wise modeling process ends when the results are accurate and meaningful enough to permit further decision-making.

Selection of Cleanup Level

Once the calculations are done for each of the exposure scenario, the scenario producing the most stringent cleanup requirement is selected

Table 1
Transformation/Transport Processes and Key Factors Affecting Them

PROCESS	KEY FACTOR
Biodegradation	Waste degradability Waste toxicity Acclimation of microbial community Aerobic/anaerobic conditions pH Temperature Nutrient concentrations
Photodegradation	Solar irradiation Exposed surface area
Hydrolysis	Functional group of chemical Soil pH and buffering capacity Temperature
Oxidation/reduction	Chemical class of contaminant Presence of oxidizing agents
Volatilization	Partial pressure Henry's Law Constant Soil porosity Temperature
Adsorption	Effective surface area of soil Cation exchange capacity (CEC) Fraction of organic content (foc) of soil Octanol/water partition coefficient (Kow)
Dissolution	Solubility Soil pH and buffering capacity Complex formation

Source: U.S. EPA, 1989b (3)

as the cleanup level. It should be emphasized that the most stringent cleanup levels are not generated by the same exposure scenario for all chemicals. In general, the drinking water scenario is expected to be the controlling one for mobile chemicals, while the direct soil contact scenario is expected to be the controlling one for chemicals that bind strongly onto the soil.

METHODOLOGY FOR DETERMINING CLEANUP LEVELS

The generic equation for calculating cleanup levels (or acceptable chemical concentrations), based on acceptable chemical intakes, can
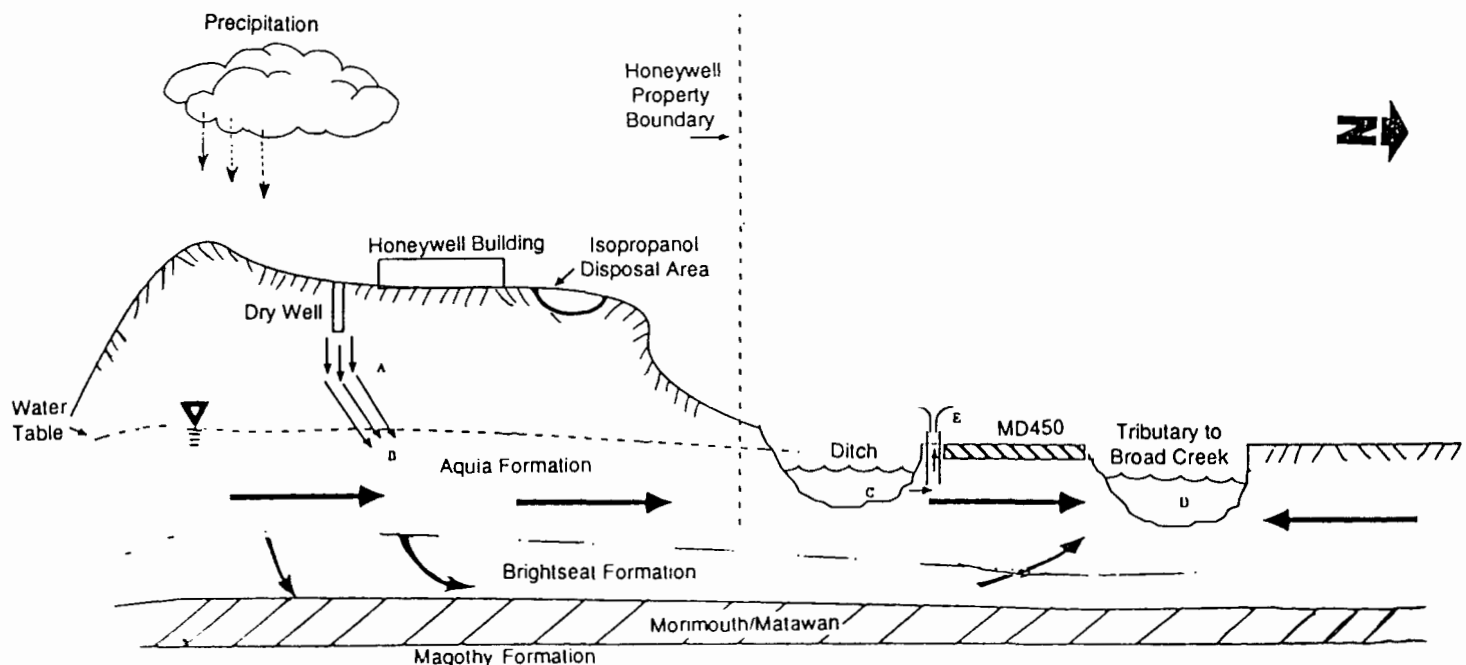
Figure 3
Schematic of Contaminant Transport Pathways

be written as (1):

$$\text{Intake} = \frac{Risk}{SF} \qquad (1)$$

where:

Intake = acceptable dose of chemical (mg/kg body weight-day)
Risk = acceptable carcinogenic risk (e.g., 1×10^{-6})
SF = carcinogenic Slope Factor (or CPF) (1/mg/kg-day)

The intake can be estimated from the following equation:

$$\text{Intake} = C \times CR \times EF \times ED/(BW \times AT) \qquad (2)$$

where:

C = the average chemical concentration contacted over the exposure period (mg/L or mg/kg)
CR = contact rate; the amount of contaminated medium contacted per unit time or event (L/day or mg/day)
EF = exposure frequency; describes how often exposure occurs (days/year)
ED = exposure duration; describes how long exposure occurs (years)
BW = body weight; the average body weight over the exposure period (kg)
AT = averaging time; period over which exposure is averaged (days)

Each intake variable in the above equation has a range of values. For Superfund exposure assessments, variable values for a given pathway are selected so that the combination of all intake variables results in an estimate of the reasonable maximum exposure for that pathway. Under this approach, some intake variables may not be at their individual maximum values but, when in combination with other variables, will result in estimates of the reasonable maximum exposure (RME). The *Exposure Factors Handbook*[5] provides the range of values for several common intake variables used in exposure assessments. For carcinogens, the acceptable chemical concentrations are determined by setting an acceptable risk level (e.g., 10^{-6}), making assumptions about the exposure factors in Equation 2 and solving Equations 1 and 2 for C.

CASE STUDY 1—SOIL CLEANUP LEVELS BASED ON FUGITIVE DUST EMISSIONS

At the King of Prussia Technical Corporation Site in New Jersey, one of the exposure scenarios involved the determination of soil cleanup levels for metals based on inhalation of fugitive dusts emitted from the site. A residual cancer risk of 10^{-6} under the inhalation pathway of exposure would provide a protective level to site contaminants. The most important parameter for this scenario was the particulate concentration in the air, which the U.S. EPA personnel set equal to 50 ug/m³ (the ambient air quality standard for particulates). However, this number represents the particulate air concentration caused by a number of sources, such as chemical plants, automobiles, etc.

The contribution to the particulate concentration by fugitive dust is very small. By performing site-specific air modeling, ERM personnel estimated this contribution to be 0.03 ug/m³, or more than three orders of magnitude less than the 50 ug/m³ concentration. This finding resulted in 1,667 times higher cleanup levels for the metals. Table 2 shows the cleanup levels obtained by use of the two different exposure levels to dust. This example (which is fairly common in soil cleanup level determinations) indicates the importance of using site-specific assumptions in the development of cleanup levels.

CASE STUDY 2—ESTIMATION OF BIOACCUMULATION OF PAHs IN FISH AT A SUPERFUND SITE IN PENNSYLVANIA

The objective of this work was to estimate the bioaccumulation of coal-tar related constituents by fish and sea lamprey tissue using actual field data and thus develop site-specific sediment cleanup levels. In the absence of actual fish-water concentration data, bioconcentration models have been used to provide estimates of potential bioaccumulation.

Table 2
Determination of Soil Cleanup Levels
Based on Fugitive Dust Emissions

Chemical	Soil Cleanup Level* (mg/kg)	Soil Cleanup Level** (mg/kg)
Beryllium	39	50,624
Cadmium	54	69,809
Chromium	8***	10,386
Nickel	129	25,490

* Assuming 50 mg/m3 as the inhalable fraction of particulates resulting from soil erosion.

** Assuming 0.03 mg/m3 as the inhalable fraction of particulates resulting from soil erosion.

*** Assuming all chromium is hexavalent chromium. That cleanup level becomes 152 mg/kg if assume that only 5 percent of the total chromium is Cr(VI).

It is generally accepted that the use of the available bioconcentration models significantly overestimates the PAH concentrations in the fish/shellfish tissue. To estimate a site-specific bioconcentration factor (BCF), measurements were taken of the subsurface soil, sediment, pore-water and biota tissue concentrations of PAHs. No PAHs were found in the fish tissue; however, the sea lamprey data indicated PAH bioaccumulation was a result of the coaltar discharges to surface water. Site-specific bioconcentration factors were calculated for each compound; these ranged between 1.0 L/kg and 378 L/kg.

Table 3 shows the calculated BCF factors along with some theoretical BCF values. It can be seen that the actual BCF values are several orders of magnitude less than the ones predicted by theoretical methods (such as using $K_o c$ or $K_o w$ values). The result of this work was to avoid cleaning up the sediments and subsurface soils due to the minimal risk posed to the aquatic life. If the theoretical BCF values were used in the sediment evaluation, then cleanup of a large portion of the site would be required.

METHODOLOGY FOR DETERMINING CLEANUP LEVELS BASED ON GROUNDWATER PROTECTION

The acceptable concentration in the leachate (C_L) emanating from contaminated soil for each chemical of concern is derived from the following relation[4]:

$$C_L = (S)(AF)(DF) \qquad (3)$$

where:

S = groundwater standard or guideline to be met at the exposure point (mg/L)
AF = attenuation or loss of contaminant during transport (dimensionless)
DF = aquifer dilution factor, defined as the ratio of the groundwater flow rate to the leachate rate (dimensionless)

Equation 3 will provide the acceptable chemical concentration in the soil water (unsaturated zone) above the groundwater table.

During soil sampling, the total (or bulk) soil concentration of a chemical is obtained. Therefore, the concentrations adsorbed onto the soil and in the vapor phase must also be taken into account. The bulk soil cleanup level is thus given by:

$$C_{bulk} = (n_w\, p_w\, C_L + p_b\, K_d\, C_L + n_a\, H\, C_L)/p_b \qquad (4)$$

where:

n_w = soil water content (cm³/cm³)
p_w = water density (kg/L)
p_b = soil bulk density (kg/L)
K_d = chemical adsorption coefficient (L/kg); for organic compounds, $K_d = (K_o c)\, (f_o c)$ where $K_o c$ is the organic car-

Table 3
Derivation of Sea Lamprey Bioconcentration
Factors at a Superfund Site
in Pennsylvania

(1) Compound	(2) Subsurface Soil Concentration (MW-11) (ug/kg)	(3) Pore Water Concentration (PS8 & PS4) (ug/L)	(4) Sea Lamprey Tissue Concentration (ug/kg)	(5) BCF* (Sea Lamprey/ Pore Water) (L/kg)	(6) Organic Carbon Partition Coefficient Koc (L/kg)	(7) Reported and Theoretical BCF (L/kg)
Naphthalene	27,000	280	1,500	5.4	1,070	96
1,3-Dimethylnaphthalene	27,000	240	2,200	11.0	1,070	96
1,5-Dimethylnaphthalene	27,000	240	3,100	11.0	1,070	96
Acenaphthylene	2,700	95	290	3.1	2,500	30
Acenaphthene	19,000	160	1,900	12.0	4,600	30
Dibenzofuran	2,700	22	160	7.3	11,000	1,350
Fluorene	15,000	79	630	8.0	7,300	1,300
Phenanthrene	34,000	240	630	2.6	14,000	30
Fluoranthene	6,400	80	56	0.7	38,000	1,150
Pyrene	15,000	120	150	1.3	38,000	12,000
1,5-Ethylindene	590	9	3,400	378.0	1,600,000	350,000

*BCF — Bioconcentration Factor
% Lipids — 4.8
Approximately 100 to 150 sea lamprey larvae were collected, weighing 100 grams; they were ground "whole body."

bon partition coefficient (L/kg) and f_oc is the fraction of organic carbon in the soil

n_a = soil air content (cm³/cm³); conservatively assumed to be zero (i.e., no volatilization is occurring)

H = Henry's Law Constant (dimensionless)

Therefore, Equation 4 becomes:

$$C_{bulk} = (n_w P_w C_L + P_b K_d C_L)/P_b \qquad (5)$$

Substitution of Equation 3 into Equation 4 results in the final equation for the estimation of the bulk soil cleanup levels:

$$C_{bulk} = (n_w P_w/P_b + K_o cf_o c)(S)(AF)(DF) \qquad (6)$$

In order to solve for C_bulk, each of variables in Equation 6 must be determined.

As a chemical travels from the source area to a potential point of exposure, it will undergo attenuation along the travel path. Attenuation results from: (1) partitioning of mass between water (soil moisture), porous media (solid matrix) and air (vapor phase); (2) dispersion; and (3) biodegradation of the chemical. The attenuation factor can be defined (if chemical losses due to biodegradation are ignored) as the ratio of the concentration at the source to the concentration at the point of compliance.

The dilution factor (DF) accounts for the mixing of the percolating leachate produced in the soils with clean groundwater originating up-gradient of the source area. The dilution factor can be calculated by means of the following equation:

$$DF = \frac{(Q_p + Q_a)}{Q_p} \qquad (7)$$

where.

DF = dilution factor

Q_p = volumetric flow rate of the leachate (ft³/sec)

Q_a = volumetric flow rate of groundwater beneath the site (ft³/sec)

The use of this equation assumes that the upgradient groundwater is uncontaminated and that complete mixing will occur.

In order to determine the volume of leachate produced, a mass balance must be performed to estimate the groundwater recharge rate beneath the affected soils. To determine the groundwater flow beneath the site, Darcy's Law is used. It should be noted that conservative estimates of several parameters are made to simulate worst-case conditions, providing minimum dilution factors.

The case study below illustrates the importance of the dilution and attenuation factors in determining site-specific cleanup levels.

CASE STUDY 3—REFUSE/SOIL CLEANUP LEVELS DEVELOPMENT BASED ON GROUNDWATER PROTECTION

At another site in Pennsylvania, the U.S. EPA determined "threshold limits" for several compounds found in leachate (not necessarily the more toxic compounds, more mobile and the ones found at the highest concentrations at the site) by use of statistical techniques. The results are shown in the second column of Table 4.

ERM determined conservative cleanup levels for soils/refuse using Equation 6, incorporating a site-specific dilution factor of 1,928 and a conservative attenuation factor of 10.0. ERM's calculations are shown in column 6 of Table 4. Also shown in that table are cleanup levels for the same compounds determined at several other Superfund sites. The importance of using site-specific dilution and attenuation factors for the development of cleanup levels is clearly demonstrated.

CONCLUSIONS AND RECOMMENDATIONS

This paper has demonstrated the importance of using site-specific factors in the development of cleanup levels at hazardous waste sites. In general, much uncertainty is associated with estimating the residual chemical concentrations that will pose no threat to human health and the environment. There are uncertainties associated with the indicator chemical selection and with the toxicity values for each substance, as well as uncertainties inherent in the exposure assessment and in the

Table 4
Comparison of Refuse/Soil Cleanup Goals with Cleanup Levels
From Other Superfund Sites and with ERM's Estimates

Key Indicator Compounds (Reference)	Lackawanna, PA USEPA Threshold Limit (mg/kg) ROD	Tysons's Lagoons, PA Cleanup Levels (mg/kg)(1) ROD	Sand Springs Tulsa, OK Cleanup Levels (mg/kg)(3) ROD	Delaware Sand and Gravel, DE Cleanup Levels (mg/kg)(4) ROD	Lackawanna, PA ERM's Estimate of Cleanup Level (mg/kg)(5)
Acetone	83.	---	---	77	1,467
2-Butanone (MEK)	125.	36.8	---	610	1,735
Ethylbenzene	16.	599	---	7,480	14,846
2-Hexanone	90.	262 (2)	---	6,300 (2)	1,215 (2)
4-Methyl-2-Pentanone (MIBK)	9.5	18.7	---	78.8	1,928
Tetrachloroethylene	2.6	5.	---	18.2	347
Toluene	59.	588	1,440	6,000	115,680
Xylene	76.	62.8	1,030	4,800	20,360
Chlorobenzene	5.	11.5	---	198	3,818

(1) Based on a dilution factor of 34.0 and an attenuation factor of at least 3.0
(2) Based on cleanup level for cyclohexanone
(3) Based on a dilution factor of 100.0 and an attenuation factor of at least 5.0
(4) Based on a dilution factor of 10.0 and zero attenuation factor
(5) Based on a dilution factor of 1,928 and an attenuation factor of 10.0
ROD = Record of Decision

site characterization process. Most of the uncertainties are associated with the exposure assessment and these need to be addressed in the development of cleanup levels: (1) characterization of the physical setting, (2) data analysis and simplifying assumptions made and (3) fate and transport of chemicals and exposure parameter values. Some of the sources of uncertainty can be quantified, while others are best addressed qualitatively.

If a site-specific cleanup level determination is made, a large amount of site- and chemical-specific data may be required. ERM recommends the collection of data in a phased approach that helps focus on the areas of a site that drive the remediation costs. The justification of collecting more data will depend on the benefit of achieving more realistic cleanup levels.

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Dynamic Compaction for Hazardous Waste Sites

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ABSTRACT

The objectives of a site closure scheme under both the Superfund and NRC guidelines are to address specific site concerns and to protect human health and environment. These objectives can be achieved by developing and combining the various available technologies which will fit the needs of the remedial action objectives of a site. Construction of an infiltration barrier or a cap over the waste material is most often considered as one alternative. The major performance requirement of a cap is its stability, which depends upon the compactness of the waste material and subsurface soils. To avoid the cracking or disintegration of the cap, it must be placed over materials which do not settle.

This paper will discuss innovative techniques to treat in situ waste materials and subsurface soils to reduce or eliminate as much as possible the risk of cap failure due to total or differential settlements. The use of the dynamic compaction method in order to reduce the permeability and increase the stability of the waste material and subsurface soils is presented.

Dynamic compaction is an innovative technique which involves repeated dropping of a heavy weight over the waste material in order to consolidate it and the underlying soils. This method has been used successfully in the past on some hazardous waste sites in the United States.

INTRODUCTION

The development of soil improvement methods started with the realization that it could be more cost-effective to increase the mechanical properties of waste materials and soils rather than ignore the problem and select other expensive options. There are various techniques available for the improvement of mechanical properties of waste fill and the soil below it using various types of energies, with and without adding new materials. This paper describes "dynamic consolidation," a method using mechanical energy to improve engineering properties of waste fill and soil at depth, both above and below the groundwater table. This method is ideally suited for loose waste fills and loose to very loose sands with some silt to a depth up to 25 feet within a minimum time frame.

The method basically consists of providing large energy impacts at the top of the waste fill which usually is covered with a few feet thick layer of granular soil. Weights ranging from 12 to 200 tons are dropped from a height varying from 15 to 120 feet. As the waste contents located on the surface or in a trench densify, backfill soil is added to the resulting depressions or craters. The backfill soil is compacted over the compacted materials. The mechanism of this process has been previously explained by many authors. In any type of unsaturated material, the shock wave generated by the impact causes compaction as in a common Proctor test. In waste or soils below the water table, P-wave first causes partial to full liquefaction and then S-wave and Raleigh waves rearrange the waste or soil grain structure into a dense state. The results of using this method are dramatic and immediate. Surface settlement achieved is typically 2 to 5 percent or more of the thickness of the loose layer treated by impacts. Porewater pressure builds up instantaneously with some boiling appearing at the surface which then dissipates rapidly. Strength, in terms of Bearing Capacity of subsurface soils, is typically improved by a factor of 2 to 4. Compressibility in terms of total and differential settlements is reduced by a factor of 3 to 10.

DESIGNING IMPROVEMENT

Designing improvement utilizing the dynamic consolidation process requires the following steps:

Pretesting

The first step, termed as pretesting, consists of determining the in situ condition of the waste material and soils below it. This condition typically can be measured in terms of standard penetration test (SPT) values (ASTM D-1586) or dutch cone test (DCT) resistance (ASTM D-3441). Based on the results of the above, test evaluations are made regarding the existing state of compactness of the waste and soils. A criterion is then established which describes to what maximum density the waste and soils below it can be effectively compacted. This criterion is in terms of higher SPT or DCT values. Sometimes a small test program of actual dynamic consolidation is performed to establish the compaction criterion for a specific site.

Equipment Selection

The next step is the selection of dynamic consolidation equipment and processes which lead to the established criterion. This phase of the program involves theoretical calculations to justify the parameters for the consolidation process. These parameters include the selection of weight and crane, height of drop, grid pattern for drops, number of blows at each drop location and number of passes required. Preliminary values of the above parameters can be established from the relationships previously established based on a large number of dynamic consolidation jobs completed in the past.

Based on 900 sites investigated, we have determined the following relationship can be used:

$$D = CS\ WH \tag{1}$$

where:

D = effective depth of waste/soil to be improved (Meters)
W = weight being dropped (Metric tones)
H = height of the drop (Meters)
C = speed factor (0.9 for cable drop and 1.2 for free fall)

S = Soil structure factor (0.7 for homogeneous fill and 0.3 for layered heterogeneous fill)

Grid pattern and number of phases are selected based on past experience on similar jobs.

Field Test

After establishing preliminary energy parameters, afield test on a small representative area generally is conducted prior to each phase to determine the optimum number of blows required for each phase. Penetration of weight into waste material in terms of depth of the crater formed is measured for each blow. After a certain number of blows, the depth of the crater formed does not increase. This result indicates that the maximum densification has been achieved. At this point, any additional application of energy will be unproductive. General practice is to obtain the number of blows at 80 percent of the cumulative weight penetration at which no significant penetration in the crater takes place. This number of blows is used as the production densification criterion for the rest of the job.

Production Densification

After selecting energy, grid and number of blows required for each phase, production densification is carried out. Instrumentation is provided to measure and control the generation of porewater pressures due to impact loadings. The time interval between two production phases is based on the time required for total dissipation of porewater pressure. If dynamic consolidation is performed in the close proximity of the existing structures, it is desirable to establish a minimum distance between the impact point and the structure based on the surface particle velocity generated by the impact. Generally, a limiting particle velocity of 25 mm per second for new structures and 8 mm per second for old, already cracked structures is used as a guideline.

Post Testing

After production densification, a post-testing program is conducted to verify the accomplished improvements. Usually the same tests are conducted which were used at the pretesting stage. Post-testing locations are selected close to the pre-test locations. Both test results are plotted together with depth to show the improvements.

EXPERIENCE ON HAZARDOUS WASTE SITES

The most recent applications of dynamic compaction on low-level radioactive waste sites are at the Oak Ridge National Laboratory and the Savannah River Project sites. Limited dynamic compaction also has been performed at the Hanford, Washington site with positive results.

Dynamic compaction for the above projects was performed on trenches containing wastes prior to installation of the cap. Penetration tests were used in order to verify that the compacted waste material and soils below it had been consolidated to the consistency similar to the adjacent in situ soils. A volume reduction ranging from 56 to 115 percent in the waste trenches was reported in one of the projects. No radiation exposures exceeding the background levels were reported on any of the above projects.

CONCERNS

There are some major concerns regarding the effects of dynamic consolidation over a hazardous waste site. One concern is that the impact

energy will cause additional leakage of the wastes due to the crushing of waste sealed in drums, fiberboard or cardboard boxes. However, experience shows that most of the sealed containers begin corroding and start progressively degrading with respect to time and are partially crushed due to the weight of overlying materials. All sealed containers must be assumed to fail at some point in the future. Therefore, it may be advantageous to accelerate this process of failure during the dynamic compaction process since any released liquids can be removed and treated more effectively prior to construction of the final closure cap. Based on the above, it is concluded that the benefits of treating wastes by dynamic consolidation process outweigh its risks.

The second concern about the dynamic consolidation process is that it may have an adverse effect on the geological and hydrologic conditions beneath the base of the waste containment. In evaluating this concern, both the vertical force and the generated seismic waves must be considered. Impact stress and its attenuation from an impact point has been researched and tested extensively by many authors.

Based on existing data, by monitoring and optimizating the stresses during the test program, an acceptable production energy level can be selected which will have no adverse effect on subsurface geologic and hydrologic conditions.

The next concern is the effect of dynamic consolidation on workers' safety. The work hazards of greatest concern are those associated with the operation of the heavy equipment such as cranes. Experience has shown that at many low-level radioactive waste sites, the radiation exposures resulting from dynamic consolidation did not exceed background levels. However, because the process has the potential risk of causing releases, the addition of a layer of clean granular material on top of waste material as suggested earlier is recommended. This step will reduce the risk of any potential releases to a minimum. This can be verified by health physics personnel during the test program as well as during the production densification.

CONCLUSION

Worldwide dynamic compaction experience and experience at some low-level radioactive waste sites provides a substantial basis to positively evaluate the possibility of dynamic consolidation on future hazardous waste sites.

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Analytical Methods For Petroleum Hydrocarbons

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ABSTRACT

There are currently a wide variety of methods available for the analysis of petroleum products in environmental samples. An indicator test like Total Petroleum Hydrocarbons by Infrared Spectroscopy (U.S. EPA Method 418.1) and analyte-specific tests like Methods 8020, 8240, 8100, or 8270 can only be indirectly related to petroleum products. The goal of our efforts has been to develop alternative techniques to provide reliable measurement of a full range of petroleum products at environmental levels at reasonable cost. These methods can be used at hazardous waste sites in addition to target parameter techniques to provide information on petroleum product contamination.

The suggested methods are all based on gas chromatography with flame ionization detection (GC/FID). This technique has been used extensively to characterize petroleum products and is the basis of many quality control procedures used in the petroleum industry. The methods are designed to provide a "Total Hydrocarbon" value based on the GC/FID area relative to a reference standard. Quantitation is reliable and consistent, and bias to specific projects can be measured. The boiling point or carbon range may be defined, and project identification also is possible.

The analytical methods include a purge-and-trap "Volatile" method termed "Gasoline Range Organics" which includes measurement of gasoline and BTEX. The "Semivolatile" method is termed "Total Chromatographable Organics" and is designed to measure other products (diesel, kerosene and motor oil) and provide carbon range information. An "Oil Spill" method is designed specifically for crude oil and is termed "Petroleum Hydrocarbons."

INTRODUCTION

At many hazardous waste sites, contamination of the environment by various petroleum products has resulted in a variety of laboratory techniques to determine the extent of contamination. An indicator test such as Total Petroleum Hydrocarbons by Infrared Spectroscopy (U.S. EPA Method 418.1) is known to have a low recovery for gasoline[1,2] and is susceptible to a significant positive bias when applied to some soil types.[3] Analyte specific tests (U.S. EPA Method 8020 and 8040) only measure selected components of gasoline (e.g., BTEX). The limitations of these tests have been well-documented.[1,2] A variety of Gas Chromatography/Flame Ionization Detection (GC/FID) methods have been developed including ASTM Method D3328-78[4] for "waterborne oil" and the California Department of Health Services "modified Method 8015."[5]

The wide array of methods available for petroleum hydrocarbon analysis provide data of varying and questionable quality. The approach used in our work was to evaluate the existing methods and establish improved methods based on GC/FID (including documented perfor-

mance). As discussed below, an analytical protocol which provides a reliable measurement of a full range of petroleum products at environmental levels at a reasonable cost was developed.

DESCRIPTION OF PETROLEUM PRODUCTS

Petroleum products are comprised of a range of individual hydrocarbons. Figure 1 condensed from the ASTM *Manual on Hydrocarbon Analysis*,[6] shows the number of carbon atoms and boiling point range of several common products.

No. of Carbon Atoms	C_2	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	$>C_{20}$
Boiling Pt., °C	-89	-0.5	69	126	174	216	253	287	316	343	

Butanes

Gasoline

Diesel

Fuel Oil

Wax

Figure 1
Description of Petroleum Products

Petroleum product specifications are based on criteria such as distillation start/end points, octane ratings for gasoline and cetane ratings for diesel fuel. Thus, the concentration of individual hydrocarbons (and groups like paraffins, olefins, napthenes and aromatics) may vary significantly from one vendor to the next for a given product. Various products may contain many of the same compounds in different relative amounts. To reliably measure petroleum products, methods must adjust for these variations.

EXISTING ANALYTICAL METHODS

Total Petroleum Hydrocarbons (TPH)

Several versions of the TPH or oil and grease methods are available. Standard Methods 5520A (formerly 503) includes three methods for liquids: the partition-gravimetric method (B), the partition-infrared method (C) and the filtration-soxhlet method (D), plus a soxhlet method for sludges (E).[7] Calibration of the infrared spectrophotometer (Method C) requires a reference oil (by volume—37.5% iso-octane, 37.5% hexadecane and 25% benzene). Method F is silica gel cleanup which removes polar fats from animal and vegetable sources and makes

the test more specific for nonpolar petroleum hydrocarbons.

Method 413.1 measures Total Recoverable Oil and Grease using a separatory funnel extraction and gravimetric determination.[8] Method 413.2 replaces the gravimetric determination with an infrared measurement. Calibration uses a reference oil (by volume 37.5% n-hexadecane, 37.5% iso-octane and 25% chlorobenzene). Method 418.1 (Total Recoverable Petroleum Hydrocarbons) is similar to 413.2 except 418.1 adds a silica gel cleanup. The foregoing are water methods, but 418.1 frequently is modified using a soxhlet or sonication extraction for the analysis of soils. The U.S. EPA has also published two methods, 9070 and 9071, in *SW 846*[9] for oil and grease with gravimetric determination in water and sludge, respectively.

A modification of the TPH method has been developed by the Chevron Research Company.[10] This Modified Oven Drying Technique (MODT) determines the oil, water and solids concentration of wastes and soils. The three phases are recovered separately, allowing for a weight closure check and further characterization of each phase if necessary.

Except for the MODT method, the TPH methods are U.S. EPA approved, well-established and most commercial laboratories are very familiar with the techniques. These methods are relatively quick and inexpensive. However, there are some definite disadvantages to the TPH tests. The extraction solvent used for these tests is Freon, which will become increasingly difficult to obtain. In addition, many heavy distillates are poorly soluble in Freon and are not effectively extracted.

TPH tests have low recovery for volatile hydrocarbons, like gasoline. Volatile components are lost during the concentration step of the gravimetric method. Infrared calibration with the required reference oil assumes the unknown sample is 25% aromatic. This assumption can lead to significant bias if a sample is 100% (or 0%) aromatic. One study[3] has indicated potential false positive TPH IR results when the test is performed on clay or limestone soils.

Without the silica gel cleanup, TPH tests will measure vegetable or animal hydrocarbons (organic acids and fats) which can bias results high. Use of the silica gel cleanup may remove complex aromatic compounds and other hydrocarbons which contain chlorine, sulfur and nitrogen which can bias results low.

Methods 8020/602

Similar to the TPH/oil and grease techniques, Method 8020 is U.S. EPA approved, well established and widely used. Method 8020 is a Gas Chromatography/Photoionization Detection (GC/PID) method which can measure the individual toxic components of gasoline directly (BTEX—benzene, toluene, ethyl benzene and xylenes). Method 602 is a similar technique designed for wastewater applications. The method has good sensitivity for these compounds; nominal reporting limits are 0.5 ug/L in water and 50 ug/kg in soil.

The primary disadvantage of Method 8020 is the difficulty in correlating BTEX values to gasoline. While BTEX is a good indicator for gasoline's presence, particularly in groundwater, the volatile aromatics can originate from sources other than gasoline. Moreover, Method 8020 does not address any of the heavier products like diesel or kerosene.

Method 8240/8270 and 624/625

Methods 8240 and 8270[9] are also target compound analytical methods but use Gas Chromatography/Mass Spectrometry (GC/MS). Methods 624 and 625 are used for wastewater analysis. These methods are U.S. EPA-approved with good sensitivity (5 to 10 ug/L in water and 5 to 330 ug/kg in soil). In addition, through the use of library searches, Tentatively Identified Compounds, and additional nontarget compounds can be measured.

The disadvantages of Methods 8240/8270 are similar to the disadvantages of Method 8020. It can be difficult to correlate individual compound data to particular products. In addition, the GC/MS methods are generally too expensive for routine screening applications.

California LUFT: DHS TPH—Gasoline and Diesel

The above methods are GC/FID techniques designed to measure gasoline and diesel fuel concentrations. Unlike the target compound methods, these techniques provide values for specific projects. The calibration process uses commercial gasoline or diesel fuel and samples are analyzed on a packed GC column. Standard laboratory quality practices including blanks, duplicates and spikes are required.

However, the California methods do have some limitations. The methods lack key method performance data such as recovery and minimal quality assurance criteria. Key details such as start/stop of integration, use of baseline projection and interpretation of weathered samples are not addressed. In addition, the analysis of gasoline is permitted by either Headspace or Purge and Trap (U.S. EPA 5030). Apparently, gasoline may be analyzed by the same extraction/concentration method used for diesel fuel. There is no indication of the equivalence or applicability of these method variations.

ASTM D3328-78

ASTM D3328-78[4] is a GC/FID method for the analysis of water-borne oils. It is designed for qualitative identification and the determination of product matches, primarily distillate fuel, lubricating oil and crude oil. Samples of known oils must be submitted with the unknown samples; there are no provisions for identification of the source of unknown oils. No quantification information is provided.

IMPROVED METHODS

The improved methods being used for oil analysis all have similar characteristics. They provide a "Total Hydrocarbon" value for a particular carbon range which is based on a GC/FID response relative to a synthetic standard. The use of a synthetic standard requires careful attention to the analytical details of the method, but provides a more universally consistent quantification the hydrocarbons present. Each method has the capability to fingerprint particular products. However, the primary goal of the method is to provide reliable, consistent quantification. The basic method can be enhanced for specific applications. The methods are listed below:

- "Volatile" Method—Gasoline Range Organics (GRO)—for the gasoline range, BTEX included
- "Semivolatile" Method—Extractable Petroleum Hydrocarbons reported as Total Chromatographable Organics (EPH—TCO)—for diesel, kerosene and other products
- "Oil Spill" Method—Petroleum Hydrocarbons (PHC)—for crude oil

Gasoline Range Organics

The Gasoline Range Organic (GRO) Method was developed through a laboratory study sponsored by the American Petroleum Institute. The project was designed to develop a reliable method for sampling and analyzing gasoline-range organics in soil. A number of professionals in the petroleum industry recognized that the current analyses for gasoline were inadequate due to the following concerns:

- Loss of volatile organics during sampling and sample handling leading to significant bias
- The wide variety of laboratory techniques for "gasoline" produced data of variable quality
- The generally poor documentation of the performance of "gasoline" methods

The results of this study have been previously described.[11]

The GRO method is a modified Method 8015 (Purge and Trap—GC/FID) for the measurement of gasoline which adds Method 8020 (Purge and Trap—GC/PID) for BTEX. (The BTEX values are based on a single column.) The method complies with the minimum criteria in the California LUFT purge and trap method for gasoline. Calibration uses a synthetic gasoline comprised of ten common components of gasoline. The synthetic gasoline eliminates potential problems from variable commercial gasoline. In addition, the first and last peaks define the gasoline "window" and correspond to the range of C_6 to C_{10}.

Various commercial gasolines had similar recoveries (53%, 58% and 62%) compared to API PS-6 reference gasoline (70%). Using PS-6 gasoline and the methanol extraction, (purge-and-trap GRO), recoveries were similar in Ottawa Sand (70%), Houston Black Clay (67%) and Norwood Loam (58%). Relative differences on the clay and loam were less than 5%.

The soil method used field preservation with methanol which stabilizes the organic components via solubilization and minimizes microbial degradation. This field sample control allows the sampler greater freedom in the actual selection of the sample. Reporting limits for gasoline are 2 to 5 mg/kg for soil and 50 to 100 ug/L for water. Reporting limits for individual components like benzene are lower (0.05 mg/kg for soil and 0.5 ug/L for water).

Extractable Petroleum Hydrocarbons
Total Chromatographable Organics (EPH-TCO)

The EPH-TCO is a modified Method 8100 (GC/FID) designed to measure diesel, fuel oil, kerosene and other products in the range of C_7 to C_{32}. It is also possible to identify gasoline and motor oil, although these products are not recovered as well as diesel. The method complies with the minimum criteria in the California LUFT extraction method for diesel. This method has been previously described in detail.[12]

Organic compounds are extracted from their matrix into methylene chloride and the extract is then analyzed by capillary column GC with a flame ionization detector. The term Total Chromatographable Organics (TCO) is defined as the total chromatographic area responding to a FID with boiling points between 100° C and 470° C as compared to the response of ortho-terphenyl. This definition is very similar to the definition of TCO set forth by the U.S. EPA in 1978.[13] The boiling range of 100° C to 470° C corresponds to the hydrocarbon range of nC_7 to nC_{32}. Quantification is performed using a baseline projection to integrate area for both resolved and unresolved components. Additional information is generated by comparing the chromatogram against standards of known petroleum products for identification and a series of alkanes for a carbon distribution range. In addition, nonpetroleum products such as vegetable oil and vegetative hydrocarbons can be identified in some cases.

The average recovery of fuel oil #2 from reagent water spiked at 250 ug/L was 66% with a relative standard deviation (RSD) of 25% (12 replicates). The average recovery of fuel oil #2 from Ottawa sand spiked at 10 mg/kg was 67% with a RSD of 18% (four replicates). The average surrogate (ortho-terphenyl) recovery was 82% in water (15% RSD) and 84% in Ottawa sand (8% RSD). The surrogate was spiked at 20 ug/L in water and 0.80 ug/g in Ottawa sand.

Petroleum Hydrocarbons

The Petroleum Hydrocarbons (PHC) method has been used extensively for oil spills and is similar to the EPH-TCO Method. The results provide information on fate, transport and weathering of crude oil. These results include a Total Petroleum Hydrocarbon value (C_{10} to C_{36}), n-alkanes (C_{10} to C_{32}), pristane and phytane. This test can be linked with a GC/MS-Selected Ion Monitoring technique to measure trace levels of Polynuclear Aromatic Hydrocarbons.

COMPARISONS OF PETROLEUM HYDROCARBON METHODS

The following tables compare the performance of some petroleum hydrocarbon methods on various soils. Following each table is a discussion of the results.

The field sample contained weathered gasoline. The laboratory spike was artificially weathered (spiked at 50 mg/kg; however, some of the lighter components were lost during the mixing process). Method 8020 results are lower than GRO because only selected components (BTEX) are measured. TPH-IR is known to have a low recovery for the volatile and aromatic components of gasoline.

These samples were field (soil) samples contaminated with diesel fuel. The tests were done to evaluate extraction solvents and the number of extraction steps for a round robin study. The CH_2Cl_2 samples were extracted three times with methylene chloride, while the Freon samples were extracted only once with Freon 113. The average surrogate (1-chlorooctadecane) recovery was 103% for CH_2Cl_2 extraction and 67% for Freon extraction. Although not conclusive, the data indicates that CH_2Cl_2 is more effective for the extraction of diesel fuel from these soils.

Table 1
Comparison of Total Petroleum
Hydrocarbon Methods for Gasoline[11]

Method	Field Sample mg/kg	Lab Spike mg/kg
API-GRO	130	8.3
CALIF-LUFT	64	0.96
8020-BTEX (Total)	5.9	1.8
8240-(RIC total)	51	0.82
TPH-IR	ND (50)	ND (50)

Table 2
Comparison of Extractable Petroleum
Hydrocarbon for Diesel Method

Method	D-S-1, mg/kg	D-S-2, mg/kg	D-S-5, mg/kg	D-S-4, mg/kg
EPH-TCO (CH_2Cl_2)	78	150	10	12
EPH-TCO (Freon 113)	29	24	2.2	6.0

Table 3
Comparison of TPH-IR and TPH-GC Methods[3]

Method	Limestone 1, mg/kg	Weathered Limestone 2, mg/kg	Weathered Silty Clay, mg/kg
TPH-IR	760	3000	366
TPH-GC	67	1000	ND, <25

This study[3] indicated a potential problem with the TPH-IR analysis of certain types of soil-weathered limestones, clays and silts. It is possible that clay-sized inorganic particles do not settle out of the Freon extract. The particles may absorb infrared light and produce a positive TPH-IR response in the absence of hydrocarbons.

ANALYTICAL METHOD SELECTION

If the source of the petroleum product contamination is known, the appropriate method can be selected. The Gasoline Range Organic (GRO) test is the recommended technique for gasoline. For other refined products like diesel fuel, kerosene and jet fuels, the Extractable Petroleum Hydrocarbons (EPH-TCO) should be used. For crude oil spills, the Petroleum Hydrocarbon (PHC) test is recommended.

For unknown situations or site characterizations, the GRO and EPH-TCO should be run to provide comprehensive information. In addition, TPH-IR or a TPH-gravimetric procedure should be considered if heavy products (motor oil, bunker oil) may be present (Fig. 2).
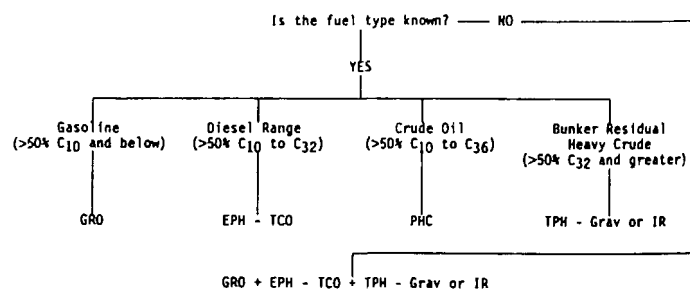
Figure 2
Analytical Method Selection

While it would be desirable to propose an additive value from the methods in Figure 2, that may not be practical in all cases. Particularly in unknown samples, interpretation of the GRO, EPH-TCO and TPH results yield useful information. For example, a high GRO value relative to EPH-TCO and TPH confirms that gasoline is the primary product present. Also, if GRO is low and EPH-TCO and TPH are equivalent, the sample is primarily in the kerosene-diesel range (the EPH-TCO should indicate the product). Finally, if TPH is high, motor oil and heavy products can be present. If interferences are suspected, the EPH-

TCO results should qualitatively confirm the presence of heavier products.

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Full-Scale Remediation at a Superfund Site Using In Situ Vacuum Extraction and On-Site Regeneration Case Study-Phase I

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ABSTRACT

A full-scale remediation of soils, bedrock and groundwater is underway at the Tyson's Superfund Site (Tyson's) near Philadelphia, Pennsylvania. Ranked number 25 on the NPL, Tyson's is a location where unknown quantities of volatile organic compounds (VOCs) and semivolatile compounds were disposed of over a period of several years. Two former waste lagoon areas are the focus of the remediation activities. The contaminated area covers approximately four ac.

The cleanup involves in situ vacuum extraction in the silty clay soils of the former lagoons and surrounding area which contains upwards of 250,000 ppm total VOCs and semivolatiles. The major contaminants of concern are 1,2,3 trichloropropane, toluene, xylenes and dichlorobenzene, although there are also approximately 20 other identified compounds. In addition, the remedy includes dual extraction of water and vapor from the underlying fractured arkosic sandstone and the collection and treatment of the seep spring water from the off-site area downgradient of the former lagoons.

The remedy includes 180 soil vacuum extraction wells, nine dual extraction wells and six bedrock extraction wells which are manifolded to a central processing plant. The process plant covers 10,000 ft^2 and contains two 700-hp vacuum units and two 250-hp vacuum units. The design air flowrate is approximately 15,000 scfm at 13 in. Hg vacuum. Vapor treatment is by activated carbon adsorption with on-site stream regeneration and solvent recovery. Water treatment is by air stripping with carbon polishing. Since the commencement of remediation activities in November 1988, more than 95,000 lb of contaminants have been removed from the site by the vacuum extraction process for off-site destruction. Overall, the vacuum extraction remedy is successfully treating soils at the site with an innovative in situ treatment process.

INTRODUCTION

Situated in southeastern Pennsylvania is the Tyson's Superfund Site (Tyson's), an abandoned quarry near the Schuylkill River which was used as a disposal facility during the 1960s and early 1970s for mixed septic and chemical wastes consisting primarily of VOCs and semivolatile compounds. Two former lagoons were excavated down to bedrock into which haulers disposed of the wastes atop the fractured arkosic sandstone. The wastes leached into the bedrock and surrounding soils, spreading contaminants laterally over an area of approximately 4 ac and vertically through the fractured bedrock where it remained as DNAPL (Dense Non Aqueous Phase Liquid). The movement of groundwater through the bedrock then carried the contaminants northward toward the floodplain of the river.

Tyson's Site was closed by the Pennsylvania Department of Environmental Regulation (PADER) in 1973. The lagoons were emptied of liquids and backfilled with soil. Following complaints of foul odors from nearby residents in 1983, the U.S. EPA began Emergency Response activities and conducted an RI. The Tyson's Site was added to the NPL in 1984 where it is ranked Number 25.

A ROD was issued, calling for excavation and disposal of the soils backfilled in the former lagoons and surrounding areas. Later, after two vacuum extraction pilot tests were conducted in the former East Lagoon, the ROD was overturned and reissued in favor of an innovative vacuum extraction remedy to address the contaminated soils and bedrock at the site.

The full-scale remedy of soils and shallow bedrock includes vacuum extraction wells, deep dual extraction wells and bedrock extraction wells. The extracted vapors enter the process plant from various manifold lines where they are treated by activated carbon adsorption prior to discharge. The activated carbon beds are regenerated on-site with steam, and the solvents are recovered and stored until they are transported off-site for final destruction.

This paper describes Phase I of the Tyson's Site remediation. The remedy description focuses on the on-site source area, and it includes a description of the site, the geologic setting and chronological chain of events, along with a description of the pilot tests and their performance objectives which led to the ROD being overturned in favor of a more effective and safer treatment using vacuum extraction. The full-scale design, facility layout and results of the first year of cleanup operations are presented with respect to recovery performance and the vacuum recovery system's operations efficiency.

SITE DESCRIPTION

The Tyson's Site is a 4-ac abandoned quarry located in Upper Merion Township, Montgomery County, Pennsylvania, near the city of King of Prussia. It is situated on the south bank of the Schuylkill River, but is separated from the river by the floodplain and a railroad switching yard as shown in the areal schematic diagram of Figure 1. A residential community is immediately adjacent to the site on the west and undeveloped property is located to the east. The fence line, shown by the dashed line in Figure 1, encloses the on-site area.

The main sources of contamination are concentrated within two former waste lagoons known as the Former East Lagoon and the Former West Lagoon. The solid lines within the dashed area represent the areas of highest contaminant concentrations within
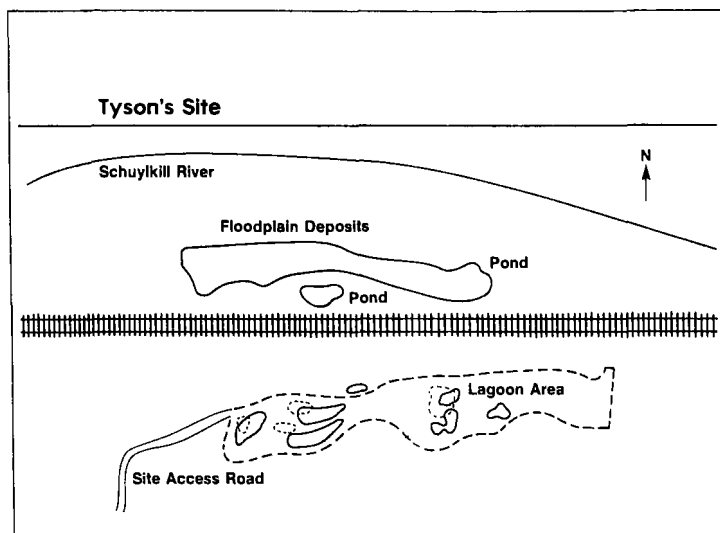
Figure 1
Tyson's Site

the two lagoons.

Figure 2 is a profile of the site looking west. The topsoils of the former lagoons were excavated to bedrock immediately adjacent to the quarry high-wall on the south. The depth of the lagoons ranges from 8 to 20 ft, making the volume of contaminated soils approximately 50,000 yd³. On the north side of the site, there are the fence line and another high-wall which overlooks the railroad tracks. Moving further north from there, one views the floodplain and then the Schuylkill River.
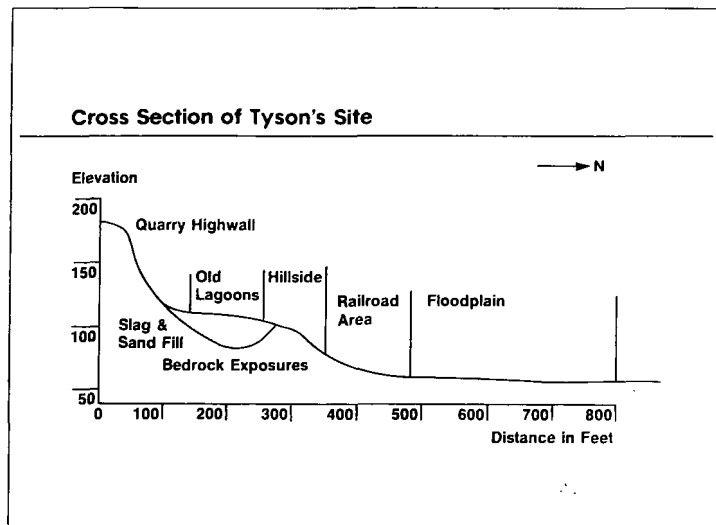
Figure 2
Cross Section of Tyson's Site

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The site is situated within the Stockton Formation outcrop area. The Stockton, of Triassic age, is approximately 4,000 ft thick and is composed of fine- to coarse-grained fractured arkosic sandstones, conglomerates, interbedded red shales and siltstones. The Stockton Formation has been subdivided into three members: (1) the upper shale member, characterized by shale and siltstone; (2) the middle member, characterized by fine- and medium-grained sandstone; and (3) the lower member, which consists of coarse grained sandstone and conglomerate. Generally,

the Tyson's Site is located within the outcrop of the lower member. Bedding planes dip to the north and northwest at an average of 12 degrees.[1]

The overburden soils consist of loam, silts and clays, but due to the extensive reworking of the soils during disposal practices, the backfilled soils are anything but homogeneous. In fact, the impact of severe heterogeneity is a primary focus of the ongoing activities of the vacuum extraction operations.

The Stockton is a relatively good water-bearing formation, and some wells in the lower members have recorded an average specific capacity of 3.0 gpm/ft of drawdown and yields of 110 gpm.[2] Beneath the Tyson's Site, however, the flow through the lower member appears to be fracture-dependent, and it is also complicated by the presence of DNAPL within the fractures. Flowrates from the wells on-site range from 5 to 20 gpm.

The groundwater gradient dips steeply to the north from the high-wall, through the lower portion of the former lagoons and down toward the floodplain. Extensive perched water rests in the former lagoons, which makes the Dual Vacuum Extraction and groundwater extraction process a logical remedy for these soils.

SITE HISTORY

From 1960 to 1973, the Tyson's Site was utilized for the disposal of a variety of septic sludges, chemical wastes and solvents. Apparently, the wastes were dispersed throughout the site, with the majority of disposal taking place in the former unlined lagoons. Some of these wastes migrated down into the bedrock and groundwater where they remained as DNAPLs and contaminated the groundwater as it flowed through the bedrock toward the floodplain.

The site was closed to waste disposal in 1973 by the PADER due to alleged regulatory violations. The lagoons were then pumped out, backfilled and vegetated. Following complaints of odors by nearby residents in early 1983, the U.S. EPA initiated emergency response activities to mitigate the direct contact threat to public health and environment posed by contaminant releases from the unsecured site. These activities included the construction of a security fence, drainage controls, topsoil cap and a leachate collection and treatment system.

During the subsequent years, 1983 to 1984, the U.S. EPA undertook a Remedial Investigation which showed that elevated concentrations of volatile and semivolatile organic compounds existed in the soils. The major constituents detected were 1,2,3-trichloropropane (TCP), xylenes, toluene and chlorinated benzenes (chlorobenzene, 1,2-dichlorobenzene and 1,4-dichlorobenzene). Well installation activities during the installation of the vacuum extraction system indicated soil concentrations of organics up to 250,000 ppm in the former lagoon soils, with several areas in the tens of thousands part per million range.

In December 1984, the U.S. EPA issued an ROD requiring excavation and removal of on-site area soils; based on this ROD, the remedial design was initiated. The plan was to excavate approximately 3,500 truckloads of soil, transport them through a residential community and then travel 600 mi up the Pennsylvania Turnpike to a disposal facility in Ohio. After the health risk became apparent, the responsible parties urged the U.S. EPA to evaluate the vacuum extraction technology for cleanup of the site. Furthermore, the ROD for excavation only addressed the soils, but did not satisfactorily address the bedrock contamination which would have recontaminated the clean backfilled soils.

In November 1988 and May 1987, the RPs initiated two in situ vacuum extraction pilot tests in the area of the Former East Lagoon. The tests consisted of four vacuum extraction wells, a water/vapor separator tank, activated carbon units and a vacuum extraction unit. The objectives of the vacuum extraction pilot tests were as follows:

• Quantify the extraction rates of volatile and semivolatile compounds

- Evaluate the radius of influence (Ri) of the extraction wells
- Evaluate the time frame for cleanup using vacuum extraction
- Extract, contain and treat the contaminants safely
- Evaluate the extraction rates in bedrock

The results of the pilot tests showed that TCP, xylenes and chlorinated benzenes had the highest extraction rates, with total extraction rates reaching 150 lb/day during the second pilot test which lasted 3 wk. The vacuum extraction system was also successful in volatilizing DNAPLs from the fractured bedrock at rates up to 15 lb/day with a radius of influence of 100 ft.

Based on the success of the vacuum extraction pilot tests, the RPs petitioned the U.S. EPA to reevaluate the ROD with the following proposed clean-up plan:

- Vacuum extraction in the former lagoon soils and topsoils
- Dual vacuum extraction and groundwater extraction from the bedrock
- Collection and treatment of the seep spring water along the railroad tracks

In March 1988, the PADER and the U.S. EPA agreed to overrule the original ROD and issue a new ROD in favor of vacuum extraction and groundwater treatment for the on-site area soils and bedrock.

FULL-SCALE VACUUM EXTRACTION AND DUAL EXTRACTION SYSTEM

Design of the full-scale vacuum extraction system began in late 1987 and was completed in May 1988. Site activities commenced in May 1988 with the clearing of trees and shrubbery, construction of the support zone and decontamination area, and initiation of the vacuum extraction well installation and process plant construction. Construction activities were completed in approximately 5 mo; system startup and testing commenced on Nov. 15, 1988.

A schematic diagram of the full-scale remedy in place at the Tyson's Site is depicted in Figure 3. The remedy includes 180 vacuum extraction wells throughout the former east and west lagoons and surrounding topsoils, nine Dual Extraction wells along the quarry high-wall and six open-hole bedrock extraction wells along the north side of the former lagoons.

The vacuum extraction wells range from 8 to 20 ft in depth and are arranged so that their radii of influence, which were measured during well development shortly after installation, overlap sufficiently to insure complete coverage of all the contaminated soil. Continuous split spoon samples were taken on each well and analyzed in the on-site laboratory with approximately 10% of the samples sent to a Certified Laboratory for confirmation. In all, approximately 1,300 soil samples were analyzed on-site with turn-around times averaging 36 hr.

The dual extraction wells along the quarry high-wall on the south side of the site are drilled from 70 to 100 ft into the bedrock. Dual Extraction is a patented process in which a vacuum extraction well is outfitted with a groundwater recovery system to simultaneously extract vapors and groundwater from the same well. Thus, the vacuum extraction process takes advantage of the drawdown cone of depression or "induced vadose zone" to extract the residual contaminants which have been left behind as the groundwater table is lowered. Typically, the Dual Extraction process increases overall system performance by removing residual contaminants while substantially accelerating the groundwater recovery process. Well yields of a dual extraction well have been shown to be from two to 15 times greater than a well which pumps groundwater alone.

The bedrock extraction wells are open-hole completions on the north side of the former lagoons. These wells range in depth from 40 to 60 ft; they take advantage of the overall depression in the groundwater elevations throughout the site to volatilize the VOCs and semivolatiles which have migrated down into the fractured bedrock.

The vacuum extraction, dual extraction and bedrock extraction wells are connected at the surface to three main mainfold lines which transect the site. The manifold lines enter the process plant where the entrained liquids are removed by vapor/water separators. From the separators, the process stream enters the vacuum extraction blowers which consist of two 700-hp vacuum units and two 250-hp vacuum units. Generally, only one of each size vacuum unit is on-line at any given time, with the duplication of equipment assuring uninterrupted operations during scheduled maintenance operations or repairs. The design air flowrate for the system is 15,000 scfm at 13 in. Hg.

After passing through the vacuum extraction blowers, the extracted vapor stream reaches temperatures of 350°+. Hence, the process stream is cooled to 100°F prior to entering the carbon adsorption units.

The activated carbon treatment system is comprised of four 7,000-lb primary adsorption units and two 7,000-lb backup adsorption units, allowing continuous operations during regeneration cycles. Vapor removal efficiency is 99.8%. An on-line flame ionization detector with continuous strip recorder automatically samples the outlet of the primary carbon adsorption units and stack discharges every 30 sec. Routine calibrations and verification samples are analyzed twice daily in the on-site laboratory.

A regeneration cycle is initiated upon breakthrough of the primary carbon units. At that time, the other two carbon units are placed on-line while the spent carbon units are regenerated using steam at approximately 7 psig. The contaminant-laden steam is then cooled, condensed and decanted, with the recovered solvents being stored on-site in a 2500-gal holding tank. When full, the tank is emptied and the solvents are transported to a permitted cement kiln for final destruction.

The aqueous phase liquids from the carbon regeneration activities are pumped to an equalization tank where they are mixed with the extracted groundwater from the dual extraction wells, the seep spring collection system and the decontamination water. The water treatment system consists of a vacuum air stripping unit and carbon polishing system prior to discharge of the treated effluent to the Schuylkill River. The air stripper is connected to the main vacuum system via control valves which maintain a constant vacuum on the stripper; in this system, both the vapors from the vacuum extraction system and the vapors from the air stripping tower are processed through the same carbon beds.

PHASE I PERFORMANCE

As of August 1990, the vacuum extraction system had removed

Tyson's Vacuum Extraction System
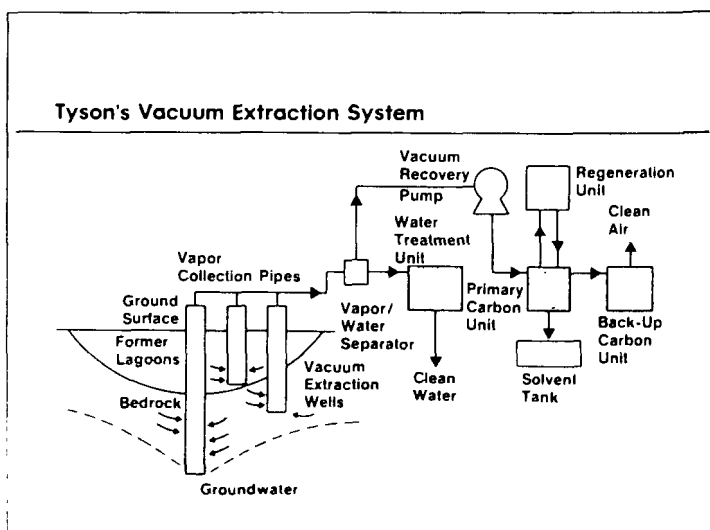
Figure 3
Tyson's Vacuum Extraction System

more than 95,000 lb of contaminants from the soils and bedrock. Approximately 80 million gallons of groundwater, process water and seep spring water have been treated to nondetectable VOC concentrations in the discharge water. The on-line operation efficiency is 99%, with nominal periods of downtime recorded for scheduled maintenance activities.

CONCLUSION

The activities which have occurred throughout the history of the Tyson's Superfund present but one of many examples of the complicated issues surrounding the presumed disposal activities, subsequent site investigations and evaluations of remedial alternatives which are inherent at nearly every Superfund Site across the nation. However, the chain of events at the Tyson's Site demonstrates the willingness of the U.S. EPA and the private sector to recognize the potential of alternative treatment technologies and to find mutually agreeable solutions to regulatory statutes while directly addressing the issues of cleanup.

Evaluation of the performance of the remedy to date shows that vacuum extraction is successfully cleaning the soils and shallow bedrock at the site. More than 95,000 lb of VOCs have been removed and destroyed, and more than 80 million gallons of groundwater have been treated. Data gathered since project commencement have indicated the extreme heterogeneity of the soils at the site and the presence of DNAPL within the soils. These phenomena are being successfully handled by the vacuum extraction operation.

Finally, the extensive communication and cooperation between the U.S. EPA, the responsible parties and the remedial contractors have resulted in a full-scale remedy at the Tyson's Superfund Site which is successfully treating soils, bedrock and groundwater with an innovative treatment process.

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A Detailed Methodology for Estimating VOC Emission Rates from Superfund Sites

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ABSTRACT

Assessment of long-term health impacts associated with air emissions from Superfund sites generally requires use of an appropriate air quality dispersion model to represent downwind contaminant dispersion and transport. An accurate source emission rate estimate is the cornerstone of any such study, yet this area typically represents the most serious data gap.

This paper presents a detailed methodology for generating accurate VOC emission rate estimates from both point and area sources and is appropriate for use at most Superfund sites. The methodology is a slight variation of the transect technique as described in the U.S. EPA air pathway analysis guidance document, *Estimation of Baseline Air Emissions at Superfund Sites* (Vol. II). The latter technique involves measuring contaminant concentrations downwind of a site at incremental points across the plume to determine the highest plume-centerline concentration. This concentration is then used as input into a basic Gaussian dispersion relationship to estimate a representative source emission rate. The methodology discussed in this paper involves contaminant mass averaging across the plume to obtain a total path integrated contaminant burden which is again used as input into a basic Gaussian dispersion relationship to estimate an emission rate. However, the mass-averaging method is shown to be easier, cheaper and far more accurate. Additionally, it provides data that are inherently more representative of the plume cross section.

The mass-averaging method can be employed using either rapid collection whole air samplers (e.g., Summa canisters) or long-path spectroscopic techniques. Application of each of these monitoring alternatives is discussed in detail and practical examples are provided.

INTRODUCTION

The assessment of health impacts associated with air emissions from Superfund sites generally requires use of an appropriate air quality model to represent downwind contaminant dispersion and transport. An accurate source emission rate estimate is the cornerstone of any such modeling study, yet this area typically represents the most serious data gap. The complexity of many Superfund sites generally makes accurate estimation of source emission rates difficult and very costly using traditional sampling techniques. This paper discusses an alternative methodology for estimating emission rates which relies upon the generation of path-integrated air contaminant data instead of the collection and analysis of contaminant samples at discrete points in space. In actuality, the path-integrated methodology can be considered an extension of the transect methodology, which is a simplistic emissions measurement technique based on the theory of point monitoring.

Accurate estimates of source emission rates are required at sites during every phase of the Superfund process. These phases consist of the site assessment, remedial and post-remedial phases. During the site assessment and post-remedial phases, time generally is not a critical factor as emission rate estimates typically are used to assess health impacts to downwind residents on a long-term basis. The sites are nearly always free of activity and emit VOCs in what may be considered an equilibrium state.

On the other hand, during the remedial phase, time is often of the essence as emission rates may vary rapidly during cleanup or removal activities. Of principal concern in these situations is the exposure to on-site workers and downwind residents on a short-term basis.

Because of these two very different objectives and data needs, a great deal of care must be exercised in specifying air sampling techniques for any given situation. Clearly, a high volume sampling technique that requires several hours of sample collection followed by subsequent off-site laboratory analysis can serve no purpose during a removal operation. Conversely, a direct-readout portable instrument would usually not be recommended for conducting air migration assessments at sites in their base line (undisturbed) states, as detection limits would generally not be comparable to most health-based standards.

THE PATH-INTEGRATED CONCENTRATION

The key to the methodology discussed in this paper concerns the concept of the path-integrated concentration. The concept is not an analytical one, but rather one of a more fundamental nature. Physically, a path-integrated concentration represents a mass average along a given distance or path length. A path-integrated concentration can be obtained instantaneously, as in the case of any of several available long-path spectroscopic techniques,[1-5] or over a short period of time (generally 15 minutes or less) by moving a constant-rate sampling device along a path at a uniform speed.[6] Path-integrated concentrations are typically normalized to a path length of 1 m or 1 km. If, for example, an integrated concentration of 30 ppm-m is reported, no information concerning the contaminant distribution can be inferred and the total mass is identical whether there is a uniform concentration of 30 ppm over a distance of 1 m, 3 ppm over a distance of 10 m, 300 ppb over a distance of 100 m, or 30 ppb over a distance of 1 km. Whether the data are generated via long-path spectroscopy or Summa canister, in each case the reported value is simply the area under the curve of instantaneous concentration versus distance. A second representation of a path-integrated concentration is g/m^3 times path length (m), or g/m^2. Although these units are not reported as extensively as ppm-m, they are frequently required for data analysis calculations as discussed later.

THE TRANSECT TECHNIQUE

Figure 1 presents an example of the transect sampling technique.[7] As discussed earlier, this is a simplistic emissions measurement tech-

nique is based on the theory of point monitoring. Concentrations of VOCs are measured at several cross-plume locations and heights at an appropriate distance downwind of the source.
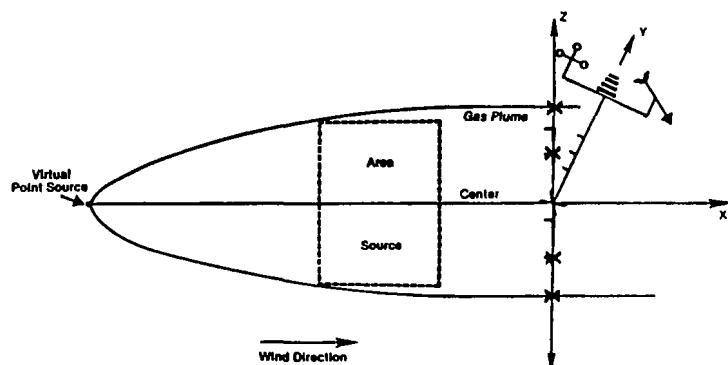
Figure 1
Example of Transcent Sampling Technique

The total VOC emission rate for a contaminant source is given by:

$$Q = \pi \chi K \sigma_y \sigma_z C u \qquad (1)$$

where:

Q = emission rate of VOC (g/sec)
χ = peak concentration of VOC (ppm)
K = conversion factor (g/ppm for VOC)
σ_y, σ_z = lateral and vertical extent of plume, 1 standard deviation (m)
C = instrument response factor
u = mean wind speed (m/sec)

In practice, σ_y, σ_z, C and u are obtained from field measurements; σ_z may be estimated from σ_y; and χ is determined by application of a Gaussian-fit curve to the VOC concentration measurements obtained by means of transect sampling.

There are several limitations associated with the transect technique. Perhaps the most significant is that the downwind sampling array will usually provide only a coarse measurement grid resulting in the possibility (and, for some sites, the likelihood) that higher contaminant concentrations advected by the wind between two sampling points may be unnoticed. Another limitation is that unless sample collection times are very short, wind fluctuations will cause a shifting plume, thus resulting in a lower peak concentration. A third limitation is the logistics associated with this approach and the relatively high degree of field labor required.

EMISSION RATE DETERMINATION

The mass-averaging measurement technique is a powerful approach for providing accurate estimates of emission rates. By knowing the on-site meteorology, the basic equations of Gaussian dispersion theory can be utilized to directly yield an emission rate. The derivations that follow begin with a continuously emitting point source and are then extended to area sources typical of Superfund sites.

Point Source

For a continuously emitting point source, the general equation for concentration of a contaminant at a ground-level receptor is:

$$\chi(x,y,0;H)) = \frac{Q}{\pi \sigma_y \sigma_z u} \exp[-1/2 (y/\sigma_y)^2] \exp[-1/2 (H/\sigma_z)^2] \qquad (2)$$

where

χ = concentration, g/m^3
x = downwind distance to a receptor, m
y = crosswind distance to a receptor, m
H = effective height of emission, m
Q = uniform VOC emission rate, g/sec

σ_y, σ_z and u are as described above.

It is noted that by setting y and H equal to zero, Equation 2 essentially reduces to the form of Equation 1 for the transect sampling technique.

Integrating Equation 2 with respect to y, from y = $-\infty$ to y + ∞, yields:

$$C(x,0;H) = \frac{2Q}{\sqrt{2\pi} \sigma_z u} \exp[-1/2 (H/\sigma_z)^2] \qquad (3)$$

where

$C(x,0;H)$ = ground-level path-integrated concentration at distance x, g/m^2.

For application of this formula at most Superfund sites, the source may be assumed to approximate a ground-level release. Setting H=0, the equation for ground-level path-integrated concentration becomes:

$$C(x) = \frac{2Q}{\sqrt{2\pi} \sigma_z u} \qquad (4)$$

This equation can be rearranged to give the emission rate, Q, as a function of ground-level path-integrated concentration:

$$Q = \frac{\sqrt{2\pi}}{2} C(x) \sigma_z u \qquad (5)$$

Equation 5 is the general emission rate equation for a point source based on path-integrated measurement data. The value of Q determined using this equation is dependent on current on-site meteorological conditions, specifically wind speed and φ^Z, the latter of which is a function of both atmospheric stability and the distance between the source and the downwind measurement. The total path-integrated contaminant burden may be determined based on data collected using either long-path spectroscopic techniques or rapid-collection whole air samplers (e.g., Summa canisters). Although most Superfund sites are represented better as area sources than as point sources, there are situations where point-source representations are not only acceptable but preferred.[8] One such situation is during air monitoring in support of site remediations, when the principal objectives are to ensure that contaminants do not create adverse off-site community health impacts and to facilitate decisions concerning on-site worker health and safety. For either objective, the concern typically is one of acute health impacts arising from short-term contaminant exposure and on-site personnel frequently cannot afford the time to develop area source inputs to a model. In such cases, the point source assumption facilitates rapid application of Equation 5 to estimate an emission rate and, most importantly, is always conservative. For a given emission rate, the maximum downwind concentration will always be greater if all of the mass is assumed to emanate from a single point within a source area.

As an example of emission rate estimation from a point source based on path-integrated data, suppose a ground-level point source has a uniform emission rate, Q, of benzene. The atmospheric stability class is determined to be D (neutral or slightly stable), the wind speed is measured at 5 m/sec and the path-integrated concentration measured at a downwind distance, x, of 100 m is 10.0 ppm-m.

From the Turner nomographs,[9] the vertical dispersion coefficient, σ_z, is 4.65 m. Based on a benzene conversion of 1 ppm = 3.25 mg/m^3 at standard temperature and pressure (STP), Equation 5 can be applied as follows:

$$Q = \frac{\sqrt{2\pi}}{2} (3.25 \times 10^{-3} g/m^2) (4.65m) (5m/s)$$

$$= (1.25) (0.76) \text{ g/sec}$$
$$= 0.95 \text{ g/sec}$$

Area Sources

As discussed earlier, most Superfund sites are represented better as

area sources than as point sources. When the objectives of an air monitoring program are more closely linked to chronic health impacts arising from long-term contaminant exposure, time is generally is not an overriding constraint and the accuracy afforded by an area source representation is preferred. Such situations would include site assessments, remedial investigation/feasibility study (RI/FS) air monitoring and post-remedial air monitoring.[10]

In practice, Equation 5 may be extended to the determination of emission rates for an area source of known location and dimensions. However, because the vertical dispersion coefficient, σ_z, varies over the along-wind dimension of the area source, an adequate treatment method for σ_z must be developed. In the simplest method, the value chosen for σ_z is based on the distance, x, from the center of the area source to the line of crosswind measurement. It is important to note, however, that because the horizontal dispersion is affected by the cross-wind width of the source, an estimate of distance to a "virtual" point source (upwind of the back boundary of the area source) is required in order to estimate the approximate plume width at the distance of measurement and to determine a path length sufficient to ensure that the mass-averaged measurement encompasses the entire contaminant plume.

As an example of an area source emission rate estimation based on this simplified treatment method for σ_z, suppose that the value for C(x) measured in the previous example, at a distance of 100 m from the center of an area source 40-m square, is used in Equation 5 to determine the total source emissions. As above, Q is calculated as 0.95 g/sec. Assuming that emissions across the area source are homogeneous, this amounts to a unit emission rate of 5.9×10^{-4} g/sec-m^2.

It is clear that a more accurate estimation of the area emission rate may be obtained without reference to a virtual point source, because Equation 5 presents Q as a function of wind speed and vertical dispersion only. For rectangular area sources with dimensions on the order of tens to hundreds of meters, a more sophisticated treatment of σ_z begins with Equation 4, from which the total path-integrated concentration, C(x), can be represented as the sum of path-integrated concentrations attributable to each of n subdivisions of the area:

$$C(x) = \sum_{k=1}^{n} \frac{2q_k}{\sqrt{2\pi}\sigma_{z_k}u} \tag{6}$$

Here, q_k is the emission rate of a rectangular subdivision of the source area with length equal to the crosswind dimension of the area and width equal to 1/n times the along-wind dimension. Because σ_y does not affect the mass-averaged concentration, the emission rate, q_k, may be interpreted as representing emissions from a point along the area centerline at the distance, x_k, from the line of mass-averaged measurement. The total area emission rate may then be written as the sum of emissions from points along the area centerline, with σ_{z_k} selected according to the distance from each subdivision center point to the line of mass-averaged measurement. Ultimately, area emissions may then be written as the limit of the sum of emissions from n subdivisions, as n approaches infinity, where σ_z is integrated over the along-wind dimension of the area.

For an area with uniform emissions, a unit emission rate, q, is usually presented in g/sec/m^2. For a given unit emission rate, an emission rate, q', for a crosswind line of length L and unit width may be defined:

$$q' = q \times L \tag{7}$$

where q' is in g/sec/m^2

It follows that for an area subdivision of crosswind length L and width Δx,

$$q_k = q \times L \Delta x = q' \Delta x \tag{8}$$

where q_k represents total emissions from the kth area subdivision, in grams per second.

Substituting for q_k in Equation 6 yields:

$$C(x) = \sum_{k=1}^{n} \frac{2q' \Delta x}{\sqrt{2\pi}\sigma_{z_k}u}$$

Rearranging, this becomes:

$$C(x) = \frac{2q'}{\sqrt{2\pi}u} \sum_{k=1}^{n} \frac{\Delta x}{\sigma_{z_k}}$$

Taking the limit as n → ∞ yields:

$$C(x) = \frac{2q'}{\sqrt{2\pi}u} \lim_{n\to\infty} \sum_{k=1}^{n} \frac{1}{\sigma_{z_k}} \Delta x$$

which may be written as:

$$C(x) = \frac{2q'}{\sqrt{2\pi}u} \int_x \frac{1}{\sigma_z}dx \tag{9}$$

Rearranging and solving for q' yields:

$$q' = C(x) \frac{\sqrt{2\pi}u}{2} \div \int_x \frac{1}{\sigma_z}dx \tag{10}$$

Solving the q' term is the key to developing an accurate method to treat σ_z. For the entire source area of width W, total emissions are given as:

$$Q = q' \times W \tag{11}$$

At this point, it is noted that the definite integral in Equation 10 cannot be evaluated without employment of some type of numerical method. Such methods rely on the idea that there is a region whose area is given by the integral and then provide a technique to approximate that area. There are several numerical techniques available for solving such a function. Each technique involves breaking up the function into a finite number of subintervals, erecting vertical lines at the division points and approximating the areas of the subregions. The simplest (and least accurate) method of approximating each subregion area is by constructing a series of rectangles, in which the value of the function across each subinterval is approximated by a horizontal line (y=constant).

The trapezoidal approximation of each subregion area is more accurate. This method replaces the horizontal line representing the function value with a first-order equation (y=ax + b), with unique values of a and b determined for each subregion.

An even more accurate method is the parabolic approximation, or Simpson's rule, in which the line representing the value of the function is replaced by a second-order equation (y=ax^2 + bx + c), with unique values of a, b and c determined for each subregion.

This rule is described briefly as follows. The integral,

$$\int_\alpha^\beta f(x)\,dx$$

is evaluated as follows:
- Break the interval $\alpha \le x \le \beta$ into n equal parts of width Δx each, where n is an even number
- Compute $y_k = f(x_k)$, k=0,1,2,...,n; $x_0 = \alpha$, $x_n = \beta$
- Then:

$$\int_\alpha^\beta f(x)\,dx = \frac{1}{3}\Delta x(y_0 + 4y_1 + 2y_2 + \ldots + 2y_{n-2} + 4y_{n-1} + y_n) \tag{12}$$

APPLICATION

Figure 2 illustrates an application of the mass-averaging measure-

.ment technique for area source emissions. Assume that a site contaminated with benzene is being monitored. The site is a rectangular area, 100 m x 80 m, with the longer side oriented in a north-south direction. The site is considered to be emitting at a relatively uniform rate across its surface and a source emission rate must be determined based upon mass-averaged concentration measurements.
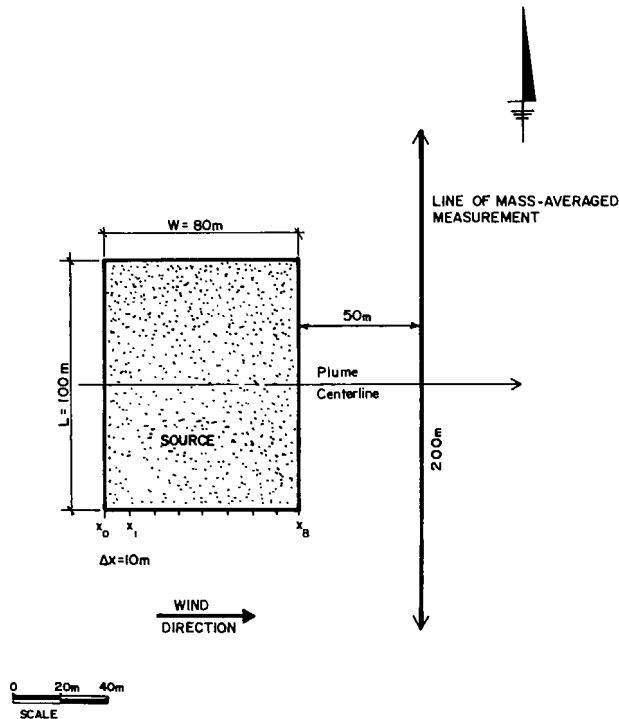
Figure 2
Line of Mass-Averaged Measurement

An on-site meteorological tower indicates that the wind is blowing steadily from the west at 5 m/sec. The downwind location for cross-plume monitoring is along a north-south line at a distance 50 m from the downwind boundary of the site. Sky conditions are mostly cloudy and a stability category of "D," or neutral-to-slightly-stable conditions, exists. A downwind path length of 200 m is determined to be sufficient to contain the plume.

Real-time monitoring yields a mass-averaged benzene concentration of 98.5 ppm-m. Based on the benzene conversion factor of 1 ppm = 3.25 mg/m^3 at STP, this is equivalent to a concentration of 320 mg/m^2.

Applying the parabolic rule for integration, we can separate the along-wind axis of the source area into eight equal parts, each of width Δx = 10 m. Constructing area subregion boundaries perpendicular to the along-wind axis at each interval yields eight area subregions, as shown in the following table, where each x_k represents the distance from the kth upwind subregion boundary to the line of mass-averaged measurement, α_{zk} represents α_z at that distance and y_k represents the value of the function, $y_k = 1/\alpha_{zk}$:

k =	0	1	2	3	4	5	6	7	8
x_k(m) =	130	120	110	100	90	80	70	60	50
(m) =	5.84	5.45	5.05	4.65	4.24	3.83	3.41	2.98	2.55
y_k =	0.171	0.183	0.198	0.215	0.236	0.261	0.293	0.335	0.393

The integral may then be calculated from Equation 12:

$$\int \frac{1}{x \, \sigma_z} dx = \frac{1}{3}(10) \, [0.171 + 0.732 + 0.396 + 0.860 + 0.472 + 1.044$$
$$+ 0.586 + 1.340 + 0.393]$$
$$= 19.98$$

Therefore, from Equation 10:
q' = (320) (1.25) (5)/19.98 = 100.10 mg/sec-m.

From Equation 11, the area emission rate is:
Q = (100.10) (80) = 8008.01 mg/sec.

In contrast to the area subdivision treatment of a rectangular area source using Simpson's rule, consider the benzene concentration, C(x), measured as in the above example and determine the total area emissions, Q, using a simplified, point source approximation of the area. Locating the point of emission at the center of the area, we have, from Equation 5:

Q = (1.25) (3.20) (4.24) (5)
= 8,480 mg/sec

This emissions estimate represents a 5.9% error when compared to the emission rate determined using Simpsons' rule. For a more conservative estimate of total area emissions, we may choose to define a point source midway along the upwind boundary of the actual source area. From Equation 5:

Q = (1.25) (3.20) (5.84) (5)
= 11,680 mg/sec

This emission rate is 45.9% higher than that calculated using Simpson's rule for integration.

CONCLUSIONS

A methodology, referred to as the mass-averaging technique, has been presented for estimating VOC emission rates from Superfund sites. The mass-averaging technique can be employed using either rapid-collection whole air samplers or long-path spectroscopic techniques. Procedures are presented for treatment of both point source and uniformly emitting area source representations.

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Field Screening of Soil Vapors at a Subsurface Gasoline Contaminated Site in West Liberty, Morgan County, Kentucky

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ABSTRACT

Leaking underground storage tanks containing petroleum products pose a serious threat to groundwater quality nationwide. Many of the releases from underground storage tanks constitute an emergency situation due to exposure to toxic or flammable vapors and contamination of potable water sources. These conditions require rapid and cost-effective acquisition of data from the contaminated area. Soil vapor field screening techniques permit a rapid assessment of the affected area.

A complaint was lodged by the Kentucky Transportation Cabinet, Department of Highways in August, 1988, concerning the quality and odor of water in its well. Preliminary sampling by the Kentucky Department for Environmental Protection revealed constituents indicating gasoline contamination. Subsequent sampling showed contamination of five potable wells in the area. One operating service station with three underground storage tanks containing gasoline and several abandoned underground storage tanks are in the immediate area where contamination had been identified.

A field investigation was initiated by the U.S. Geological Survey, and the Kentucky Department for Environmental Protection. The objectives of this investigation were to:

- Determine the degree and extent of contamination from gasoline constituents
- Locate and confirm the source(s) of contamination
- Assess the impact of contamination on the quality of soils, groundwater, and surface water in the vicinity

Soil vapors were obtained using an Environmental Instruments soil vapor sampling device. Soil vapors were drawn to the sampling probe via an electric peristaltic pump. A milliliter syringe was inserted through a Teflon septum and vapor was removed from the sampling device. Soil vapor samples were analyzed in the field using a HNU Model 311 portable gas chromatograph. These samples were analyzed for gasoline constituents. Results of the soil vapor and groundwater analyses indicate the contamination originated from the operating service station's underground storage tank system.

Problems encountered with this soil vapor technique included: sampling under dissimilar meteorological conditions produced varying results; extraction of soil vapors at a rate of one liter per minute did not produce optimum results. Advantages of this soil vapor technique included: a cost-effective screening of samples; prompt results in a safe manner; and non-disruption of site hydraulics.

INTRODUCTION

Subsurface hydrocarbon contamination may exist in four phases: as free product on the ground water surface; as a dissolved fraction; as residual contamination of soil particles; or as vapor (Figure 1).[1] Soil vapors are air that fills the space between soil grain surfaces. Soil vapor

surveys utilize the volatility of gasoline components to determine subsurface contamination. The advantages of soil vapor surveys include:

- Non-disruptive of site hydraulics
- Safety
- Cost effective
- Prompt results
- Allows for a detailed assessment of a site.[2]
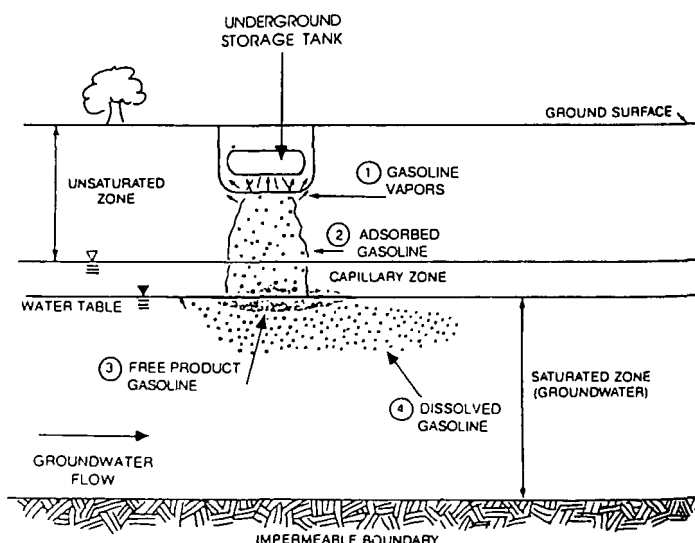
Figure 1
Depiction of Four Phases of Gasoline
Contamination in the Soil[2]

Several limitations exist with the use of soil vapor surveys. If bedrock or groundwater is near the ground surface, it is difficult to acquire representative samples. Soil vapors acquired from less than two feet below the ground surface may be mixed with ambient air causing dilution of the sample. Dense clay lenses and deep groundwater will decrease soil vapors. Biodegradation will alter the components of soil vapors.[2]

Meteorological conditions will also affect the results of soil vapor surveys. High barometric pressure will result in suppression of volatile flow in near ground surface samples. Ambient air temperature will affect the rate at which volatilization occurs.[2]

SITE DESCRIPTION

A complaint was lodged by the Kentucky Transportation Cabinet,

Department of Highways in August, 1988, concerning the quality and odor of water in its well. Preliminary sampling by the Kentucky Department for Environmental Protection revealed constituents indicating gasoline contamination. Subsequent sampling showed contamination of five potable wells in the area. One operating service station with three underground storage tanks containing gasoline and several abandoned underground tanks are in the immediate area where contamination had been identified (Figure 2).

and naphthalene.

A magnetometer survey of an area approximately 200 feet south of Gose Branch has indicated the possible location of an abandoned underground storage tank (Figure 2). Local residents indicate a store had operated at this location 20 to 25 years ago and did sell fuel oil and possibly gasoline.

A wet weather spring has been noted along Little Caney Creek in the affected area (Figure 3). Analyses of wet weather spring samples have shown the presence of constituents associated with gasoline contamination.

Figure 2
Location of Underground Storage Tanks
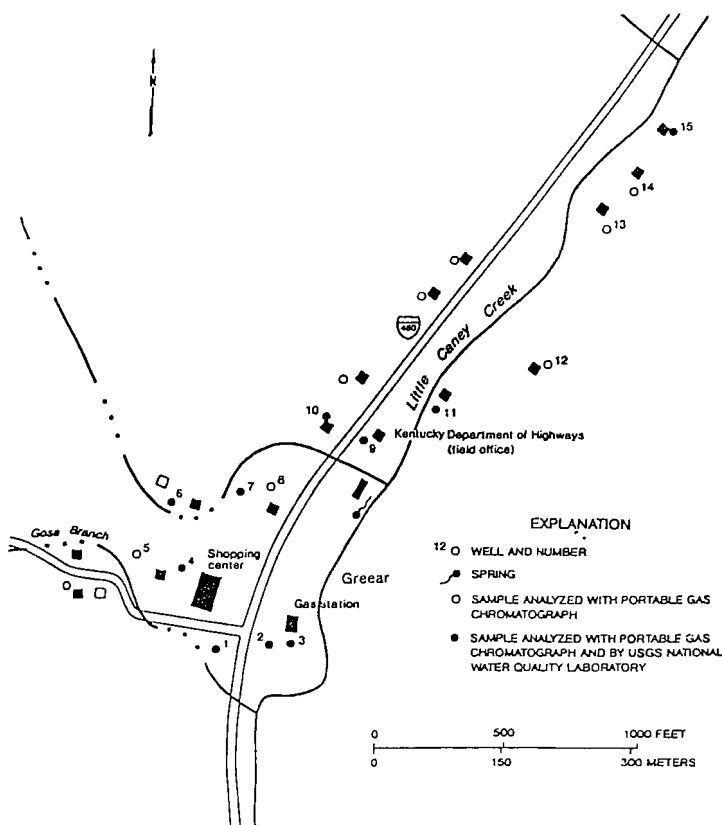
Figure 3
Location of Groundwater Wells in the Study Area

A field investigation was initiated by the U.S. Geological Survey and the Kentucky Department for Environmental Protection. The location of this investigation was approximately four miles south of West Liberty on U.S. Route 460. The objectives of this investigation were to:

* Determine the degree and extent of contamination from gasoline constituents
* Locate and confirm the source(s) of contamination
* Assess the impact of contamination on the quality of soils, groundwater, and surface waters in the vicinity

Information received from Department of Highways personnel indicated the removal of three abandoned underground tanks south of the operating service station in 1982, when US Route 460 was rerouted. This area was the former site of Jones' Restaurant, which did sell fuel and operated through the late 1950s (Figure 2).

Reconnaissance of the area resulted in the discovery of an abandoned underground tank west of the operating service station (Figure 2). Local residents indicate that this area was the former site of Hall's service station which had closed in the 1950s. The 550-gallon underground tank at this location was removed by the Kentucky Department of Highways in May, 1989. This tank was badly corroded and pitted. Soil samples obtained from the bottom of the excavation basin showed no gasoline constituents above the limits of detection. A sample taken from the approximately ten gallons of liquid remaining in the tank showed the presence of benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes

Groundwater is the sole source of potable water in the contaminated area. Twelve potable wells were inventoried during the investigation (Figure 3): five wells are developed in the Lee Formation, five wells are developed in the Breathitt Formation and two wells are developed in the Quaternary fill. The Lee Formation is characterized by sandstone and siltstone with lesser amounts of clay, claystone, coal, ironstone and limestone. The Breathitt Formation is characterized by siltstone, sandstone and claystone. The Quaternary fill consists of gravel, sand, and silt.[3]

METHODOLOGY

Soil vapors were procured using an Environmental Instruments soil vapor sampling device. This sampling train consists of a slotted stainless steel screen and several 30-inch steel rod connections with an outer diameter of 0.5 inch and an inner diameter of 0.25 inch. The probe was topped with a "T" junction. Sampling probes were driven into the ground by an electric rotohammer. Modeling clay was packed around the sampling probe at ground level to prevent ambient air from being drawn into the sampling train.

Soil vapors were drawn to the sampling probe via an electric peristaltic pump. An electric pump was used because a gasoline-operated pump might contaminate the samples. Vacuum was applied to the sampling train for one minute at a rate of one liter per minute. However, extracting soil vapors at a rate of one liter per minute may have caused a larg-

er sphere of influence than desired.

A milliliter syringe was inserted through a Teflon septum in the "T" connection and vapor was removed from the sampling train. The syringe plunger was drawn back and allowed to remain in the septum for 5 to 10 seconds with vacuum continuing to be applied. The locking mechanism of the syringe was engaged, and the syringe was withdrawn from the septum. Duplicates were taken at each sample location. The syringes were labeled with the sampling location and transported to the mobile laboratory for analyses.

Samples were analyzed using a HNU 311 portable gas chromatograph with a 20-inch column. The gas chromatograph was set with an isothermal injection temperature of 130 °C and an oven temperature of 75 °C. The carrier gas rate was set at 20 ml/min, and the attenuation was set at the lowest gain setting.

To insure quality assurance and quality control, several measures were instituted. Ambient air was sampled and analyzed using desultory syringes to examine the cleanliness of the syringes. The soil vapor probes were decontaminated after each sampling location using a laboratory grade detergent wash followed by a deionized water rinse and a hexane rise. The probes were then allowed to air dry. Ambient air was periodically sampled through the soil probe and analyzed to insure the effectiveness of the decontamination.

Four plots were chosen for examination using soil vapor survey techniques in areas known or suspected to be contaminated. These areas included Well 3, Well 6, the unidentified abandoned underground tank and the operating service station (Figures 2 and 3). Ten sample points were chosen in the vicinity of Well 3 ranging in depth from 3.5 to 4.5 feet. Four sample points were chosen in the vicinity of Well 6 ranging in depth from 5.5 to 7.5 feet. Eight sample points were chosen in the vicinity of the unidentified abandoned underground tank ranging in depth from 3.8 to 5.5 feet. Forty-one sampling points were chosen in the vicinity of the operating service station ranging in depth from 4.5 to 7.0

feet. Sampling depth was dependent upon depth to saturated soils, physical character of the soil and depth to bedrock.

RESULTS

All soil vapor analyses in the vicinity of the unidentified abandoned underground tank and Well 6 were negative for benzene, toluene, ethylbenzene, and xylene constituents. Soil vapor analyses in the vicinity of Well 3 and the operating service station's underground storage tank system exhibited increased benzene, toluene, ethylbenzene and xylene concentrations. One area was defined by sampling points 14, 15, 16 and 17. The second area was defined by sampling points 22, 23, 36, 37 and 39 (Figure 4). Chromatograms of the standard, background, and sampling point 17 are found in Figure 5.

DISCUSSION AND CONCLUSIONS

This site investigation consisted of groundwater, surface water, soil and soil vapor sampling. Samples were qualitatively screened in the field with a portable gas chromatograph. Duplicate groundwater, surface water and soils samples were quantitatively analyzed by the U.S. Geological Survey, National Water Quality Laboratory.

Qualitative analyses of soil vapors indicated gasoline contamination only on the property of the operating service station. Soil sample quantitative analyses also indicated gasoline contamination only on the property of the operating service station. Quantitative analyses of groundwater and surface water showed gasoline contamination of Wells 2, 3, 6, 9, and 11 and a wet weather spring entering Little Caney Creek north of the operating service station (Figure 3). Quantitative analyses of groundwater from monitoring Well 2 and Well 6 indicated the presence of methyl-tertiary-butyl ether. Methyl-tertiary-butyl ether is an additive commonly used in unleaded gasolines and has been commercially produced since 1979.[1] The increased concentrations of volatile compounds in soil vapors and soil, in addition to the presence of
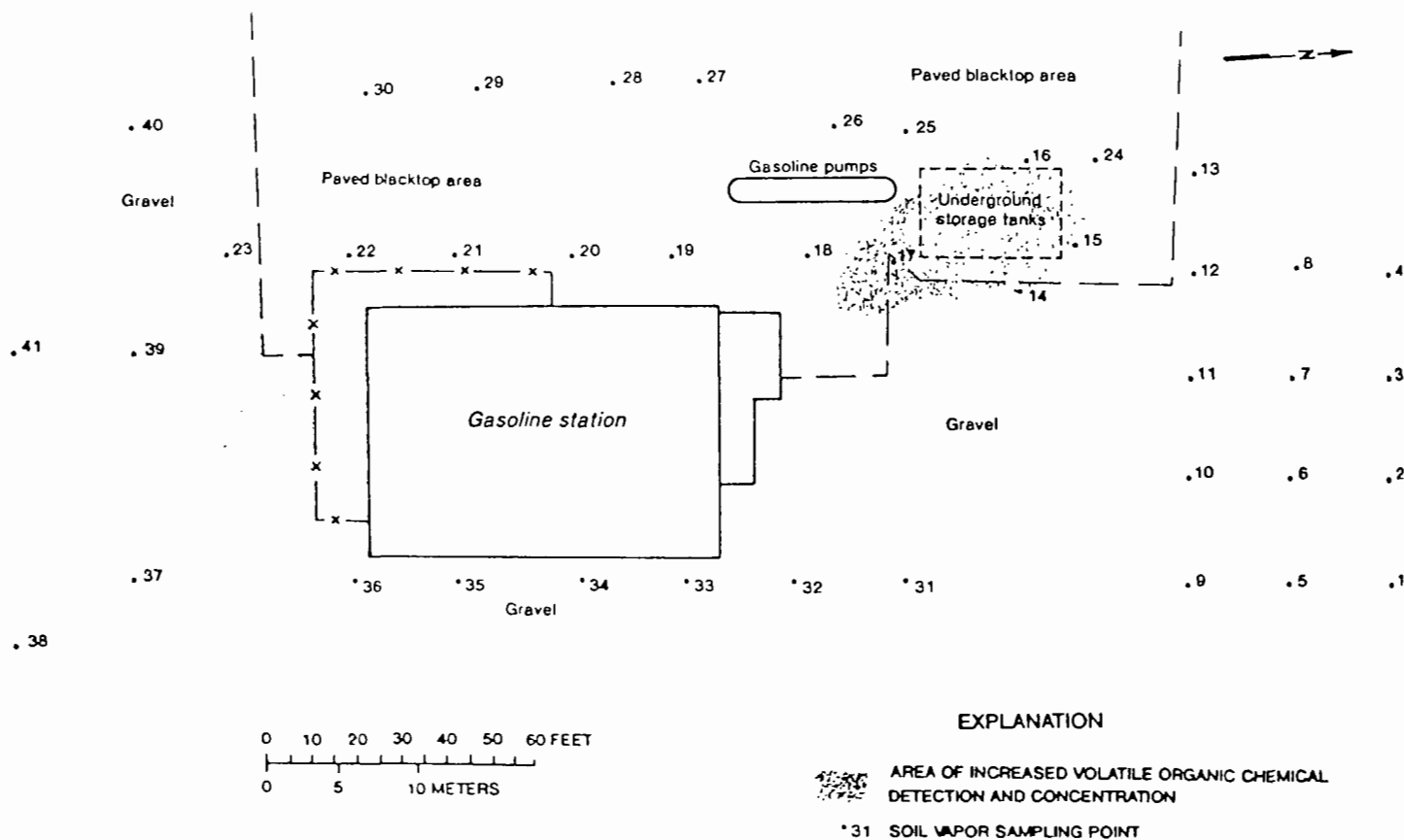
Figure 4
Location of Soil Vapor Sampling Points
on the Property of the Operating Service Station

methyl-tertiary-butyl ether at two groundwater sampling points, indicate that the source of gasoline contamination is the operating service station's underground storage tank system.

SAMPLE POINT 5 (BACKGROUND)

1 Hexane
2 Unidentified
3 Unidentified
4 Unidentified

STANDARD

1 Hexane
2 Benzene
3 Toluene
4 Ethylbenzene
5 m-Xylene
6 p-Xylene
7 o-Xylene

SAMPLE POINT 17

1 Hexane
2 Benzene
3 Unidentified
4 Toluene
5 Unidentified
6 Ethylbenzene
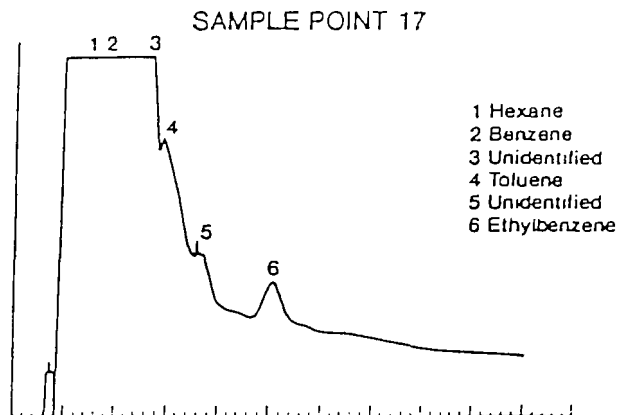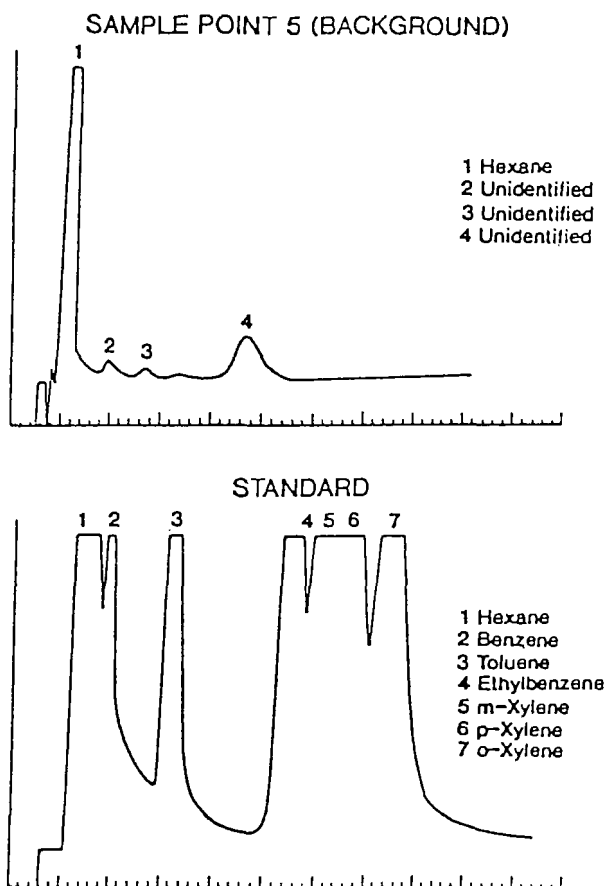
Figure 5
Example Chromatographs

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Case Study on the Application of Air Sparging as a Complimentary Technology to Vapor Extraction at a Gasoline Spill Site in Rhode Island

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ABSTRACT

Vapor extraction (soil venting) is a successful and cost-effective remediation technology for removing VOCs from vadose (unsaturated) zone soils. However, in many cases, seasonal groundwater table (GWT) fluctuations, GWT drawdown associated with pump-and-treat remediation techniques and spills involving dense, non-aqueous phase liquids (DNAPLS) create residually saturated soils below the water table. Vapor extraction alone is not considered to be an optimal remediation technology to address these areas of contamination.

Artificial water table drawdown is one approach that may be utilized to expose the contaminated soils, thereby increasing the efficiency of the soil venting process. However, in some cases, this neither practical, nor cost-effective. An alternative approach is the use of air sparging (injection) wells to inject hydrocarbon-free air into the saturated zone below the areas of contamination. The contaminants dissolved in the groundwater and adsorbed on the soil partition into the advective air phase, effectively simulating an in situ air stripping system. The stripped contaminants are transported in the air phase to the vadose zone, within the radius of influence of the vapor extraction system. The contaminant vapors are drawn through the vadose zone to a vapor extraction well where they are treated utilizing standard vapor extraction off-gas control system(s).

This paper presents a case history of the application of air sparging as a complimentary technology to vapor extraction in the remediation of residually saturated soils below the water table at a gasoline spill site in Rhode Island.

INTRODUCTION

In 1985, remedial activities were implemented at a gasoline spill site in Pawtucket, Rhode Island. The engineering company contracted to perform the remedial activities designed, installed and operated a free gasoline product recovery and groundwater pump-and-treat system. An air stripping tower was utilized to removed volatile organic hydrocarbons (VOCs) dissolved in the groundwater. Gasoline hydrocarbon vapor migration into nearby basements was controlled through the operation of a soil gas venting system (SVES), also installed in 1985. The groundwater treatment and free product recovery systems were shut down in May 1987; however, the soil venting system remained in operation, and additional vacuum wells were installed to remediate gasoline-contaminated vadose zone soils and to recover hydrocarbon vapors in the vicinity of the spill location. Approximate locations of the monitoring wells, vacuum wells and treatment equipment existing on the site as of May 1987 are shown in Figure 1.

The Rhode Island Department of Environmental Management (DEM) set closure limits of 10,000 parts per billion (ppb), 500 ppb, and 500 ppb total BTEX for monitoring wells MW-3, MW-11 and MW-12, respec-tively. While BTEX levels at MW-11 and MW-12 have remained below the closure limit prior to VAPEX's involvement at the spill site, levels at MW-3 have fluctuated around 25,000 ppb total BTEX with a relative deviation of 16% over the period from July 1988 through July 1989, displaying a high of 29,000 ppb in July 1988 and a low of 19,000 ppb in October 1988. The last sample reported during that period was 21,000 ppb in July 1989.

VAPEX were contracted in August of 1989 to evaluate site conditions for the purpose of developing a specific strategy to meet the DEM's total BTEX closure limits for MW-3. An evaluation of the existing soil gas venting system concluded that the SGVS was influencing and had achieved remediation of the vadose zone soils in the area of concern. It was concluded that the local source of groundwater contamination was located on the soils below the water table level in that area.

Under non active remediation conditions, transport of immiscible phase hydrocarbons from the saturated zone to the vadose zone requires dissolution of the hydrocarbons into the aqueous phase followed by diffusion/dispersion of the dissolved hydrocarbons through the aqueous phase to the air-water interface, where volatilization into the vadose zone occurs. The hydrocarbon vapors are then removed from the vadose zone by the SGVS. Where total hydrocarbon concentrations in the saturated zone are moderately low, as was the case at this site, and conditions are relatively static, the intraphase transport of hydrocarbons occurs very slowly, requiring long periods of time for hydrocarbon source reduction. Therefore, the utilization of the soil gas venting system alone would be expected to be a very inefficient means of achieving the DEM closure criteria at MW-3.

VAPEX performed a cost/benefit analysis on three potential treatment methodologies to achieve the DEM Closure Criteria in the vicinity of MW-3. The three proposed treatment methods were: (1) re-activate the existing groundwater pump-and-treat system, (2) install and operate a new pump-and-treat system centrally located within the area of concern and (3) in conjunction with the existing soil gas venting system, install and operate an air sparging system centrally located within the area of concern. As a result of the cost/benefit analysis, VAPEX proposed that an air sparging system be designed, installed and operated at the site. The air sparging process involves the introduction of hydrocarbon-free air to the saturated zone below the contaminated soils in order to expedite transfer of saturated zone hydrocarbons to the SGVS influenced vadose zone.

The air sparging process involves the introduction of hydrocarbon-free air to the saturated zone below the contaminated soils in order to expedite transfer of saturated zone hydrocarbons to the SGVS influenced vadose zone. Air flow in a previously water-saturated soil involves a displacement process. The air displaces the water filling the soil pore spaces. When a continuous air phase through the previously water-filled
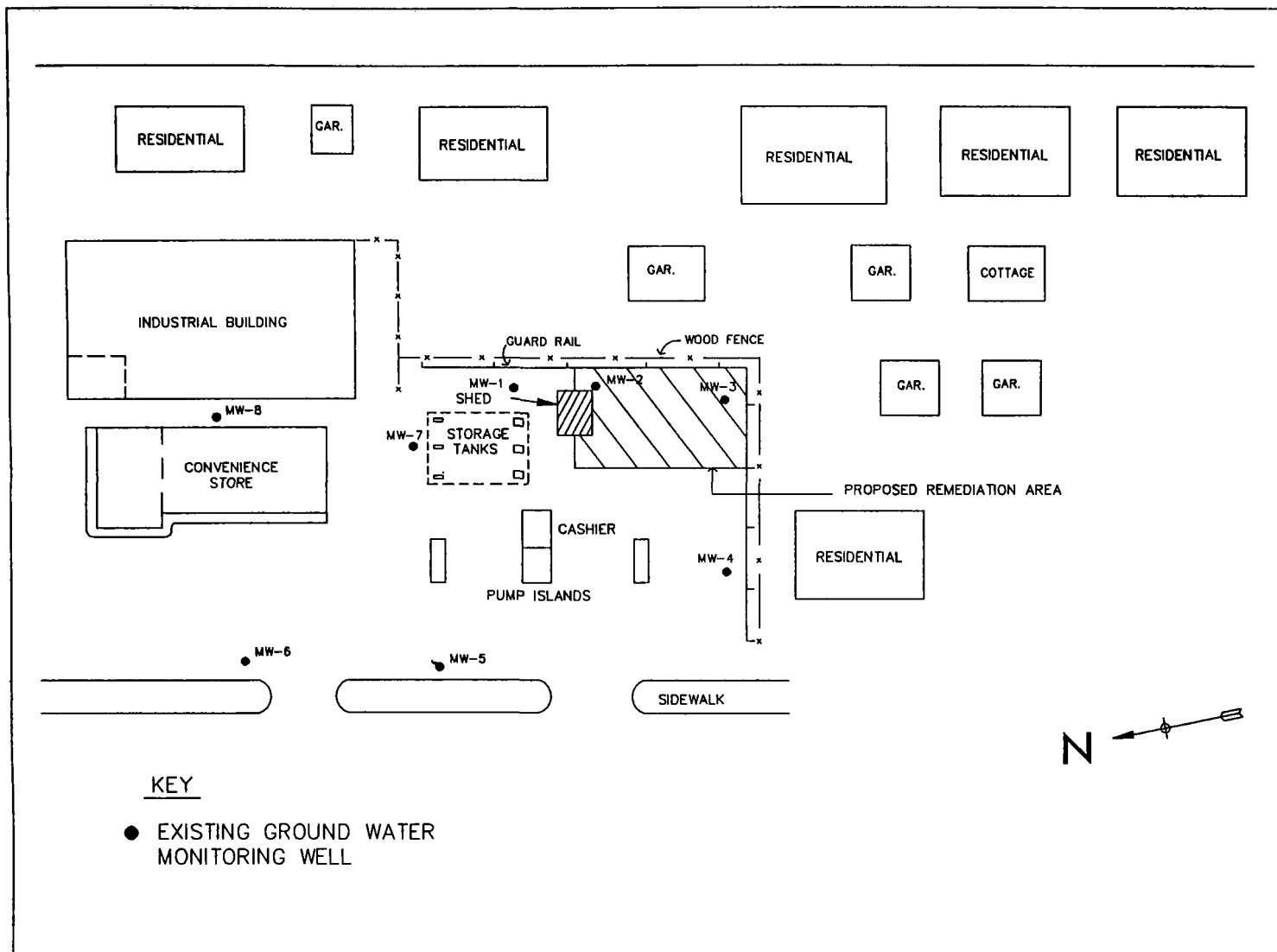
Figure 1
Site Plan
May, 1987

pores is attained, the air permeability of the soil will be a function of the degree of water saturation of the pore as shown in Figure 2.

Before the air can pass as a continuous phase through the contaminated soil, the air pressure must attain a minimum value termed the air entry pressure (pe). Figure 3 displays a typical porous media capillary pressure curve depicting the related value of the air entry pressure. The sparging system would be designed to ensure that the air would pass through the contaminated soils providing the hydrocarbons with a more efficient transfer pathway to the vadose zone.

SYSTEM INSTALLATION AND OPERATION

Site Geology

The general stratigraphy of the investigated area is defined by a fine to coarse brown sand with no silt and 5 to 15% fine to medium gravel extending from grade to 19 to 20 feet below grade. The coarse, highly permeable material is underlain by a much less permeable brown/grey, well sorted, dense, fine sand. Groundwater was observed at 15.5 to 16.0 feet below grade and displays and approximately 3 feet seasonal fluctuation in level.

Design Parameter Evaluation

To verify the presence of the contaminated soils below the water table

level and to develop design parameters for a full-scale air sparging system, eight borings were advanced in the proposed remediation area. Soil samples were taken during the advance of the borings and were analyzed utilizing U.S. EPA Method for volatile aromatics. The results of the analysis confirmed the presence of low levels of weathered gasoline components on the saturated soils from 15 feet down to approximately 25 feet below grade. BTEX compounds detected ranged in concentration from 835 micrograms per kilogram (ug/kg) to nondetectable, with levels generally decreasing with depth.

Two test air injection wells, (AIW1S and AIW2S) and three monitoring points (VP-1, VP-2 and VP-3) were installed at the site where the soils analyses had indicated the presence of relatively high levels of hydrocarbons in the soil and/or groundwater. The approximate locations of the test injection wells and monitoring points are shown on Figure 4.

Major design parameters to be evaluated were: achievable contaminant removal rates, air entry and operation pressure requirements at the injection wells, achievable injected air flow rates, achievable effective radius of influence of the injection system and an evaluation of pulsed versus continuous air injection.

A 1-day pilot test was performed on the test wells (screened from 18 feet to 20 feet below surface grade). Pressures and achievable air flow rates were measured at each well and monitoring point during the pilot test. The discharge from the SGVS was monitored prior to, during

Figure 2
Relative Permeability Relationship
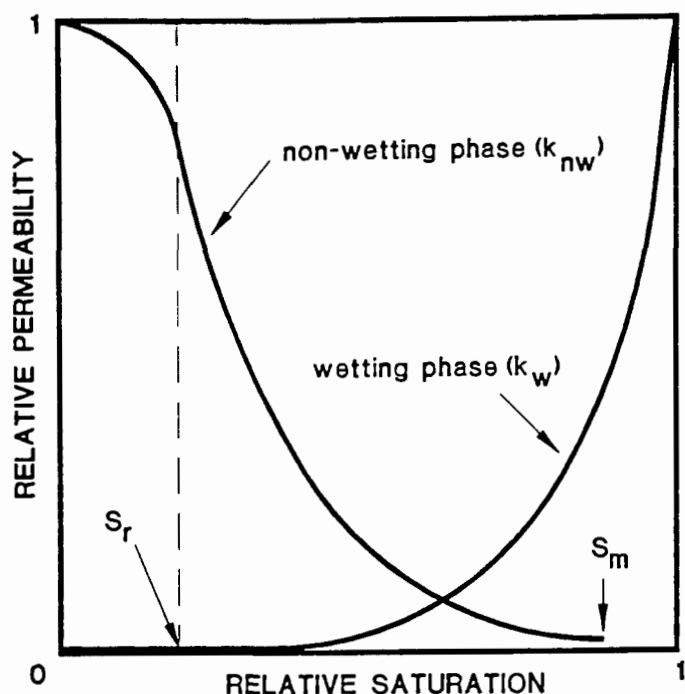
S_r - Residual Saturation of Wetting Phase

S_m - Maximum Relative Saturation at which k_{nw} exists
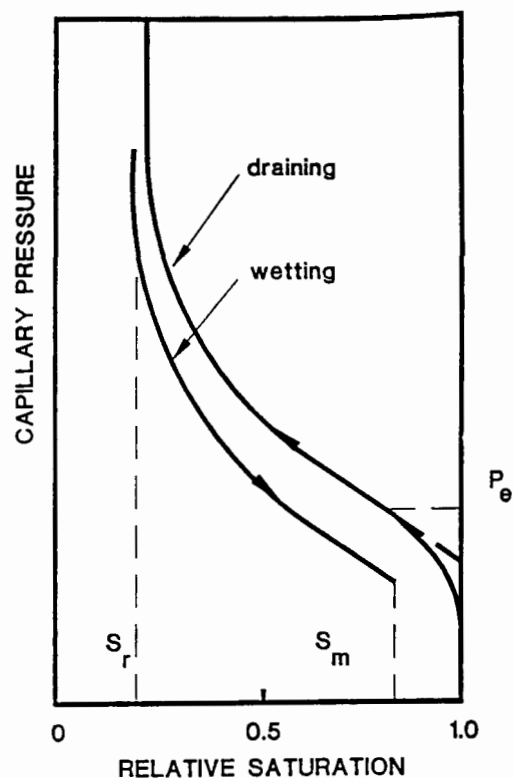
P_e - Air entry pressure

S_r - Residual saturation

S_m - Maximum saturation due to entrapped air

Figure 3
Capillary Pressure Relationship

and after the pilot test.

A portable gas chromatograph (HNU Model 321, equipped with a photoionization detector) was utilized to analyze the discharge data from the soil gas venting system. Prior to the initiation of the injection test, the background discharge reading from the soil gas venting system was 13 parts per million by volume (ppm-v/v) as gasoline. During the injection tests, the discharge from the soil venting system reached a maximum level of 300 ppm-v/v. The SGVS was operating at an air flow rate of approximately 100 cubic feet per minute, while injection air flow rates varied between 10 and 20 cfm, providing a minimum withdrawal to injected air flow ratio of five to one. SGVS discharge concentrations, generally, decreased relatively rapidly during the conduct of the injection test at a well. Approximately 0.7 pounds of gasoline range hydrocarbons were removed from the groundwater and saturated zone soils during the short-term test.

Relatively low air entry and operation pressures of 1 to 2 pounds per square inch (psi) were required to achieve air injection flow rates of 5 to 10 cfm. As expected, during the air injection process, slight positive pressures were measured at the monitoring points in the vadose zone and a rise (0 to 1 inches) in the water table level was detectable within the area local to the injection well. As the shallow injection well screen was located 3 to 5 feet below the water table level in a coarse sand, it was anticipated that the radius of influence of the injection wells would be relatively small. Based on the air pressure readings at the monitoring points and the local water table rise, the radius of influence was calculated to be approximately five feet. No significant differences were observed in mass removals during the injection test under pulsed versus continuous operation. However, with respect to energy conservation and to prevent the development of short-circuiting pathways for the air flow under continuous operation, pulsed injection was considered to be the most advantageous mode of operation.

Full-Scale System Installation and Operation

Based on the parameters evaluated during the pilot test, VAPEX designed and installed a full-scale air sparging system. The full-scale system consisted seven shallow air injection wells and six deep injection wells enveloping the area of concern. Figure 4 shows the remediation area layout. The deep air injection wells were screened from 25 feet to 27 feet below grade in the fine sand material. Two 2.5-hp Ingersoll-Rand oil-less compressors were utilized to provide the hydrocarbon-free air supply to the injection wells. The shallow air injection wells were operated on a 3 hours on, 9 hours off schedule, at an air pressure of 1 to 2 psi and 3 to 6 cfm air flow rates. The deep injection wells were operated on a 6 hours on, 6 hours off schedule, at an air pressure of 6 to 8 psi and 2 to 6 cfm air flow rates.

RESULTS

The operation of the full-scale air sparging system consisted of a 60-day run time within the period from March 21, 1990 through July 14, 1990. During that period, approximately 5 to 10 pounds of gasoline range hydrocarbons were removed from the groundwater and soils within the remediation area. Groundwater samples were collected and analyzed utilizing U.S. EPA Method 602 prior to, during and after the operation of the full-scale air sparging system. The results of the groundwater analysis are presented in Table 1. In Table 1 it can be seen that following 2 to 3 weeks of operation, the level of BTEX in the groundwater had declined in non-detectable levels with the area of concern.

One to two weeks prior to groundwater sampling, the system was shut off to allow the system to come to equilibrium. Dissolved oxygen levels within the area of concern rose from an average level of 1.4 milligrams per liter (mg/l) to approximately 6 to 8 mg/l, reflecting the aer-

WOOD FENCE

SHED

MW2

VW7

AIW7S

AIW6S

AIW5D

AIW2S

VW8

AIW2D

VP2

AIW4D

MW3

AIW1S

AIW1D

AIW6D

AIW5S

VP3

AIW3D

AIW3S

AIW4S

VP1

N

KEY

● EXISTING MONITORING WELL

⊕ EXISTING VACUUM WELL

⊙ SHALLOW AIR INJECTION WELL

⊠ DEEP AIR INJECTION WELL

▲ VAPOR PROBE
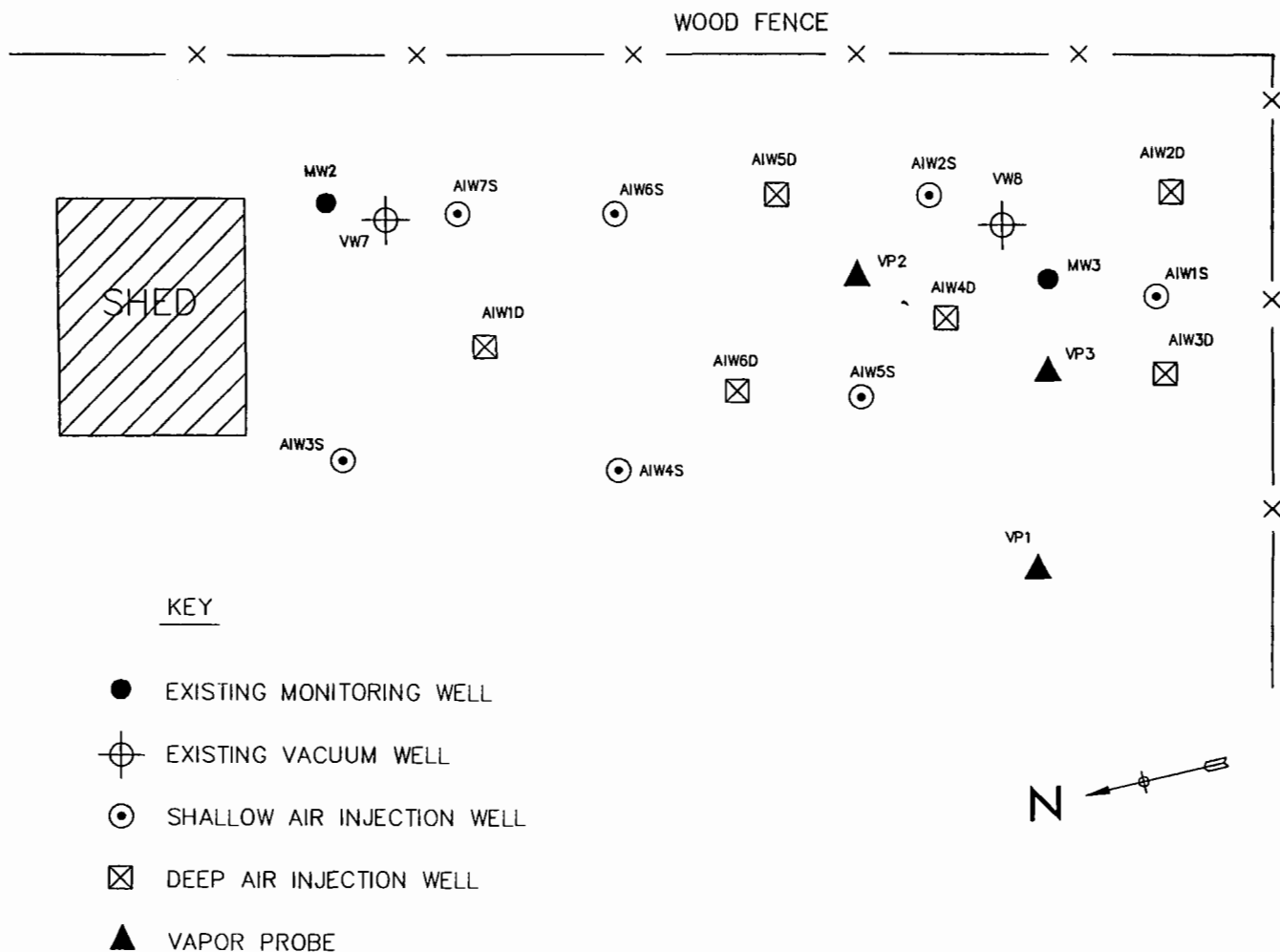
Figure 4
Remediation Area Layout
September 1989

Table 1
Groundwater Sample Analysis

WELL	COMPOUND	Results expressed in uG/L									
		4/5/89	7/3/89	10/13/89	01/30/90+	03/05/90*	04/03/90	04/23/90	4/24/90	06/18/90	07/18/90
MW2	BENZENE	31	26	6.9	11	-	ND	ND	ND	-	7
	TOLUENE	110	59	21	ND	-	ND	ND	ND	-	7
	ETHYL BENZENE	210	250	110	ND	-	ND	ND	ND	-	1
	XYLENES	1,900	1,700	850	710	-	ND	ND	ND	-	68
	TOTAL BTEX	2,300	2,000	990	721	-	ND	ND	ND	-	83
MW3	BENZENE	160	65	79	225	-	15	ND	ND	ND	20
	TOLUENE	6,200	6,000	5,600	3,710	-	152	ND	ND	ND	440
	ETHYL BENZENE	2,600	2,000	1,800	590	-	6	ND	ND	ND	80
	XYLENES	16,000	13,000	11,000	8,610	-	1,760	ND	ND	ND	1,000
	TOTAL BTEX	27,000	21,000	18,000	13,135	-	1,933	ND	ND	ND	1,540
MW4	BENZENE	-	-	-	500	1,450	269	1,500	-	ND	210
	TOLUENE	-	-	-	1,430	4,050	640	1,000	-	ND	450
	ETHYL BENZENE	-	-	-	1,570	200	460	250	-	ND	280
	XYLENES	-	-	-	14,460	19,400	8,450	9,700	-	46	1,250
	TOTAL BTEX	-	-	-	17,960	25,100	9,819	12,450	-	46	2,190

ND   Not Detected   +   Post Pilot Test of 1/30/90
      Not Sampled   *   Full Scale Startup on 3/21/90

ation of the groundwater within the zone of influence of the air sparging system. As determined by pressure measurements in the vadose zone, the air sparging system as designed displayed an effective radius of influence that enveloped the area of concern.

CONCLUSIONS

An air sparging system was designed, installed and operated at a gasoline spill site in Rhode Island. Formerly, the site had undergone five years of remediation utilizing a combined system of groundwater pump-and-treat and a soil gas venting system. While the soil gas venting system was effective in remediating the vadose zone soils, gasoline con-tamination remained on the soils below the water table level and the DEM closure criterion of 10,000 ppb at MW-3 was not achieved.

Following 60 days of operation of the air sparging system, approximately 5 to 10 pounds of gasoline range hydocarbons were stripped from the groundwater and water saturated soils. Within 2 to 3 weeks of operation the closure criteria were achieved at MW-3 and the site is now on a quarterly groundwater monitoring program to ensure that the closure levels are maintained.

The results of the case study demonstrate the potential for air sparging to be utilized as a complimentary technology to vapor extraction (SGVS) to attain a cost-effective, turnkey solution for remediation of gasoline spill sites.

On-site Vapor Extraction—Demonstrated Effectiveness

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ABSTRACT

Vapor extraction technology has been successfully used to remediate soils contaminated with volatile organic compounds (VOCs). The majority of vapor extraction remedial actions have involved application of a vacuum to contaminated soils in situ.

Soil pile venting employs vapor extraction to reduce VOC levels in soils that have been excavated and stockpiled on the site. Soil pile venting has been used as a successful remedial response action at sites contaminated with VOCs, however, limited published information on design requirements and demonstrated effectiveness is available. Additionally, most of the previous applications have not involved use of a closed system.

A former paint and varnish manufacturing facility in Massachusetts which stored bulk petroleum hydrocarbons and other organic chemicals underground served to demonstrate the effectiveness of vapor extraction in an on-site, above ground, closed system. The application involved excavation of soils containment with toluene, ethylbenzene, xylenes, MEK and vinyl acetate as a of leaking underground tanks and piping.

Soils were excavated during underground storage tank and piping removal placed containment in a closed system for application of vapor extraction technology. The system was comprised of a specifically designed sand bed overlain by an impervious liner; stockpiled contaminated soils on top of the liner in a specifically designed structurally competent manner; vapor vent and vapor extraction piping systems; condensate collection system; and complete enclosure of the stockpiled soils with an impervious liner using extrusion welding processes and attachment of a vapor extraction system blower, a thermal oxidizer vapor treatment system, sampling ports, monitoring devices and electronic controls. A description of the design, including system monitoring requirements and results, perimeter air monitoring results and a cost effectiveness analysis are provided.

INTRODUCTION

This paper discusses an on-site, aboveground treatment technology for remediating soils at a paint and varnish manufacturing site contaminated with esters, ketones, aromatic and halogenated organic compounds. The volatile nature of these compounds allows them to be stripped from soils by inducing a negative pressure over the soil particles surface area. An effective negative pressure can be maintained by connecting a vacuum blower to a piping system installed in the contaminated soils. Vapor extraction, or soil venting as it is also known, has been successfully applied to soils contaminated by releases of gasoline, degreasing solvents and dry cleaning solvents. Soils with grain sizes down to silty fine sands have been effectively remediated by this cleanup technology.

The majority of vapor extraction remedial designs have been applied in situ. Source removal becomes increasingly important where groundwater contamination is present or there is a significant threat of pending groundwater contamination. The operational period of an in situ vacuum extraction system may be greater than desired to remediate a contaminant source in an environmentally sensitive area. On a limited number of sites, contaminated soils have been excavated and stockpiled for above ground remediation using vapor extraction. As a result of a risk assessment performed at Paint and Varnish Site, it was recommended that leaking underground piping and contaminated soils be excavated for above ground, on-site treatment. The excavated soil was stockpiled on a high density polyethylene liner. The liner was folded over the stockpile and extrusion welded along three edges, encapsulating the contaminated soil. Vapor extraction and air intake piping were installed in the soil pile during construction.

SITE DESCRIPTION AND HISTORY

The Paint and Varnish Site comprises approximately three acres in Central Massachusetts, and contains buildings, paved areas and woods (Fig. 1). The main manufacturing building was used to store and mix oil-based primers and paints. An adjacent laboratory building was used to develop and test paint and varnish products. Both buildings were connected to a pump house by underground product distribution lines. The pump house distributed product from 14 underground steel storage tanks ranging in volume from 2,500 to 5,000 gallons each. A list of each tank, its contents and estimated age is presented in Table 1. The site also contained a 55 gallon drum burial area in the southwest, wooded area of the site.

The majority of the site topography slopes to the east towards a nearby residential community. The topography is influenced by the underlying bedrock which outcrops in the northwest corner of the site. The southern half of the site is mainly wooded.

The site has been vacant since late 1985. In late 1986 and early 1987, 14 underground storage tanks were removed. The associated underground piping transferring product to the laboratory and main building was left in place. In June 1987, approximately 80 55-gallon drums were excavated from the drum disposal area in the southwest corner of the site. J.B. PLUNKETT ASSOCIATES, INC. has been involved with the site since August 1988.

SITE GEOLOGY

The geology observed during subsurface exploration programs is fairly consistent beneath the site. A surface soil layer consists of light brown silty fine sand with little amounts of coarser materials. This one to two foot layer has been classified as fill material due to the presence of metal and wood debris. Underlying this unit is a dark brown silty fine sand approximately one foot thick. Beneath this stratum to an average

WOODED AREA

Quonset Hut

Tin Shed

Laboratory Building

Office Building

Main Manufacturing Building
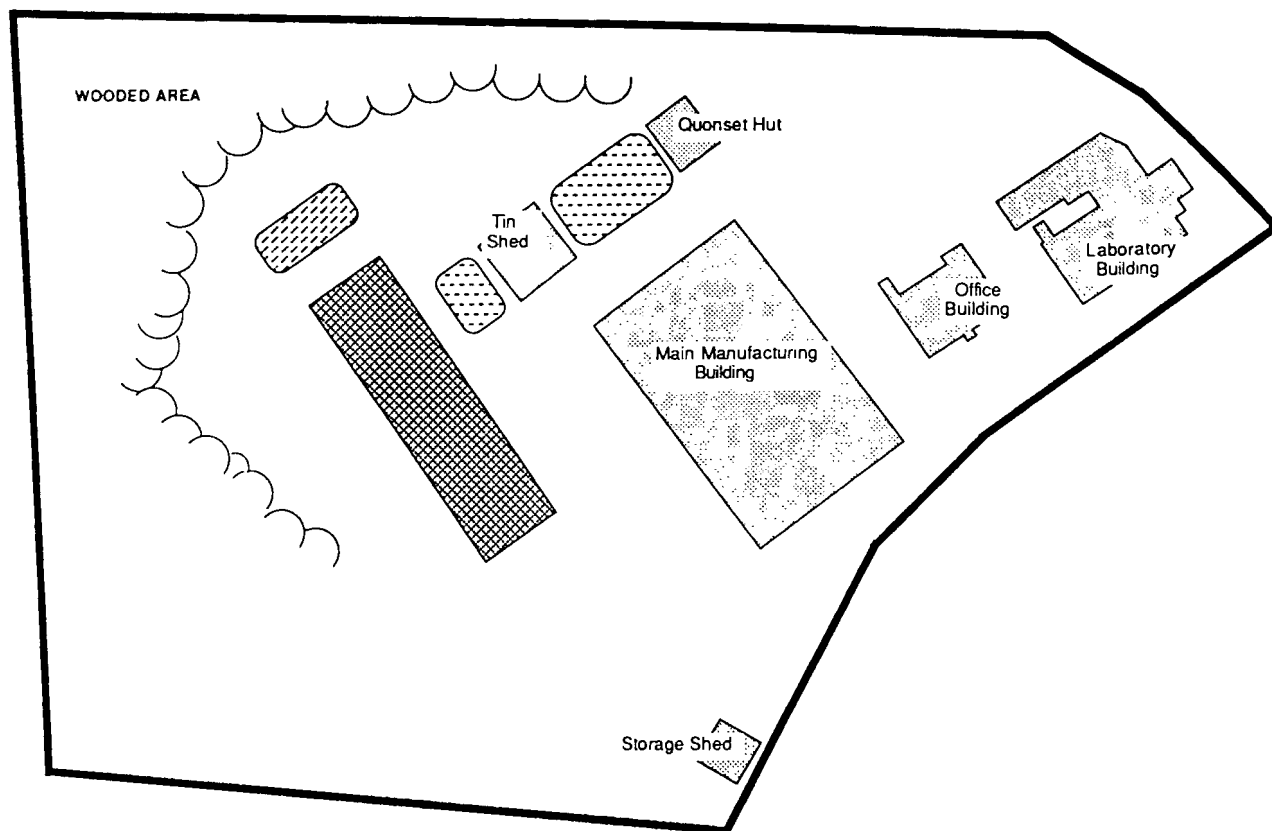
Storage Shed

LEGEND

FORMER DRUM DISPOSAL AREA

FORMER UNDERGROUND STORAGE TANK LOCATIONS

LINER ENCAPSULATED SOIL PILE

EXISTING BUILDINGS

SITE PERIMETER

NOTES:

1. Underground Storage Tank Pump House was located between the Tin Shed and Quonset Hut

2. Site Boundaries from Topographic Plan of Land Scale 1"=40', Drawn 4/22/88 by Dunn Engineering Co., Inc.

Figure 1
Site Plan P and V Site

three foot depth is an orange silty fine sand layer containing angular rock fragments. Below approximately three feet, down to the weathered bedrock surface, the soil consists of brown to gray medium to fine sand with secondary amounts of coarse sand, silt and boulders. The silt content of this layer increases with depth. The bedrock surface exposed in the northwest property corner was encountered at approximately 24 feet along the eastern border of the property. The bedrock has been identified as a moderately fractured, biotite granite.

PRIMARY CONTAMINANTS

The results of previous soil and groundwater sampling associated the primary source of contamination with the former underground storage

Table 1
Description of Excavated Underground Storage Tanks

DESCRIPTION OF EXCAVATED UNDERGROUND STORAGE TANKS

NO	GALLONS	CONTENTS	ESTIMATED AGE
1	3,000	VMP Naphtha	8
1	5,000	Toluene	16
1	2,500	Acetone	22
1	3,000	Isopropanol	8
1	3,000	MIBK	8
1	2,500	Xylol	16
2	2,500	Mineral Spirits	22/16
1	2,500	MEK	16
1	2,500	Ethyl Acetate	16

Table 2
Primary Contaminant Properties
of On-site Organics

Contaminant	Vapor Pressure(1) (mm/hg)	Vapor Density(2) (Air = 1)	Henry's Law Constant (3) (Dimensionless)	Evaporation Rate (2) (butyl acetate = 1)
Xylenes	20	3.7	0.18	0.7
Toluene	22	3.2	0.16	1.90
Ethyl-benzene	7	3.66	0.14	0.89
MEK	77.5	.81	.01	N/A
Vinyl Acetate	83	.93	N/A	N/A

tank farm and the existing underground piping. The primary contaminants identified in the soil excavated from these areas and stockpiled on the liner include xylenes, toluene, ethylbenzene, methyl ethyl ketone (MEK) and vinyl acetate. Total concentrations of volatile organic contaminants as high as 70 ppm in groundwater and 380 ppm in soils have been found.

A review of the physical/chemical properties of the primary contaminants in soil identified vapor extraction as a feasible on-site treatment alternative.

Physical/chemical vapor phase properties for the primary contaminants at the site are listed in Table 2. [2]

Henry's Law Constant is an expression of the distribution of a volatile compound or solute at equilibrium between liquid and vapor phases. A review of available literature on vapor extraction systems suggests chemicals with a Henry's Constant greater than 0.01 can be remediated effectively using this technology.[1] While Henry's Law describes the proportion of a compound in the gaseous phase at equilibrium, vapor pressure describes the pressure exerted by the compound in the vapor state.

Figure 2
Cross-sectional View of Liner and Soil Pile

SOIL PILE CONSTRUCTION

The soil pile dimensions after construction are 36 feet by 140 feet by six feet high (Fig. 2). The sides of the soil pile are graded at a 2 to 1 slope for stability. The pile pitches at a 10% grade towards the blower. The liner consists of Permalon® Ply, X-210 high density poly-

ethylene laminate (18 mil). Each laminae is oriented at 45° in succession to provide increased strength. The liner material was selected for its tear resistance, low vapor permeability, contaminant compatibility and photodegradation resistance. The contaminated soil was piled on the liner in sections which minimized contaminant loss through volatilization. The piping was built into the pile at the specified heights and locations as each section was under construction.

Four vent pipes installed at the corners along the pile length consist of 4 inch diameter Schedule 40, PVC slotted screen (Fig. 2). Each vent pipe is slotted in widths of 0.020 inch. A four inch PVC extraction pipe installed lengthwise through the pile center is slotted in widths of 0.010 inch to distribute the vacuum pressure equally over the length of the pipe. The smaller openings provide a more uniform draw on the contaminated soils. Each pipe is surrounded by approximately six inches of filter stone with a median grain diameter of 3/8 of an inch. The vent pipes and the extraction pipe extend through the liner at both ends. The piping configuration is designed to draw contaminated soil vapor atmosphere air radially inward through the pile, flushing the contaminated soil vapor towards the extraction pipe. The vapor flushing method will improve and increase recovery rates and volumes.

The vent pipes at the bottom corners of the pile also function as condensate traps. The vent pipes pitch at a 10% slope towards solid, clear PVC pipe which will collect condensate buildup inside the line. Ball valves installed on the ends of the clear pipe allow the condensate to be drained off. An identical ball valve also has been placed on the downgradient end of the extraction pipe to permit regulation of vapor flow from the pile.

SOIL VAPOR TREATMENT

Contaminated vapor extracted from the pile will be treated to maintain atmospheric air quality standards. A preliminary design has been completed. (Fig. 3).

The estimated maximum influent vapor concentrations of the primary contaminants are: 74 ppm vinyl acetate, 58 ppm methyl ethyl ketone, 38 ppm total xylenes, 14 ppm ethylbenzene, and 5 ppm toluene. These values represent the maximum concentration of the compounds in soil samples collected from the soil stockpile prior to heat sealing the liner.

A blower flow rate between 150 and 350 scfm will be selected which will extract the volume of contaminated vapor in the soil pile every 15 to 45 minutes. These air flow rates will produce the desired vacuum pressure of approximately 40 inches of water.

The vapor stream drawn out of the pile will be directed to a thermal oxidizer which will incinerate the VOCs in a ceramic burner chamber at 1400°F. The minimum destruction efficiency of this unit for these compounds is 95%. Increased destruction efficiency can be obtained by reducing the air flow rates. The estimated operation time of the system to remove the contaminants from the soil stockpile at 250 scfm is 13 weeks.

COST ANALYSIS

Depending upon the objective, excavation and on-site treatment or in situ treatment may prove to be the most cost-effective alternative for remediation of contaminated soils at the site. Typically, the excavation and on-site treatment option is more effective when limited data on subsurface site conditions and occurrence of contaminants are available,

Figure 3
Containment Vapor Treatment
System Flow Diagram

Table 3
Cost of Potential Cleanup Options

ON-SITE TREATMENT		IN-SITU SYSTEM	
Excavation	$ 12,486.00		
Excavation Monitoring	8,018.00		
Extraction System Design	6,130.00	Extraction System Design	$ 8,371.00
Extraction System Materials	22,187.00	Extraction System Materials	17,300.00
Extraction System Construction	12,500.00	Extraction System Construction	10,202.00
Extraction System Construction Monitoring	8,018.00	Extraction System Construction Monitoring	8,799.00
Treatment System Design	5,702.00	Treatment System Design	13,000.00
Treatment System Materials and Construction	15,000.00	Treatment System Materials and Construction	27,338.00
Treatment System Operation	6,000.00	Treatment System Operation	6,000.00
Monitoring System Construction	2,500.00	Monitoring System Construction	8,875.00
System Monitoring	6,000.00	System Monitoring	5,060.00
TOTAL	$104,541.00	TOTAL	$ 104,945.00
Per Cubic Yard	$ 130.68	Per Cubic Yard	$ 131.18

OFF-SITE DISPOSAL		OFF-SITE INCINERATION	
Excavation	$ 12,486.00	Excavation	$ 12,486.00
Excavation Monitoring	8,018.00	Excavation Monitoring	8,018.00
Transportation	100,000.00	Transportation	100,000.00
Disposal	240,000.00	Incineration	1,680,000.00
TOTAL	$360,504.00	TOTAL	$1,800,504.00
Per Cubic Yard	$ 450.63	Per Cubic Yard	$ 2,250.63

especially when excavation of a subsurface storage facility is planned. The cost-effectiveness of this option is obtained through advance planning and preparedness. This goal is accomplished by a system design such as that described in this paper which can be constructed during the excavation operations.

For soils contaminated with hazardous substance list compounds, only four alternatives (other than no action) are available: (1) excavation and on-site treatment, (2) in situ treatment, (3) excavation and off-site disposal or (4) excavation and off-site incineration. Table 3 details a breakdown of costs for these four alternative.

The on-site vapor extraction treatment costs were derived using data on expenditures made during design and construction of the vapor extraction system discussed in this paper. The in situ treatment costs were derived from a vapor extraction design project being performed by JBP at a different site. Although site conditions for the in situ system are different, the design is comparable to what would have been required to remediate soils in situ at the Paint and Varnish Site. The operation costs for the on-site system and the in situ system were based on manufacturer information and the costs of propane and electricity usage associated with a three month operating period for the thermal oxidizer. The off-site alternative costs were derived directly with communications with licensed contractors. All figures are 1990 dollars.[3]

As shown, the off-site alternatives are substantially more expensive than the on-site alternatives. The on-site costs shown for the system described in this paper, in our opinion, represent a near worst case scenario due to the levels of contamination which occurred in the soils, the types of material excavated and the difficulty of the excavation process due to the high levels of vapors.

CONCLUSIONS

Soil contaminated with VOCs can be excavated and encapsulated on-site with an impermeable liner, resistant to chemical and photochemical degradation, secure from human contact and infiltration of precipitation, and designed so that no uncontrolled releases of vapors or leachate occur. Encapsulation is an effective method for temporarily isolating contaminated soils from the environment. Installation of a piping network during soil pile construction prior to encapsulation allows access to contaminated soil vapors inside the liner. By attaching a vacuum source to the piping, the contaminated vapor can be extracted from the enclosed pile, treated and released to the atmosphere. Including vent pipes at strategic locations during the soil pile construction will permit enhanced vapor recovery.

This remediation design is a low cost on-site alternative to soil remediation at sites contaminated with VOCs. This design has particular merit when applied to locations in highly environmentally sensitive areas (i.e., sole source aquifer) where rapid contaminant source removal is the foremost priority. This design also is appropriate in high water table areas or in areas where soil moisture contents are high.

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Operating Principles and Case Histories of Soil Vapor Extraction Systems

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ABSTRACT

An overview of the principles and use of soil vapor extraction, or SVE, is presented. In many cases, SVE provides an economical and practical approach to mitigating hydrocarbon-contaminated soils.

The implementation of SVE measures are demonstrated for both silt-sized, very fine grained sands and for coarse grained soil matrices, for shallow water table as well as dry (moist) soil conditions and for volatile and semivolatile contaminants. Special emphasis is placed on the soil conditions, contaminant characteristics and SVE system operating variables.

Two case histories are presented to demonstrate the effectiveness and simplicity of an SVE system as well as the importance of design and operating considerations. In the first case history, gasoline contamination of a shallow water table aquifer resulted from a leaking underground storage tank located in southeastern Canada. The site was mitigated in 1982 using SVE. Though site conditions were not optimum for SVE application, the shallow water table coupled with a very fine grained soil matrix produced a 'wick effect' which enhanced the impact of SVE on residual gasoline in the capillary fringe.

The Canadian case shows the effect of marginal soil permeability and a high water table/capillary fringe condition on the volatile organic compounds (VOC) removal efficiency of a typical SVE system. The impact of induced, atmospheric air recharge to the SVE system also was evaluated and was determined to have little or no impact on the SVE system efficiency. However, the subject SVE operation successfully extracted approximately 7 gallons of gasoline per day from the SVE impact zone.

The second case history, recently completed in California, involved both light-end volatile chemicals and heavier semivolatiles in a dry, generally coarse, permeable soil matrix. In the California case, a 40-foot thick unsaturated soil zone afforded excellent SVE pressure distribution and effect. The VOCs were removed over a 9-month period of SVE operation, while the majority of the semivolatiles were biodegraded in conjunction with the SVE-induced aeration of the contaminated soils. Approximately 5 gallons per day of product were removed from the impact zone.

INTRODUCTION

Soil vapor extraction (SVE), or soil venting, has been commonly used to remediate hydrocarbon-contaminated sites since the late 1970s. As current trends indicate, SVE is fast becoming the in situ soil treatment method of choice for many sites contaminated by hydrocarbons and other volatile organic compounds (VOC). Two decades of using SVE for soil air containment and interception and for soil remediation have provided the engineer and scientist with many examples of effective site cleanup and mitigation.[2]

In general, SVE is the removal of volatile constituents from unsaturated soils using a vacuum, or negative pressure source. The SVE equipment (exhaust pump or blower, production wells, piping, vapor aftercooler and knockout drum, and granular activated carbon (GAC) canisters, if required) is easily deployed and installed. The appropriate SVE deployment and operating requirements for a specific site are determined from pilot studies which are used to define the design criteria.

Following regulatory approval of the system operation and configuration, VOC contamination can be mitigated within a matter of months. Contaminant concentration gradients which may threaten the public health (ambient air, adjacent structures, the groundwater quality, etc.) may be effectively reversed shortly after implementation of the SVE program.

SVE is a generally nondisruptive, cost-effective technology which can be coupled with conventional pump-and-treat methods to remove adsorbed contaminants from unsaturated soils. Free product removal is an attainable goal, while containing and extracting the VOC contaminant, restricting hydrocarbon migration to the water table and minimizing overall cleanup time[1,5] are attractive results of SVE implementation. Moreover, while removing soil vapor, the negative pressure created within the soil zone also enhances the extraction and removal of carbon dioxide generated during the dieoff of bacterial growth within the soil pores.

These biomasses are associated with biodegradation of the 'heavy-end' semivolatiles,[8,16] those hydrocarbon molecules having carbon numbers greater than C_{12} or C_{14}. Aeration of the biomass stimulates biodegradation while withdrawal of the carbon dioxide waste product permits active biomass regrowth.

SVE is commonly used to extract lighter volatile compounds from the vadose and capillary zones of the subsurface soils (the unsaturated zones lying above the water table). The SVE procedures also effectively minimize secondary contamination of the water table due to percolation of groundwater downward through contaminated soil zones. SVE also aids in reducing floating hydrocarbons on the water table by enhancing volatilization from the surface of the floating product, often as a result of the wick effect encountered in fine grained capillary fringes.[4]

Factors influencing desorption of a compound from the soil, diffusion into the soil air and into the atmospheric air are the soil's adsorptivity, the soil-water partition coefficient and the solubility, vapor pressure and Henry's Law constant for the VOC molecule. The speed with which this desorption and diffusion takes place is a function of the soil porosity, grain size, moisture content and bulk density and the chemical characteristics of the compound and the operating characteristics of the SVE system.[14,15] The next section of this paper describes

these variables and the diffusion mechanism in detail.

PRINCIPLES OF SOIL VAPOR EXTRACTION

Basically, SVE is the volatilization of a chemical compound from a soil matrix. The physical and chemical processes by which this occurs comprise a co-dependent suite of actions and reactions which determine the rate and degree of volatilization and subsequent success of an SVE project.

Volatilization, the basic mechanism of SVE, relies on the ability of a compound to evaporate or volatilize to the soil-air atmosphere from a nonvapor environment. Various mathematical models and procedures have been developed which help to evaluate this process.

These methods of analysis permit the estimation of chemical concentrations in the soil as well as the volume of the compound diffused to the soil air and subsequently to the SVE system discharge. Such analytical methods should be used as indicative tools and are considered reliable only when corroborated by the results of field conditions as defined by pilot studies, performance results and field and laboratory measurements.[21]

Mobility Factors

Volatilization of a compound from a soil particle requires desorption of the compound from the soil and subsequent migration of the compound to the surface of the soil particle or soil layer. The rate of movement of the compound to the soil surface significantly impacts the length of time required to remediate a site and the cost-effectiveness of an SVE program.

A successful SVE program is defined by attaining a controlled rate of soil vapor extraction by which an appropriate chemical vapor concentration is maintained at the soil surface. An equally appropriate rate of removal of that vapor occurs such that the flux of chemical vapor away from the soil surface to the atmosphere neither limits nor reduces the ability of the compound to continue to migrate from the soil surface and into the soil moisture surrounding the particle with subsequent diffusion into the soil vapor.

The relative volatility of VOCs when not adsorbed on a soil particle or soil layer can be determined from the vapor pressure and water solubility of the subject compound. VOCs of low water solubility will volatilize quickly from water if little or no sediment is present; likewise, colloidal materials, if present, will limit such volatility. Thus, volatilization of compounds from a water-atmosphere interface is a relatively simple process; VOC volatilization from a soil-water-air interface is more complex.

The equilibrium distribution of the soil-water-air matrix is affected by the inherent saturated vapor pressure of the compound; the vapor pressure at the soil surface; the compound solubility; the adsorption coefficient; the various soil-water, compound-water and compound-air partition coefficients; Henry's constant; and the rate of movement of the compound to the soil particle or soil layer surface.

The two processes most critical to SVE success are the movement of nonvapor and vapor from the soil particle to the particle surface (or from a layer of soil particles to the layer surface) and the movement of vapor away from the soil surface to the atmosphere. The two most common mechanisms of VOC movement to the evaporating surface (the surface of the soil particle or soil layer and the thin layer of soil moisture which lines the soil pores), include molecular diffusion and convection.

Both convection (mass flow in the evaporating soil moisture) and advection (soil vapor transport within the soil pores) as well as molecular diffusion (within the soil and at the soil surface) often occur together during SVE processes.[13] These factors are addressed in the following two sections which describe the transport mechanisms of VOCs to the soil particle surface and from the particle surface to the soil air.

VOC Flux within the Soil Layer

The initial volatilization rate of a compound from the soil surface will depend on the compound's vapor pressure at the soil surface. This is determined by the adsorptive interaction of the compound with the soil[19] and by the presence or absence of soil moisture. Where water is not present and able to evaporate from the particle or layer surface,

molecular diffusion dictates the rate of compound movement.

Thus, the presence of soil moisture on and within the soil layer enhances the volatilization of a compound; it increases the desorption rate of the compound, subsequently increasing the vapor pressure of the compound within the soil pores. Conversely, the evaporation of soil moisture increases the adsorption of the compound to the drying soil, thereby reducing the volatilization rate. Without soil moisture, molecular diffusion must occur and the VOC concentration must be sufficiently high whereby the VOC can migrate to the soil surface in a nearly pure form.

As well, the soil bulk density, percent compaction and effective porosity are important factors in the effective transport of VOCs from the soil surface to the soil vapor and to the atmosphere. The chemical characteristics of the subject compound are also particularly important as the vapor pressure, water solubility, basic structure and molecular charge affect such critical factors as adsorptivity and volatile fraction.

VOC Flux from the Soil Surface to the Soil Air

The flux of VOC as a vapor and nonvapor from the soil particle or soil layer surface to the soil vapor within the soil pores is a diffusion-controlled mechanism. The compound moves into the soil moisture or through a thickness of soil water of at least one monolayer (a one-molecule thick layer of water surrounding the particle) and into a solution phase and thence to the soil air in the vapor phase.

As described in the preceding section of this paper, the absence of soil moisture of less than one surrounding water monolayer minimizes the compound volatility. In such circumstances, the compound concentration must be sufficiently large that adsorption to the soil surface is exceeded by direct vapor-phase diffusion of the compound from the soil surface to the soil air. Diffusion pathways of a VOC usually include a vapor-phase and/or as many as three nonvapor phases. The three nonvapor or liquid-phase diffusion pathways include water-to-water, air-to-water and water-to-soil.[21]

These nonvapor phases or pathways are significantly slower than vapor-phase diffusion. However, significantly greater volumes of compound are usually found in the liquid phase (adsorbed to the soil particles or layers and in solution in the soil water contained in the capillary fringe of the unsaturated zone).

Moreover, the rate of vapor-phase diffusion is generally higher than liquid-phase diffusion; the vapor-phase diffusion coefficient is approximately 10,000 times greater than the solution) or liquid-phase coefficient.[21] Thus, a soil water-soil vapor partition coefficient of 1 x 10^{-4} (the distribution of the VOC in grams per cubic centimeter in soil water divided by the distribution of the VOC in the soil air in grams per cubic centimeter) defines the approximate point where vapor/nonvapor phase diffusion becomes dominant.

Thus, the partition coefficient of a compound (soil water-soil air) can be used to predict diffusion pathways. Partition coefficients much less than 1 x 10^{-4} indicate diffusion pathways in the vapor phase whereas compounds having partition coefficients much greater than 1 x 10^{-4} will likely diffuse in the solution phase.[21]

Vapor phase diffusion, which would dominate SVE-induced effects, is inversely proportional to the soil vapor pressure.[6] That is, a decrease in the ambient soil air pressures between the soil particles produces a proportional increase in the diffusion of the compound vapor from the soil-water phase to the soil-air phase.

Moreover, without at least one water monolayer about the soil particles to permit such diffusion, the volatilization rate of the compound once again depends on the compound concentration and subsequent liquid-phase diffusion to the soil surface. Liquid-phase diffusion is much slower than vapor-phase diffusion and reportedly occurs at a rate of only a few centimeters per month.[21]

Nevertheless, total mass transport of the compound by vapor-phase diffusion often equals that of the total transport of compound through the three nonvapor, or liquid phases.[21] The application of negative SVE soil air pressures (decreased ambient soil air pressures) has been demonstrated to significantly enhance the total mass transport of the vapor-phase compound.[3,4]

Release Mechanisms

Adsorption of the VOC to the soil is a critical factor affecting the release of the compound to the soil air during SVE operations. The adsorptivity of the soil matrix (organic fraction; clay content; relationship to compound charge and structure; and the general available surface area of the soil) will affect the chemical activity of the compound and subsequently reduce the vapor density and volatilization rate. Adsorption will reduce the soil-water partition coefficient and limit the amount of available compound for partitioning between the water monolayer and the soil air.

The concentration of the compound in the soil air will depend on this soil-water partition coefficient which in turn is dictated by other previously mentioned parameters, including:

- The soil/soil vapor temperature
- Soil moisture content
- Molecular diffusion coefficient
- Vapor-phase diffusion coefficient
- Solution-phase diffusion coefficient
- Compound partition coefficient
- Ambient and atmospheric vapor pressure
- Soil characteristics (grain size, density, porosity, etc.)
- Rate of air flow over the evaporating surface
- Soil particle geometry and roughness coefficient
- Compound structure (polar/nonpolar, charge, etc.) as well as the changing physical environment induced by the SVE process itself

Upon desorption of the compound from the soil to the soil water, the VOC can then move from the soil water to the soil air depending on its partition coefficient. The concentration of the compound in the soil water will determine the vapor density of the compound in the soil air surrounding the soil particle.

The general formula for VOC partitioning into an adsorbed, solution and/or vapor phase when spilled or leaked to the soil zone has been expressed by Spencer[19] and Jury (University of California, Riverside) as:

$$C_T = (p_A) + (\theta)(C_L) + (a)(C_G) \qquad (1)$$

where

C_T = the total quantity of compound per soil volume
C_A = the adsorbed chemical concentration in ug/g
C_L = the dissolved compound concentration in ug/cm^3
C_G = vapor density in ug/cm^3
p_b = soil bulk density in g/cm^3
θ = volumetric water content
a = volumetric air content

Henry's constant is expressed as C_G divided by C_L; i.e., vapor density divided by dissolved chemical concentration. This constant is dimensionless (ug/cm^3 over ug/cm^3).

Thus, Henry's constants may be used to predict the partitioning and mass transfer effects of VOCs in the soil/ soil-water/soil-vapor system. Calculated or laboratory values such as the distribution coefficient, K_D, and the organic carbon partition, or adsorption coefficient, K_{OC}, can then be used to determine relative vapor-pressures and densities in the soil air surrounding the soil particles. The relative volatility of the compound in the soil given specific physical conditions can then be calculated using the compound's vapor pressure, solubility and adsorption coefficient. Both Spencer[19] and Ehlers[6] have demonstrated this procedure for calculation of lindane volatilities in various soil matrices.

Other factors affecting the release of VOCs to the vapor phase include the polarity of the compound itself. Organic compounds that are weakly polar (nonionic) require low concentrations of the compound in the soil to achieve a saturated vapor phase. Moreover, the weakly polar compounds will volatilize much more easily than strongly polar compounds given equivalent increases in temperature and chemical concentration. Note that the compounds that exhibit weak polarity are also significantly affected by decreases in the soil moisture content; a soil

moisture film less than one monolayer thick significantly reduces the vapor pressure of that compound in the soil pores.

For VOCs that are weakly polar, the organic carbon partition coefficient (or adsorption coefficient) is a significant factor in the release of VOCs to the vapor phase. An increase in the organic matter in the soil increases adsorptivity and decreases vapor pressure; thus, the potential volatility of the compound also is reduced.

Highly polar compounds which exhibit ionic molecular bonds are more affected by the presence of clay minerals rather than organic matter. The ionic VOCs may exhibit reduced vapor pressures and volatilities due to a high adsorptivity on specific clay minerals. The majority of the more volatile compounds are not ionic, are weakly polar and exhibit high adsorptivity on organic matter.

Other physical factors which affect the release of VOCs to the soil-water and subsequently the soil-vapor phase include temperature and rate of air flow across the soil surface. Increased temperature increases vapor pressure and thus volatility. Temperature also affects the soil-water adsorption/desorption equilibria whereby increased temperature will accelerate molecular diffusion and mass transport of the compound to the soil surface.

In general, Henry's constant will increase significantly with increasing temperature (the more volatile compounds are less soluble in warmer water [soil moisture] and therefore produce greater vapor concentrations and densities with increased temperatures). Therefore, with increased temperatures, vapor-phase diffusion increases while mass transport of the compound and liquid-phase diffusion remain stable or decrease.

However, increased temperature and, in a similar manner, excessive airflow across the soil surface will dry out the soil moisture. Reduction of the soil water to less than one monolayer inhibits vapor-phase diffusion and volatilization. Vapor density is decreased and volatilization is reduced. Note that induced airflow across the soil surface enhances vapor-phase removal through ambient pressure reduction and encourages biomass growth and VOC biodegradation if appropriate airflow rates are applied.

An important consideration when discussing air flow effects is the occurrence of a stagnant boundary layer of soil vapor adjacent to the soil particle through which molecular diffusion of the compound must occur. With SVE-induced soil air flow, this stagnant boundary layer is replaced by a moving face of turbulent soil air. The geometry of the soil (effective porosity, granularity and tortuosity) determines the effectiveness of the induced air flow.[17]

The following table demonstrates the relationships of the various release and attenuation factors as well as volatility characteristics of specific VOCs.[9,10] Some of these characteristics are discussed in the succeeding sections of this paper which describe two SVE case histories.

COMPOUND	HENRY'S CONSTANT (atm-m^3/mole)	VAPOR PRESSURE (mm Hg at 25 C)	ADSORPTION COEFFICIENT*
vinyl chloride	1.07×10^{-2}	2660	0.40
acetone	3.67×10^{-5}	231	very low K_{oc}
benzene	5.43×10^{-3}	95	32 – 143
trichloroethylene	1.03×10^{-2}	69	100
toluene	5.94×10^{-3}	28	37 – 178
dichlorobenzene	1.80×10^{-3}	2.3	300 – 2500
naphthalene	4.83×10^{-4}	0.082	400 – 1000

* based on a 'standard soil' type

Given the above Henry's constants and vapor pressures, it is apparent that compounds such as vinyl chloride and acetone have excellent volatilities and are amenable to SVE. Their low adsorption coefficients also reduce the potential for attenuation to the soil matrix.

In general, the extraction of these and similar compounds is easily accomplished by minimal generation of negative soil air pressures within the pore spaces of the soil and continuous movement of soil air across the soil/soil-water surface. High pressure soil air extraction as opposed to low) and moderate-pressure extraction, usually is not required unless the soil matrix is poorly permeable.

The implementation of SVE for compounds like trichloroethylene

and toluene is well suited to granular soil matrices (moderate to good permeabilities with minimal amounts of clay and/or organic matter). The vapor pressures of these compounds are moderate; they have appropriate Henry's constants. However, their adsorption coefficients are also moderate, thus there is an advantage to an extraction site which exhibits a low percent of clay and organic matter in the soil matrix. The presence of such clay and organic matter may increase the potential for attenuation of these compounds which will subsequently limit their potential volatilization.

Also, as suggested by the above table, SVE of dichlorobenzene and naphthalene generally is not cost-effective given the low vapor pressures of these compounds and their comparatively high adsorption coefficients. If organic soils and clays are present, the potential for effective volatilization of these compounds is severely limited. In general, the biodegradation effects generated in the soil matrix due to the aeration of the soils will have a more significant impact on the concentrations of these and other heavy-end VOCs than the SVE process itself.

OPERATING REQUIREMENTS AND VARIABLES

Based on the discussions presented above, the applicability of a cost-effective, efficient SVE program will depend on the chemical nature of the compound involved and the physical environment in which the compound has been introduced. The physical environment may be modified by the operation of the SVE system to increase the volume of VOC extracted from the soil; conversely, inappropriate operation may reduce volatilization rates to ineffective levels. The factors which most significantly impact the operation of SVE systems are described below.

Site Conditions

A site investigation carried out prior to SVE implementation establishes the site history and general site conditions. The investigation addresses the general amount of contaminant believed lost to the soil and the distribution of VOCs and other compounds in the soil (and groundwater if appropriate), the depth to groundwater and the local geologic variations encountered at the site.

The site condition factors which are most important to the successful operation of an SVE program include:

- The areal extent and distribution of the VOCs in the subject area
- The depth to groundwater (shallow vs. deep water table)
- Rainfall and infiltration rate (migration of surface water into the unsaturated soil zone)
- Location of soil matrix heterogeneities (clay and/or organic matter, grain size changes, etc.)
- Ambient temperature and atmospheric pressure
- Location and type/use of nearby structures

During the site investigation phase of a SVE design, these factors are evaluated in an effort to determine the applicability and cost-effectiveness of the proposed SVE mitigation measure. These conditions must be evaluated as the investigation proceeds to maintain an overall understanding of the project as well as to develop the most appropriate SVE design.

Sound engineering principles and practices are then applied to the SVE designs and implementations to assure cost-effective mitigation of soil contamination. The use of equally sound hydrogeologic and geologic principles insures implementation of an appropriate SVE system design which accommodates the specific soil type, condition and other environmental factors of the subject property.

Soil Properties

Typical soil properties defined during the site investigation include particle size distribution, soil structure, porosity and permeability. These properties, which are used to determine the depositional environment of the subject soils, sometimes reveal preferential soil-vapor flow patterns that may permit 'short-circuiting' of the SVE pressures. This short-circuiting may result from layers or zones of coarser-grained sediments and similarly intervening layers of less permeable clays and silts. Thus,

the distribution of fine-grained soils (very fine sands, coarse silts and clays) will not only impact contaminant distribution, but also will deflect and direct SVE pressure distributions.

As addressed earlier, one of the dominant factors determining the success of any SVE system is the soil moisture content. This factor has a significant impact on the ability of the soil to permit diffusion from the soil particle, through the surrounding soil moisture and into the soil vapor between the soil particles. However, soil moisture also impacts soil plate count (the quantification of existing microorganisms that may biologically degrade the VOC) and influences soil pH. The pH of the soil can significantly affect microbial populations. In general, a healthy microorganism biomass is dependent on the subject VOC concentrations, the soil moisture and pH, and the soil/soil vapor temperature.[8]

Thus, where the subject VOC is marginally acceptable for SVE (exhibits ionic bonding and is not weakly polar, has a low vapor pressure and has a high adsorption coefficient, etc.) the presence of natural microbial populations in the soil may enhance the removal of these compounds. Moreover, where natural populations of such microbes are lacking, they may be artificially introduced and subsequently encouraged through addition of soil nutrients and soil moisture.

Control Variables

Following the decision to use SVE as a mitigative measure, existing blower configurations with appropriate pressure and flow ratings should be selected. Numerous companies prepare explosion proof skid-mounted blowers, filters, condensate collection bowls and electrical switches required for SVE implementation.

SVE design parameters include installation of the extraction well near the center of the soil contamination. Generally, the SVE effect is to enhance migration of soil air from adjacent areas across and into contaminated soils thus minimizing cross-contamination of the adjacent soils.[17,18]

Piping, valving and well materials should be chemically resistant to the soil vapor being extracted. Air flow control valves should have Teflon or Viton seals for prolonged use while other piping materials may include stainless steel or fiberglass.

A particularly important SVE factor which affects operation efficiency is the type of surface cover. During SVE, coarse-grained, nonvegetated soils can channel atmospheric air around well installations as well as directly through the ground surface thus impairing system efficiency. In such cases, the soil may be covered with plastic sheeting or an asphalt surface. This cover will also minimize surface water infiltration and pore space reduction in areas having abundant rain.

The operating requirements of an SVE system include accurately monitoring pressures and VOC concentrations at the negative (or inlet) pressure side of the blower and at the positive or outlet pressure side of the blower. Pressure and VOC measurements prior to and after an emissions treatment unit are also required.

These measurements are then used to demonstrate regulatory compliance; i.e., these measurements verify that the SVE operation is functioning as designed and that VOC emissions to the atmosphere are controlled (where required). The analytical information subsequently is used to calculate product recovery rates as well as to determine when termination of the SVE program is appropriate.

Response Variables

In some geographical locations, vapor emissions must be controlled to minimize degradation of the atmosphere. This factor is especially important in California where most air quality management districts require an operating permit. Included in these permits are strict guidelines for monitoring effluent concentrations, installing and operating soil vapor extraction equipment and implementing effluent treatment measures. Additional permits may include electrical, plumbing, excavation or extraction well permits.

Parameters that should be monitored are pressure gradients within specific soil regimes in the vertical and lateral directions from the SVE well. Additional SVE program verification parameters include the final

areal and vertical distribution of VOCs, final moisture content and volume of VOCs removed.

CASE HISTORIES

The application of SVE programs to the mitigation of VOC-contaminated sites can be aptly demonstrated by the following two case histories. The first example involves the remediation of gasoline-contaminated soils in the vadose zone of a shallow water table aquifer located in southeastern Canada. The SVE program was implemented in May 1982. The SVE measure was implemented as the final phase of groundwater and soil cleanup at the subject property.

Case 1: VOC Extraction from a Shallow Aquifer Vadose Zone

The subject property is located in southeastern Canada near the Lake Ontario shoreline. The site was a former service station located near residential and commercial properties. Attention was focused on the service station property as a source of leaking hydrocarbons when reports of gasoline odors in the station and adjacent structure prompted a site investigation. Implementation of free-phase product removal and SVE procedures followed the completion of the site investigation.

The SVE program was originally designed to intercept gasoline vapors migrating from the free-phase product pools floating on the shallow water table. The hydrogeologic conditions at the site were appropriate for groundwater/product recovery wells and SVE production wells. Though the aquifer in which the gasoline leak occurred was comprised of coarse silt-sized aeolian (windblown) sand and was subsequently very

fine-grained, the permeability of the unit was, nevertheless, acceptable for SVE.

The shallow water table (12 to 14 feet below grade) limited the vertical extent of the SVE pressure generation and the unsaturated aquifer thickness available for well screen installation. However, the shallow depth to water and the height of the capillary fringe were not significant problems in this specific application.

SVE System Design

The design of the SVE testing and implementation program included the construction of four gas production, or hydrocarbon recovery, wells located as shown in Figure 1. The wells consisted of 8 feet of 2-inch diameter schedule 40, polyvinylchloride (PVC) pipe and 4 feet of 2-inch diameter stainless steel well screens. Each pipe/screen assembly was placed in an augered 6-inch diameter borehole and backfilled with coarse sand to 3 feet below grade. The remaining borehole/PVC pipe annulus was then filled with a cement/bentonite seal.

The recovery wells were connected to a simple forced-draft blower system (12-in. water column, negative pressure exhausters) installed on the roof of the subject service station. The blowers and piping configurations are shown in Figure 2.

Figure 2
Wells and Fan piping Configurations
Canadian Case History

Figure 1
Location of Gas Production Wells
Canadian Case History

The blowers were operated in sequence or in parallel depending on the need for increased negative SVE pressures or for increased soil-air volume. Two fans operating in parallel produced an approximate doubling of the flow volume of the system with minimal reduction in negative inlet pressure. Connecting the exhausters in series approximately doubled the static pressures at the exhauster inlet while maintaining minimal volume reduction. No emissions treatment or monitoring of soil vapor concentrations was required by the local agency.

Given the comparatively poor permeability of the silt-sized sands at the site, increased negative SVE pressures were desirable. Connecting

the two exhausters in series achieved this effect.

The SVE program included various consecutive phases of pilot testing. These phases were designed to determine the most appropriate method of VOC extraction from the shallow vadose zone of the water table aquifer.

The Canadian SVE pilot tests included:

- A Phase 1, short-term extraction of gasoline VOCs and soil vapor from the vadose zone with limited soil air recharge
- A Phase 2, long-term SVE test coupled with induced atmospheric air recharge
- A Phase 3, long-term SVE test coupled with natural soil air recharge

The following discussion describes the results of the Phase 2 testing of the system. In this phase, SVE was coupled with enhanced recharge of atmospheric air along the site perimeter.

The program was restricted to a circular area having a 20-foot radius from a centrally located group of soil air extraction wells. The perimeter of the test area was a natural soil vapor recharge boundary created by opening to the atmosphere the vadose zone wells located immediately outside the 20-foot radius.

The unsaturated thickness of the soil zone above residual gasoline (floating product) was 12 to 14 feet. The capillary fringe containing water, gasoline and soil air immediately above the water table was calculated to be 3.4 feet thick.

The following equation was used to calculate height of capillary rise.

$$h_k = 0.45 \times (\frac{1-\sigma}{\sigma}) \times (\frac{1}{d_{10}}) \qquad (2)$$

where

h_k = height of capillary rise
σ = porosity
d_{10} = average effective diameter of the soil particles as defined by grain size distribution curves and as measured in millimeters

In the uniform, silt-sized very fine aeolian sand deposits of the subject property,

σ = 0.3
d_{10} = 0.1

therefore

h_k = 3.4 feet

Estimated Hydrocarbon Removal Rates

Using a height of capillary rise of 3.4 feet, a gasoline vapor recovery area of 1,260 square feet (with a radius of 20 feet) and the data measured during the Phase 2 pilot test, the volume of gasoline recovered per day was calculated.

Two methods of calculation were employed. The first calculation, based on mass diffusivity and mass flux laws in a binary gas system,[7,18] was used to calculate theoretical gasoline vaporization in the 40-foot diameter test circle. The second calculation, using standard gas coefficients and measured SVE volumes and vapor concentrations, was used to calculate actual gasoline volumes generated.

In the first method, calculation of mass diffusivity and flux in a binary gas system, where the system was assumed to contain air and n-hexane at 1 atmosphere (atm) pressure, 80% relative humidity, and 60 °F, the following equation was used:

$$D_{AB} = 0.0069 \frac{T^{\frac{3}{2}}}{P(M_A^{\frac{1}{3}} + M_B^{\frac{1}{3}})^2} \sqrt{\frac{1}{m_A} + \frac{1}{m_B}} \qquad (3)$$

where

T = Degrees Rankin
P = 1 atmosphere
M_A = molecular volume of n-hexane C_6H_{14} in ft^3 /lb mole
M_B = molecular volume of air in ft^3 /lb mole
m_A = molecular weight of n-hexane C_6H_{14}
m_B = molecular weight of air

Upon calculation,

$$D_{AB} = (6.9 \times 10^{-3}) \frac{(520)^{\frac{3}{2}}}{[1][(140.6)^{\frac{1}{3}} + (29.9)^{\frac{1}{3}}]^2} \sqrt{\frac{1}{86.2} + \frac{1}{27.4}} \qquad (4)$$

D_{AB} = 0.26 ft^2/hr

With these calculated values, mass flux N was determined using the fictive film theory and mass transfer process:

$$N = \frac{\rho D_{AB}}{\delta} \ln \frac{P_a}{P_a - P_g} \qquad (5)$$

where

D_{AB} = coefficient of diffusion in ft^2/hr
σ = density of air in lb$_m$/ft^3
δ = film thickness in feet (capillary equation h_k)
P_a = pressure of 1 atm (14.7 lb/in.^{2})
P_g = vapor pressure of gasoline = 2 lb/in.^{2}

Using the above calculated and assumed factors,

$$N = \frac{(0.076)(0.26)}{3.4} \ln \frac{14.7}{12.7} \qquad (6)$$

therefore

N = 8.5 x 10^{-4} lb$_m$/hr-ft^2

The gallons of gasoline vaporized in the system over a period of one day can then be calculated. Using an average density of gasoline of 6 lb$_m$/hr-ft^2, the value of N was calculated to be 8.5 x 10^{-4} lb$_m$/hr-ft^2. Thus, the volume of gasoline volatilized in gpd as V can be calculated:

$$V = \frac{(t)(A)(N)}{\rho_g} \qquad (7)$$

where

t = time in hours
A = area of film surface in ft^2
N = mass flux in lb$_m$/hr-ft^2
ρ_g = the average density of gasoline in lb$_m$/gal

By substituting these variables and constants in the equation for V,

$$V = \frac{(2.4 \times 10^1)(1.26 \times 10^3)(8.5 \times 10^{-4})}{6} \qquad (8)$$

approximately 5 gallons per day (gpd) of gasoline are theoretically recoverable from the SVE impact zone.

A second method for calculating V, the volume of gasoline recovered per day, was used as a check on the validity of the above calculations. Using measured flowrates and gasoline vapor (as hexane) concentrations recorded during the pilot study, the following calculations were made:

Q_{AB} = discharge rate of air and n-hexane mixture at exhaust stack of gas extraction unit in ft^3/min

C = concentration of n-hexane vapors in discharge as a percent total sample volume

ρ_{AB} = density of air/hexane mixture in lb/ft^3 at a discharge temperature of 80 °F, a relative humidity of 80%, and a pressure drop of 1 inch Hg induced within the fan

ρ_g = average density of gasoline in lb/gal

Given the above values, the calculated value of V is

$$V = (Q_{AB})(C)(F)(\rho_{AB})(\frac{1440}{6}) \qquad (9)$$

V = (70)(0.02)(0.3)(0.070)(1440)/6

and the calculated recovered gasoline volume was determined to be approximately 8.5 gal/day.

The calculated values obtained from the two methods used to estimate the volume of gasoline, V extracted per day from the SVE impact

zone are approximately 5 and 8.5 gal/day, respectively. These values suggest an average gasoline recovery rate of approximately 7 gal/day.

Results

The Canadian case history demonstrated the effectiveness of SVE for removal of VOCs (in this case, volatiles associated with a gasoline spill) from a silt sized, fine-grained unsaturated sand as well as from the capillary fringe. The effectiveness of SVE in similar soil and site conditions has been documented by Hutzler.[11,12]

Of particular note, is the volume of gasoline vapor that was removed from the soils at a moderate SVE pressure. Even with fine-grained soils and a system configuration such that atmospheric air was allowed to recharge the perimeter of the SVE area, effective VOC removal was achieved. If the atmospheric air recharge had been eliminated (as it was during subsequent full-scale operation of the system), the areal extent of the negative soil-vapor pressures would have been increased and the volatilization rate enhanced. Soil-vapor pressures within the pore spaces would have become more negative, thus increasing the flow of soil air across the particle surface and allowing more compound to volatilize into the pore space.

The increased negativity of the soil air pressures also would have encouraged greater extraction of VOCs from the capillary fringe due to the shallowness of the water table and the significant rise of water and floating product into the fringe area (a result of the very fine-grained character of the soil and the wick effect enhanced by the SVE). The following case history further demonstrates this general advantage of limiting atmospheric air recharge to a SVE system.

Case 2: VOC Extraction from Thick Unsaturated Soils

In accordance with a California county's (County) guidelines for the monitoring of underground storage tanks (UST), a site investigation was conducted on the subject property. The subject investigation indi-
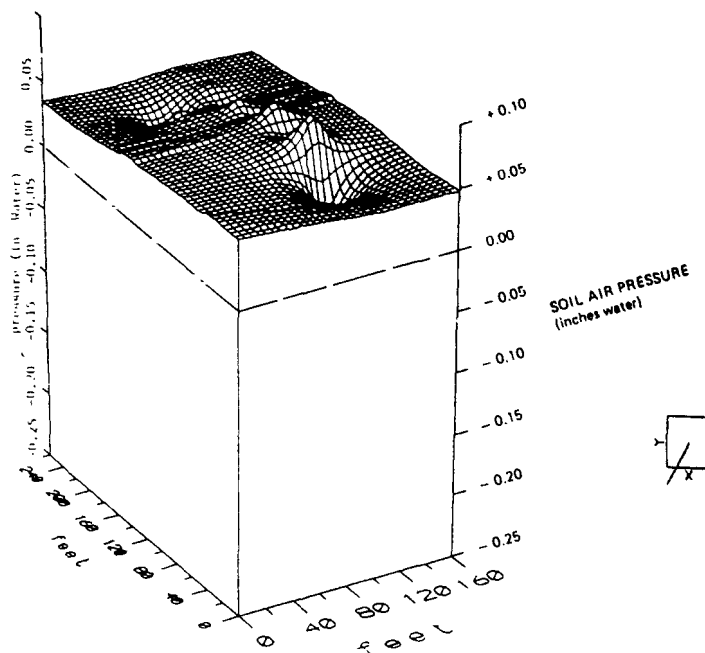
Figure 4
Soil Vapor Pressures at One Hour Before SVE Startup,
California Test

Figure 3
Pilot Test Well and Monitor Location Grid,
California Case History

Figure 5
Soil Vapor Pressures at One Hour after SVE Startup,
California Test

cated hydrocarbon leakage from one UST and possible leakage and/or spillage in other localized areas of a UST facility. Chemical analyses of soil samples collected near the USTs indicated that the hydrocarbons present were generally light-end to moderate and heavy-end oils (not gasoline) with low levels of aromatic compounds.

The County approved SVE as an acceptable mitigation procedure if such hydrocarbon volatilization could be verified by: (1) development and demonstration of a degradation curve showing a leveling-off of total VOC concentrations in the soil-air extracted from the subsurface soils (2) by final verification samples of the subsurface soils showing reduc-

tion in the amount of hydrocarbons in the soil as originally documented at the site.

Soil samples collected during the site UST excavations and prior to SVE implementation indicated the presence of hydrocarbons in the soil at concentrations of 10,000 to 100,000 milligrams per kilogram (mg/kg) in three general areas of approximately 10,000 square feet each. Upon facility closure and initiation of a SVE pilot program, three hydrocarbon recovery wells were installed in the highest soil contamination areas.

In addition to recovery well installation and subsequent pilot testing, an air quality management agency permit process for the control of VOC emissions was implemented. A formal risk analysis was performed and County approval was received. The potential risk to the public health generated by the pilot test emissions was assessed and the risks (with emissions treatment) were accepted as reasonable. The results of the pilot study indicated that effective VOC removal and treatment could be accomplished at the site using SVE. The results of the pilot test are demonstrated by Figures 3 through 5. The pilot test generated an appropriate SVE impact zone which encompassed the site.

Regional and Site Geology

The property of concern is located in an area of continental deposits of coarse gravels and fine-to-medium sands and silts. The local geology near the site has been defined through various test drilling programs conducted during earlier UST investigations as well as during the SVE program.

The surficial sediments in the subject area generally consist of moist, poorly graded sand with minor clay/silt interbedding. These granular surface deposits appear to average 35 feet in thickness and are reportedly separated from an underlying, deeper sand and gravel unit by 55 feet of silty clay.

On the property, surface water infiltration is inhibited by the concreted plant surface area and by the paved surfaces surrounding the plant. No water table has been observed in the shallow sand deposits. All monitoring and recovery wells which were installed to the aquiclude contact at 35 feet below grade evidenced dry to moist soils (no standing water).

SVE System Design

The SVE system employed the basic fundamentals of volatilization; i.e., the extraction of hydrocarbons from the soil surface and from liquids contained within the soil pores. The soil-air extraction system provided the impetus to promote volatilization of the VOCs through generation of negative pressures in the soil pores and enhanced movement of soil-air across the soil particles and adsorbed VOCs. The soil-air extracted from the SVE impact zone was ultimately directed through granular activated carbon where the VOCs were adsorbed before discharge to the atmosphere.

Factors which directly affected the degree and rate of hydrocarbon volatilization included the equilibrium distribution of the VOCs in the soil air, the amount of soil moisture and the type of soil matrix as well as the vapor pressure, solubility and adsorption coefficient of each VOC. SVE not only increased the rate of VOC volatilization from the contaminated soils, but also enhanced the growth of naturally occurring aerobic and facultative bacteria which, in turn, increased natural biodegradation of the heavy-end (C_{12} to C_{14} range and up) spectrum of the hydrocarbon compounds.[3]

System Components

The SVE system included two 4-inch diameter recovery wells screened from 15 to 35 feet below grade. The recovery well locations were selected based on their location in the center of the inactive UST facility and the contaminated area.

The recovery wells were connected to a SVE centrifugal blower/exhauster via buried 4-inch polyvinylchloride (PVC) pipe. Soil vapor extracted from the wells and containing the volatilized VOCs was pumped through a vapor aftercooler (to lower the vapor temperature), a knockout drum (to collect condensed water vapor) and a backdraft valve (to prevent desorption of the granular activated carbon [GAC] during system shutdown).

Ultimately, the extracted soil air passed through two 1,000-pound GAC canisters connected in series to the SVE system. The cleaned soil vapor was exhausted to the atmosphere via a 2-inch diameter PVC pipe leading from the final GAC canister to a discharge point located above the existing plant roof line.

Field Monitoring

The effectiveness of the SVE system was monitored using four distinct methods. These methods consisted of GAC canister breakthrough monitoring, measurement of VOC concentrations at numerous vadose zone monitoring wells, soil vapor pressure response measurement

Contour Interval = 40 ppm

SCALE 1":40 feet

LEGEND

—40— OVM CONCENTRATION CONTOUR, ppm (dashed where inferred)

⊕ VADOSE ZONE MONITORING WELL

⬦ RECOVERY WELL
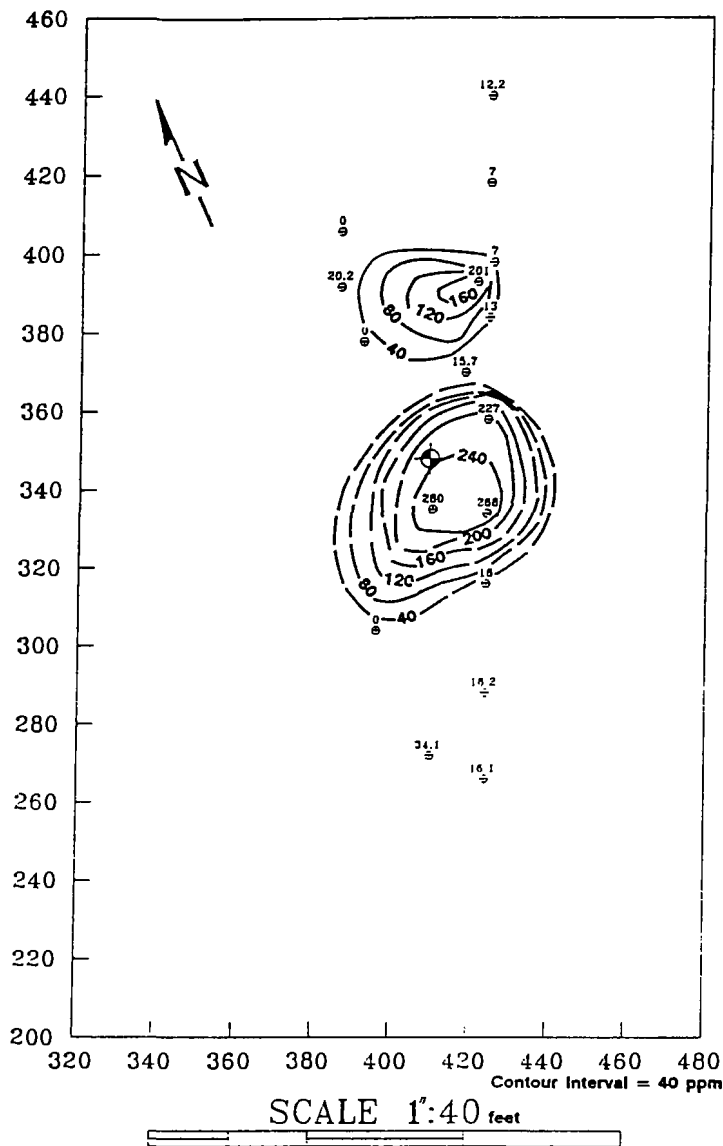
Figure 6
VOC Concentrations in Soil Vapor before SVE Operation,
California Program

throughout the subject property and periodic monitoring of the system's flowrate.

Using an organic vapor monitor (OVM), the VOC concentrations in the surrounding vapor monitoring wells were monitored to track the effectiveness of the SVE system over time. Prior to the testing and sampling of the ambient soil vapor monitoring wells, each well was purged and sampled with the OVM and the maximum VOC concentration was recorded. Contour maps illustrating the OVM data are included in Figures 6 and 7.

The negative soil-air pressures created by pumping the vapor extraction wells were initially measured on a daily basis (subsequently reduced to weekly measurements) to determine the radius of influence of the soil-air extraction system. The soil-air pressures were measured in inches of water using a low pressure gauge.
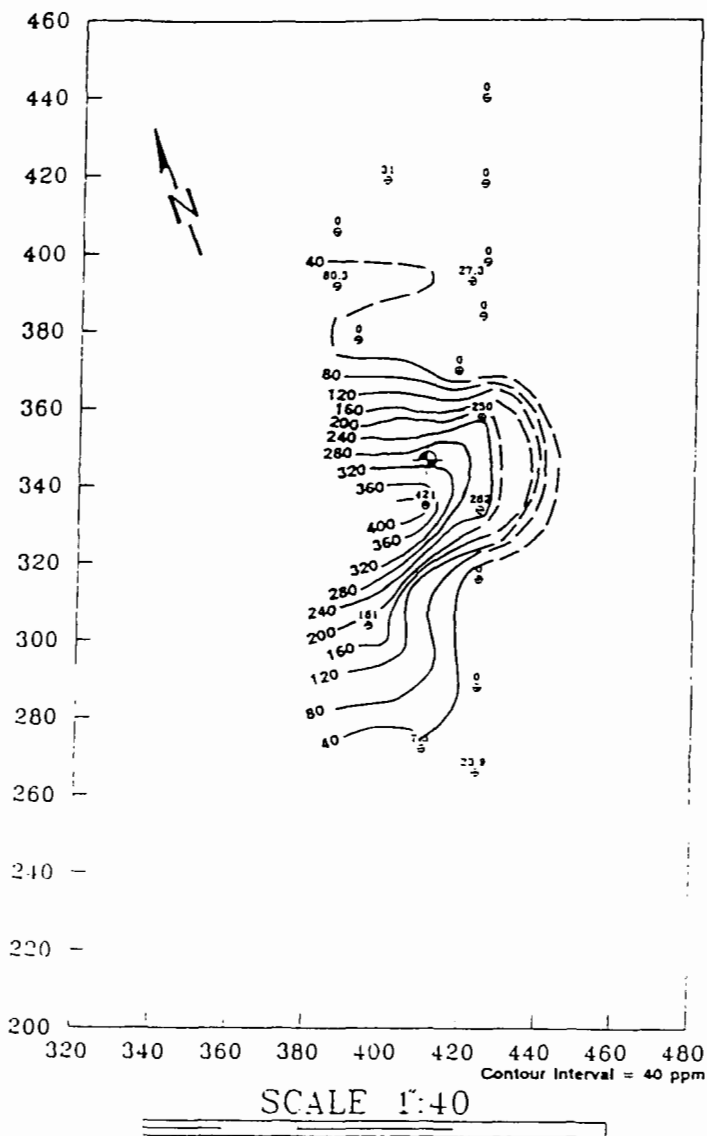
Parameters impacting the soil-air pressures included the pump discharge (or flow rate) and the atmospheric pressure. Barometric pressures and influent vapor temperatures were recorded hourly.

The pump discharge rates (volumes of soil vapor extracted) were measured using an anemometer inserted at the exhaust stack outlet located on the roof of the plant structure. Flowrates recorded during the SVE operation averaged approximately 30 cubic feet per minute.

Soil vapor samples were collected at the exhaust inlet and outlet of the SVE system to enable correlation between OVM field measurements and laboratory analyses. Also, laboratory samples were collected as required by the County's permit for construction and operation of an SVE system.

Each vapor sample was analyzed for total hydrocarbons (TH) as methane and for volatile priority pollutants (U.S. EPA Method 8240). Additional influent soil-air samples were also analyzed for TH as methane on a weekly basis.

Results

The soil-air pressure data were evaluated using the pressure measurements obtained prior to system initiation, at one month after system initiation, prior to system flow rate increase, and after this flow rate increase. Figures 8 through 11 present the soil-air pressure configurations as pressure contours for the specific periods cited above. These soil vapor pressures were consistently negative in the wells nearest the VOC recovery or impact zone.

LEGEND

——— 40 ——— OVM CONCENTRATION CONTOUR, ppm (dashed where inferred)

⊕ VADOSE ZONE MONITORING WELL

◈ RECOVERY WELL

Figure 7
VOC Concentrations in Soil Vapor after two Months Operation,
California Program

LEGEND

——— .04 ——— PRESSURE CONTOUR, Inches water (dashed where inferred)

⊕ VADOSE ZONE MONITORING WELL

◈ RECOVERY WELL

Figure 8
Soil Vapor Pressures before SVE Program Startup,
California Case History

Figure 9
Soil Vapor Pressures at One Month Operation,
California Case History

Figure 10
Soil Vapor Pressures at Two Months Operation,
California Case History

Moreover, the soil-air pressures decreased as the distance from the recovery well increased. These data reflected the expected diminishing radius of influence of the SVE impact zone as distance from the pumping source became greater.

In an effort to demonstrate the reduction in VOC concentrations in the system exhaust over time, the analytical measurements of TH were compared to flowrate; i.e., TH per unit of flow expressed as ppm/scfm was graphed versus time in days since pump startup (Figure 12). Field measurements of VOCs as determined using the OVM were also plotted versus time as shown in Figure 12. Additionally, the total VOCs expressed as TH (methane) were graphed versus time since pump startup (Figure 13).

The heavy-end, lower volatility hydrocarbons remaining in the sub-surface soils at the subject property appeared to be essentially kerosene and mineral oil types having low vapor pressures and moderate adsorption coefficients. These heavy hydrocarbons also appeared to be susceptible to enhanced, natural biodegradation in the soil.

Estimated Hydrocarbon Removal Rates

The estimated hydrocarbon removal rate between GAC canister changeouts was established based on the total operating time between GAC changeouts, average system flow, average TH concentration of the inlet vapors between changeouts, and average molecular weight of the inlet vapor. The following calculation was used to determine V_r, the vapor recovery rate per day:

$$V_r \text{ (lb/day)} = (V_c)/(1 \times 10^6 \text{ ppm}) \times (103.5 \text{ lb/lb-mole})$$
$$\times (1.0 \text{ lb-mole}/385 \text{ scf}) \times (Q \text{ scf/day}) \qquad (10)$$

or

$$V_r \text{ (lb/day)} = (V_c) \times (Q) \times (2.69 \times 10^{-7})$$

where

V_r = vapor recovery rate (lb/day)
V_c = vapor concentration in ppm (by volume)
Q = venting rate (scf/day)

The hydrocarbon removal rates estimated between carbon canister changeouts were then converted to gpd using an assumed liquid hydrocarbon density of approximately 7 pounds per gallon. From system startup through the third GAC changeout, the estimated hydrocarbon removal rate was approximately 1.1 gal/day. Between the third and fourth GAC canister changeout, the estimated removal rate was approximately 5.5 gal/day.

The hydrocarbon removal rate from each GAC changeout was also estimated based on moisture and VOC content in the spent GAC as reported by the GAC recycler. The recycler's analytical results (in percent VOCs) reported for the GAC canisters was multiplied by 2,000 pounds of GAC per changeout (two canisters per occurrence). The total pounds of VOCs were then converted to gallons. This value was subsequently divided by the total number of days between changeouts. The estimated average VOC removal rate was estimated to be approximately 4.5 gal/day.

Results

The California case history demonstrated an application of SVE to
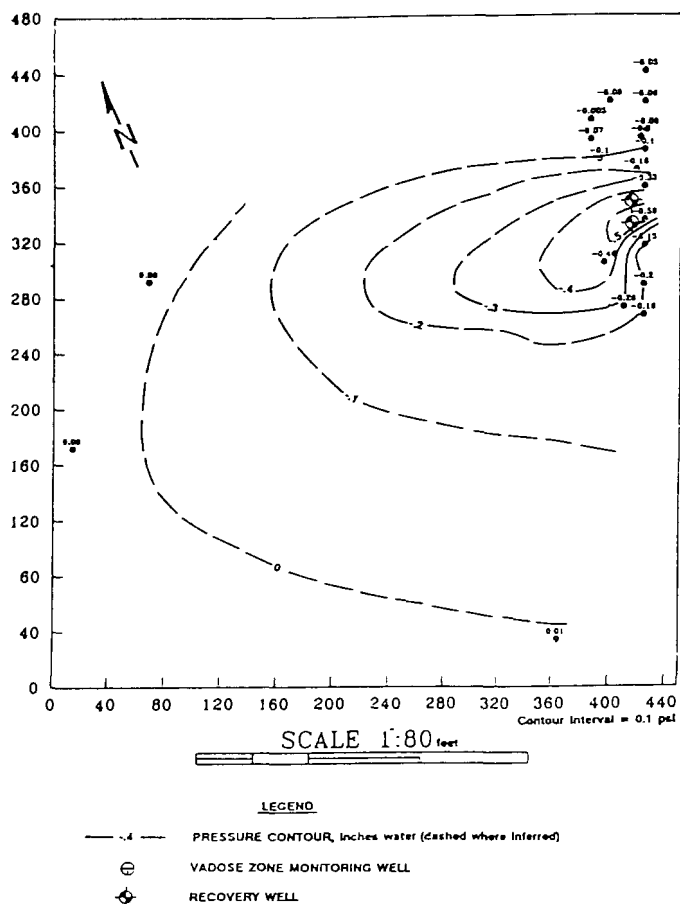
Figure 11
Soil Vapor Pressures at Three Months Operation,
California Case History

Figure 12
Total VOCs per Unit Flow per Elapsed SVE Operating Time,
California Program

Figure 13
Total Hydrocarbons per Elapsed SVE Operating Time,
California Program

an ideal unsaturated aquifer situation (granular soil, thick deposits with generally moist but unsaturated soil conditions, paved surface cover, etc.): i.e., the physical conditions for SVE were ideal. However, the chemical conditions (i.e., compound volatility) were not totally suitable for direct SVE impact.

The results of the project indicated that the light-end VOCs (C_{12} to C_{14} and less) were volatilized and extracted during SVE operation while subsequent soil sampling showed that the heavier hydrocarbons were also affected by the SVE induced biodegradation. The heavy-end hydrocarbons were effectively biologically degraded and their concentrations were reduced.

CONCLUSIONS

The foregoing discussion and case histories demonstrate the applicability of SVE for many different types of soil conditions and remediation requirements. Of particular importance in all cases, however, is the need for a soil type which is amenable to soil vapor flow and movement; a contaminant type which can be volatilized or, at least, biodegraded during SVE operation; and soil moisture which can be controlled and/or replenished by manipulation of the natural soil conditions.

There are a multitude of ways to judge the success of an SVE operation. The surest evidence of a successful site mitigation and soil cleanup is demonstration of:

• Effective SVE pressure generation (appropriate negative pressure contours in the SVE impact zone)
• Measurable volumes of VOCs extracted and discharged to the treatment system
• Reproducible evidence of decrease and/or consistent reduction in VOC concentrations in the SVE emissions

- Acceptable levels of the VOC and other regulated contaminants in the subject soils

These methods, as described in the above case histories, were used to meet regulatory requirements and to demonstrate effective mitigation of hydrocarbon-contaminated sites.

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Reverse Osmosis for Leachate Treatment Case Study: V.A.M., Wijster, the Netherlands

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ABSTRACT

Reverse osmosis installations for leachate processing have already operated for several years. The large unit installed at VAM's waste disposal site in the Netherlands has proven that reverse osmosis is a reliable and useful technology for treating this leachate.

Field experience gained over 2 years with this installation at a processing capacity of 102.5 gpm (154 gpm after expansion) is as follows:

With a two-section system high retention rates can be achieved:

BOD   98.8 %
COD - 99.9 %
N.Kj. - 99.5 %
Cl⁻   - 99.8 %

High retention rates are also achieved for heavy metals and extractable organic halides.

On average, the following effluent quality was achieved:

BOD   2 mg/L
COD - 8 mg/L
N.Kj. 10 mg/L
Cl⁻ - 45 mg/L

The operating costs are roughly consistent with the design and are approximately 1.7 cents per gallon of purified water, or approximately 1.3 cents per gallon of leachate.

The use of cellulose acetate tubular membranes in the first section has proven its worth. A service life of approximately one year was achieved. Using the spiral-wound composite membrane in the second section has also proven its worth, although the achieved service life of approximately 1.5 - 2 years is not yet optimal.

INTRODUCTION

For some years, installations utilizing the reverse osmosis principle have been used for waste disposal site leachate treatment in Europe. A reverse osmosis installation has been operational since 1984 at the waste disposal site in Uttigen, Switzerland, where 13,000 gpd of leachate are processed. The installation is operating in batch mode as a single-pass unit. The RO unit has 1075 ft² of tubular composite membranes. The daily production is approximately 10,500 gpd of permeate and 2,500 gpd of concentrate; the latter stream is returned to the waste disposal site.

Currently, another installation is being constructed for the new waste disposal site in Trliachen, Switzerland.

In Western-Germany, an RO plant has operated at the Rastatt disposal site since 1986. Here, a 5-stage single section unit with a total membrane area of 5920 ft² is being used to treat leachate. The unit processes approximately 50,000 gpd in a fully automatic cycle.

In the Netherlands, there are now two operational units and a pilot

plant. A mobile pilot plant was installed in 1985 at the Bavel disposal site. Since 1987, a two-section installation has been used at the Wieringermeer disposal site, where building and industrial waste is dumped. There is also an on-site composting plant. This RO unit produces approximately 38,000 gpd of dischargeable permeate. The installation at the VAM disposal site went on stream in 1986. More details of this plant are reported in the following section of this paper.

VAM DISPOSAL SITE

N.V. Vuil Afvoer Maatschappij (VAM) is a waste processor, of which the Dutch state is the sole shareholder. Currently, VAM's workforce consists of 170 employees. In 1986, well over 1,000,000 tons of waste from nine provinces and more than 88 municipalities were collected and processed. VAM is one of the largest waste processors in the Netherlands. There has been large-scale waste processing at VAM's disposal site at Wijster in the Netherlands since 1930. Until 1980, the waste was mainly composted, but in the last few years mechanical waste separation is rapidly gaining ground. In the years ahead, developments will focus on the composting of biological waste (> 50,000 tons/year) and processing of residual waste partly to produce RDF (refuse derived fuel), which will be used as a fuel for power generation plants.

The Problem of Water

Until 1975, there was an annual water shortage because of the water consumption of the composting process. Since then, this shortage has gradually changed into a water surplus as a result of some operational adjustments, for instance:

* Lower water consumption in the composting process
* Enlarging the disposal site area
* Improved drainage and other actions which were taken for environmental protection.

Since 1979, the framework governing the overall water issue has been structured. This structuring, as a result of government regulations, resulted in the following package of measures:

* Reorganization in order to limit volume of wastewater. The following were created based on the quality of wastewater streams: white, grey and black water. Buildings were disconnected and work was started to cover the site.
* Determination of the ultimate wastewater stream
* Research into the purification potentials of various processes.

In anticipation of the findings of a research project, a temporary solution was found in the off-site discharge of the wastewater to the sewage treatment plants at Beilen and Hoogeveen. Additionally, the equalization (holding) capacity was enlarged to 26,400,000 gal. and a simple prepurification process was installed.

A water management plan was prepared, in which the annual wastewater stream to be purified was calculated to be approximately 63,400,000 gallons. This figure was based on:

- The operating conditions as they will probably be in 1996
- A wet year every other year.

Searching for an Appropriate Purification Method

In 1984, research was done to develop a purification technology which would be suitable for wastewater. Several systems and system combinations were checked for:

- Quality of the effluent that would allow it to be discharged into a regional sewage water treatment plant or into surface water
- Optimum and maximum conditions (capacity and retention)
- Operational at high and low temperatures.

The following systems were investigated:

- Submerged nitrification system
- Activated sludge plant
- Denitrification plant (with addition of methanol)
- Activated sludge with nitrification and denitrification
- Physico-chemical treatment (precipitation with flotation)
- Reverse osmosis installation

Some of the findings are shown in Table 1.

Table 1
Survey of Systems, Effluent Grades and Costs
(VAM Wijster)

System	Effluent (ppm)					Costs (1985, $cts/gal)
	COD	BOD	NH4-N	NOx-N	SO4	
Discharge into surface water						
Activated sludge + physico-chemical post-purification	1500	5	<2	<5	500	1.2
Two-section RO	10	1	8	<1	<1	1.2
Single-section RO + activated sludge	40	2	2	2	11	1.1
Discharge into the sewerage						
Activated sludge + physico-chemical post-purification	1500	50	100	<100	500	1.0
Single-section RO	75	10	240		11	1.1

This research shows that:

- Systems not working on the reverse osmosis principle are unsuitable for the production of dischargeable water
- The biological purification method unsuitable, because many substances cannot be sufficiently biologically degraded
- When used alone, reverse osmosis is relatively expensive, but it produces a dischargeable effluent
- The costs are in the region of 1 to 1.2 cents per gallon. of clean water at a capacity of 127,000 gpd (on the 1985 price basis).

Selection of Purification Method

The selection criteria for the purification system were as follows:

- Discharge requirements, i.e. Cl- and COD (Table 3)
- Water quality and cost of treatment systems
- Availability of relatively inexpensive energy (landfill gas)
- System flexibility (uprating, disconnection, etc.)
- Avoiding odor
- Guarantees for reliable operation, etc.
- Area required for installation

In the end a two-section reverse osmosis system, with tubular mem-branes in the first section and spiral-wound membranes in the second section, was selected.

Design

Together with Grontmij consulting engineers, Stork Friesland has designed a purification installation for VAM's wastewater. The inlet capacity is 102.5 gpm; 79 gpm can be discharged off into the surface water as permeate. In its basic configuration, this installation is suitable for being enlarged to an inlet capacity of 154 gpm and a purified and dischargeable effluent capacity of 119 gpm (which was achieved in 1988).

Process Description

The RO process is shown in Figure 1. The water is filtered in a reversible flow filter (200 μm), so the largest dirt particles are removed to protect the high pressure pumps. Subsequently, the water is heated to approximately 25 C in three heat exchangers. In the feed tank, the leachate is mixed with the concentrate from the second section and the pH is lowered to approximately 6.7 by the addition of sulphuric acid. The first section is fed from this feed tank by a plunger type pump. The pressure is approximately 500 psig. There are six stages to separate the feed into dirty and clean water streams. The concentrate generated in the first section (dirt) is temporarily returned to the disposal site. The clean permeate from the first section is sent into the second section. The second pass is fed from a buffer tank and through two filters (10 μm). The concentrate from the second section is returned to the feed tank of the first section. The permeate from the second section is discharged into the surface water. Further data are given in Table 2.
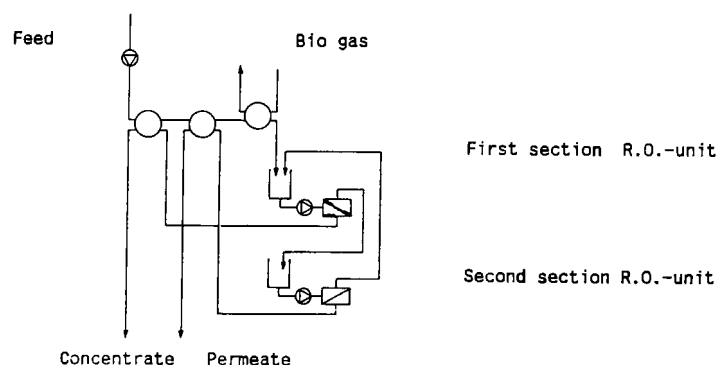
Figure 1
Process Concept: Reverse Osmosis Process

Table 2
Design Data of the RO Installation

	Design (1986)		After enlargement (1988)	
	First section	Second section	First section	Second section
System	tubular	spiral	tubular	spiral
Number of stages	6	4	7	6
Membrane area sqft	15,540	4,960	22,900	7,440
Leachate gpm	102		154	
Feed RO gpm	126	102	187	151
Permeate gpm	102	79	151	119
Concentrate gpm	23	23	35	32

Tubular cellulose acetate membranes are used in the first section of the RO unit, because of the:

- Presence of undissolved substances in the feed
- Possible deposition in the concentration process
- Minor.risk of tubular membrane clogging
- Ability to be mechanically cleaned

- Potential for chlorine disinfection
- Low membrane replacement cost

Spiral-wound composite polyamide membranes are used in the second section, because of the:

- Good quality of the permeate coming from the first section
- Small space required for fitting the spiral modules
- Low cost (investment and power consumption)
- High retention rate

FIELD EXPERIENCE AT VAM, WIJSTER

Feed and Permeate Quality

Since January 1987, data on the quality of the feed and effluent of the RO installation have been collected. Each week COD and BOD, Kjeldahl-nitrogen and chloride contents as well as the pH have been established. Figure 2 shows the COD results as a function of time since 1987. Generally, the COD is rising. The fluctuations are not consistent with particular periods, i.e., summer or winter. The chloride content shows the same fluctuations and the same trend as the COD. The average composition over the period January 1987 to February 1988 is shown in Table 3, which also indicates the average permeate quality. The calculated standard deviations for both parameters are also given.

Figure 3
COD Concentration of the Influent and Permeate of the RO System

Figure 2
Variation of COD and Chlorine of the Influent Leachate
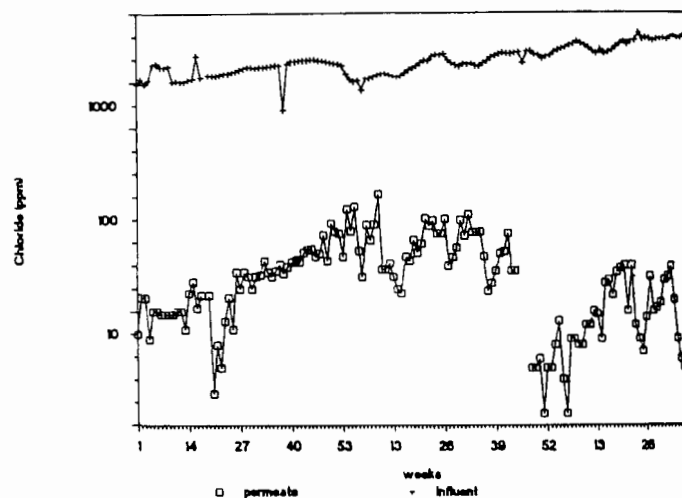
Figure 4
Chloride Concentration of the Influent and Permeate of
the RO System

Table 3
Leachate and Permeate Composition

Value		Leachate		Permeate		Requirement
		Average	Standard deviation	Average	Standard deviation	
pH		8.2	0.2	5.6	0.4	6.5 - 8.5
COD	ppm	1,600	500	8	9	< 100
BOD	ppm	60	55	2	2	< 5
N-Kj	ppm	480	185	10	7	< 10
Cl⁻	ppm	2,250	470	45	30	< 50

Figures 3 and 4 show the weekly trends in influent and effluent concentrations for the COD, N-Kjeldahl and chloride contents, on a logarithmic scale.

A comparison between the effluent and the allowable concentrations, which are proscribed in VAM's discharge permit (Table 3), shows that the average effluent quality (Table 4) satisfies the discharge conditions.

In 1988, the average permeate figures shown in Table 4 were worse for the following reasons:

- Poorer membrane quality
- Higher concentration of influent than envisaged at the design stage

Table 4
Leachate and Permeate Composition

Value	Average annual figures					
	1987		1988		1989	
	Leach-ate	Permeate	Leach-ate	Permeate	Leach-ate	Permeate
pH	8.1	5.6	8.2	5.6	8.3	5.2
COD ppm	1258	4	1726	12	2859	3
BOD ppm	40	2	59	2	217	2
N.Kj ppm	386	8	495	13	955	5
Cl⁻ ppm	2068	32	2287	60	3156	7

The pH-value of the permeate is declining. Generally speaking, the pH of the effluent from the installation has decreased too much. Therefore, before being discharged into surface water, the effluent is passed through a bed with calciferous material and spray aerated. This process increases the pH to 6.5.

Table 5 shows the feed design figures on which the guaranteed performance figures rates have been based. the data also include the concentrations measured in the periods July 1984 to December 1984

(approximately 40 samples), January 1987 to December 1988 (approximately 104 samples) and January 1989 to February 1989 (8 samples).

Table 5
Leachate Composition

Value		Design	7-12/1984	1/87-12/88	1/89-2/89
pH			8.4	8.2	8.3
COD	ppm	3,000	2,870	1,510	2,860
BOD	ppm	300	218	50	220
N.Kj.	ppm	800	750	440	960
Cl⁻	ppm	2,000	2,900	2,180	3,160

In the first two months of 1989, the concentrations (except for the chloride content) are consistent with those of 1984 (measured during the tests done at VAM's pilot plant) and with the design figures. The system performance in this period met the guaranteed performance (Table 6).

Table 6
Comparison of Retention Rates

Parameter		Guarantee	1/89-2/89	1/87-12/88
COD	%	99.8	99.9	99.5
BOD	%	99.7	98.8	95.7
N.Kj.	%	97.4	99.5	97.4
Cl⁻	%	98.4	99.8	97.9

In addition to the above analyses, heavy metal and organic micropollutant concentrations are measured every three months. Since January 1987, eight samples have been analyzed. The average figures are shown in Tables 7, and 8 and Figure 5.

Table 7
Heavy Metal Concentrations (µg/L)

Parameter	Feed		Effluent		Discharge requirement	Retention rate %
	Average	Standard Deviation	Average	Standard Deviation		
Zinc	630	440	27	16	200	96
Copper	170	45	17	14	50	90
Lead	100	15	3	1.5	50	97
Chromium	170	60	2	1	50	99
Nickel	150	40	15	0.5	50	99
Total	1220	600	50		200	96
Cadmium	1.3	0.7	0.4	0.3	25	67
Arsenic	12	4	3	3	10	73
Mercury	0.5		< 0.1		0.5	> 80

All effluent concentrations are lower than the requirements specified in the discharge permit. The heavy metal concentrations expressed as the total of zinc, copper, lead, chromium and nickel are shown in Table 7, which relates to the feed and effluent since 1987.

Capacity and availability of installation

The installation has been designed for the flowrates shown in Table 9. In November 1988, the installation was expanded to its current capacity.

The permeate produced since January 1987 is shown in Figure 6. In the second quarter of 1987, the permeate production was lower, because work was carried out on the installation. In this period some membranes in the first section (stages 4, 5 and 6) were replaced because of fouling. At the same time some adjustments were made to reduce the pH of the feed to 6.7.

Table 8
Concentrations of Organic Micropollutants (µg/L)

Parameter	Feed		Effluent		Discharge requirement
	Average	Standard Deviation	Average	Standard Deviation	
EOCL *	4.9	3.6	0.7	0.6	10
Mineral oil	380	210	<40	-	100
Total PCA**	8.3	6.8	0.6	0.6	10

* = Extractable organic chlorides

** = Polychlorinated aromatics
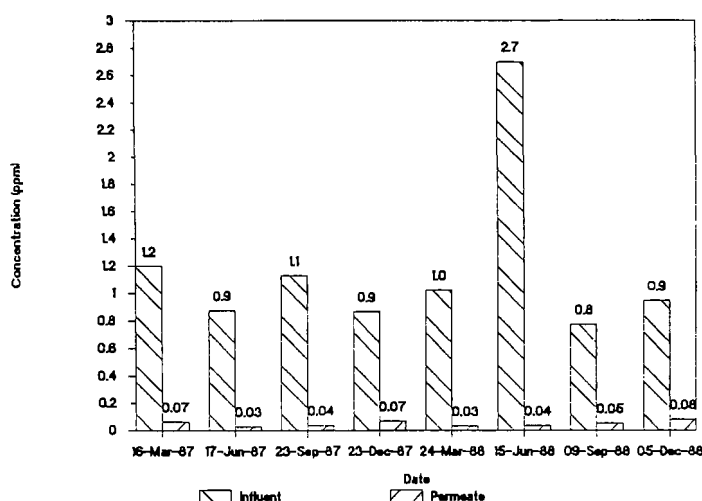
Figure 5
Reduction of Heavy metals Concentrations as a Result of Treatment in the Reverse Osmosis Unit; Summation of Concentrations of Zn, Cu, Pb, Cr and Ni

Table 9
Design Capacities of the RO Installation

		Initial capacity	Uprated
Feed	gpm	102	154
Permeate	gpm	79	119
Concentrate	gpm	23	35
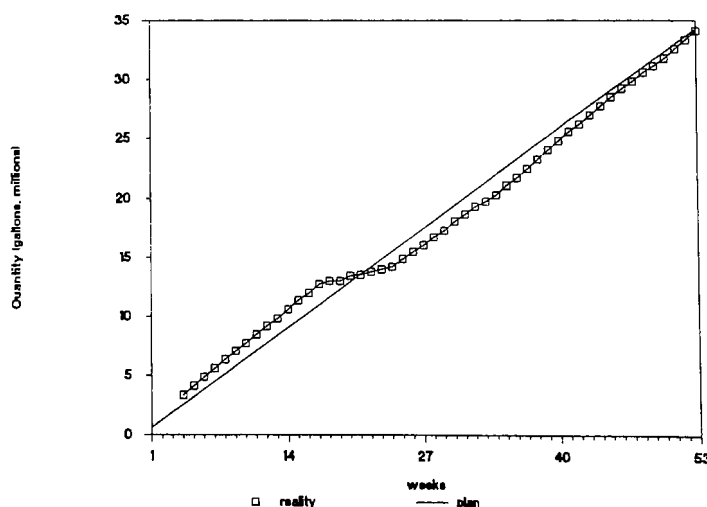
Figure 6
Total Flow Through the Reverse Osmosis System in 1987
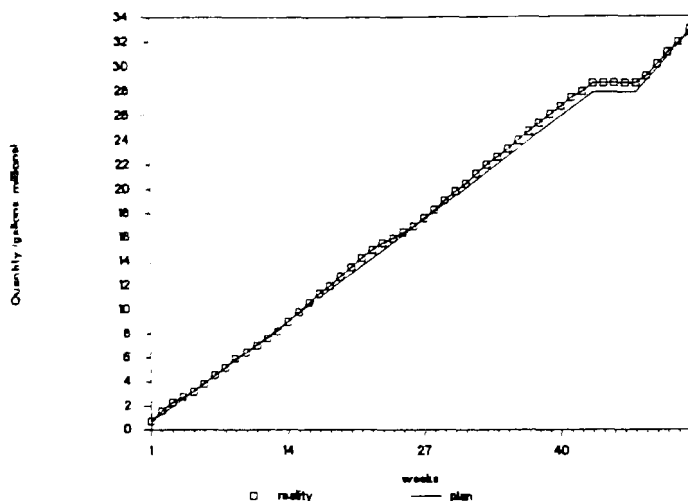
Figure 7
Total Flow Through the Reverse Osmosis System in 1988

In Figures 6 and 7 and the cumulative permeate capacities for 1987 and 1988 are compared with the target figures. The number of operating hours in 1987 and 1988 is shown in Table 10, which also indicates the hours spent on cleaning, maintenance and other outages.

Table 10
Survey of Operating Hours

	1987	1988
- Production	7,158	6,764
- Cleaning		365
- Maintenance]	1,260	374
- Miscellaneous	340	1,257*

In 1987, the availability of the installation was approximately 82%, or, when the downtime for equipment installation is disregarded, approximately 86%. The total production of purified permeate was 34,600,000 gallons.
In 1988, the availability of the installation was approximately 78%, or, when the outage for expansion (580 hours) is not considered, approximately 83%. The total production of purified permeate was 35,000,000 gallons.

CONSUMPTION FIGURES

Power

The installed power of the installation is:
- 1987 182 kw
- 1988 225 kw (after uprating)

The average power consumption per gallon of permeate produced is 0,0044 kwh/gallon. Additionally, gas is needed to heat the leachwater and the building.

Chemicals

The average consumption of chemicals needed to acidify the feed to pH 6.7 was 0.3-0.7 gallon of H_2SO_4/1,000 gallons of leachate.
The total consumption was as follows:
- 1987 79 tons of H_2SO_4 (98%)
- 1988 146 tons of H_2SO_4 (98%)

The consumption of chemicals for cleaning and disinfection of the installation were the following: Ultrasil 53--approximately 220 lb/cleanup--and the disinfectant active Oxonia--approximately 90 lb/cleanup. Moreover, to avoid bacterial growth in the second section,

4.5 lb of active Oxonia are injected daily. The total consumption was as follows:

	Ultrasil (lb)	Oxonia (lb)
• 1987 :	5500	2750
• 1988 :	7700	4200

Manpower Costs

The manpower costs incurred by VAM are shown in Table 11.

Table 11
Manpower and Maintenance Costs

		1987	1988
- Operation	USD	40,000.-	30,000.=
- Maintenance	USD	20,000.-	10,000.=
Total	USD	60,000.-	40,000.=

Membranes

As described, this is a two-section reverse osmosis installation, where the permeate from the first section is subsequently purified in the second section (Table 12).

Table 12
Installed Membrane Area

	First section		Second section	
	Stages	sq.ft.	Stages	sq.ft.
December 1986	6	15,500	4	5,000
December 1988 *)	7	22,900	6	7,400

*) Expansion from 102,5 gpm to 154 gpm.

For membrane replacement, VAM has concluded a multiyear contract with the membrane producer, Stork Friesland. A fixed annual payment is made and as many membranes as are deemed necessary are replaced, by the contractor to ensure optimum system operation and to meet the guaranteed quality and capacity.
The following conclusions can be drawn from the membrane replacements which have taken place so far:

- The membrane replacement in 1987 was caused by premature calcium deposition in the last three stages, which was due to temporarily insufficient acid dosing of the feed.
- The need for the membrane replacement in the second section may partly be explained by a too low retention rate in the first section. The higher concentrations of calcium and organic substances may have contributed to the attack and/or fouling in the second section.
- The service life of the membranes in the first two years proved to be as follows:
  First section, tubular membranes: approximately 1.0 years
  Second section, spiral-wound membranes: approximately 1.5-2 years

It seems as if the service life in the first section of the RO unit is mainly governed by the chemical attack and/or accelerated hydrolysis of the substances contained in the leachate. The length of the service life in the second section seems to be dominated by the combination of:

- A flux decline as a result of fouling caused by bacteria and/or deposits
- A drop in retention rate due to mechanical and/or chemical attack

Membrane Cleaning

Generally, the membranes in the first section can be cleaned without any trouble.
Cleaning procedure:

- Frequency: every 1-2 weeks
- Cleaning agent: Ultrasil 53: 160-220 lb/cleanup
- Disinfection: Oxonia active: 70 lb/cleanup

Mechanical cleaning the first section appears to have little effect, when it is used for leachate processing. It is rarely possible to clean the spiral-wound membranes in case of severe fouling and/or depositing.

Standard cleaning procedure for the spiral-wound membranes:

- Frequency: every 1-2 weeks
- Cleaning agent: Ultrasil 53: 70 lb/cleanup
- Disinfection: active Oxonia: 4 lb./clean up

Costs

The project was implemented in the period from May to December 1986.

Building costs and Investment costs (based on 1 U.S. dollars = 2 Netherland guilders)

RO installation, complete	$1,300,000
Buildings	$220,000
Infrastructure	$230,000
Engineering	$110,000
Total amount	**$1,860,000**

The following investments were needed for the expansion in 1988:
Uprating of the RO installation $500,000

Operating Costs

Based on the operational results described in this paper, the following operating cost calculation was made by VAM. This calculation relates to the RO installation only (Table 13). The following costs were not considered: leachate gathering and concentrate processing.

FURTHER DEVELOPMENTS

Leachate Quality

To improve the feed (leachate) quality, a study is being conducted

Table 13
Operating Costs in U.S. Dollars of the
VAM WIJSTER Reverse Osmosis System

	DESIGN 1986	1987	1988
A. OVERHEAD	230,000	265,500	275,000
B. RUNNING COSTS			
- MAINTENANCE	45,000	40,000	60,000
- MEMBRANE REPLACEMENT	115,000	115,000	115,000
- GAS (7,6 cts/1,000gal.	10,000	10,000	10,000
- ELECTRICITY (5 cents/kWh)	75,000	65,000	65,000
CHEMICALS	10,000	25,000	55,000
- COST OF ANALYSIS	25,000	25,000	25,000
- OPERATION	35,000	40,000	30,000
	315,000	320,000	360,000
TOTAL	545,000	585,500	635,000
C. PRODUCTION OF PURIFIED WATER gpd	98,000	95,000	96,000
COSTS PER GALLON OF LEACHATE ($ CENTS)	1.2	1.3	1.4

into the optimization of nitrification processes in the storage tanks. This may result in lower BOD and NH_4-N-contents in the feed, which may have a positive effect on the permeate capacity and the concentration factor for the RO installation.

Using Tubular Composite Membranes

Based on the tests which were conducted in the Netherlands, Western Germany and Austria in 1988/1989 on the composite membrane for leachate processing, it may be expected that tubular composite membranes will be more widely used for this application, for the following reasons:

- Improved chemical resistance and, thus, an increased life expectancy
- Higher retention rates at the same flux rate.

Table 14 shows retention rate of composite versus cellulose acetate membranes for leachate processing.

Table 14
First Section, System Retention Rate (%)

	Composite	Cellulose acetate
Conductivity	> 90	60 - 80
COD	> 98	80 - 97
BOD-5	> 99	90 - 95
NH4+	> 90	60 - 80
Cl-	> 90	50 70

Concentrate Processing

According to the original plan, the concentrate was to be returned to the waste disposal site, which was actually done in 1987 and 1988. As VAM's waste disposal site does not completely meet the Dutch IBC-criteria (isolation, management and inspection) and a survey in 1988 proved that the water buffer capacity of the waste disposal site is insufficient for returning the concentrate to the waste disposal site for many more years, research was started for a different solution.

According to VAM's plans, a waste-to-energy plant will go on stream in 1995. A portion of the waste that is unfit for composting will be burned in this plant. The residual substances (approximately 450,000 tons/year) will be discarded.

With a view to this development, a final solution for the complete wastewater stream is being sought, which includes processing of the concentrate.

Other options, such as evaporation, steam stripping, drying and nitrification will also play a role in the selection process. In 1988, tests were conducted to investigate the various options for concentrate processing. Table 15 shows the effluent quality that can be achieved.

Table 15
Effluent from Concentrate Processing

	COD ppm	N.Kj ppm	Cl- ppm
RO concentrate (feed)	13,000	3,500	13,000
Evaporation/stripping	100	50	65
Nitrification/evaporation	125	225	65
Nitrification/physico-chemical	6,200	160	13,000

During the evaporation tests, the concentration was up to 15% dry solids. Further concentration by evaporation is possible. In the Netherlands, research is being done into drying of this evaporated concentrate. After mixing with the dried product, the concentrate is introduced into a superheated steam circuit. The product is pneumatically transported through the installation at high speed (65-130 ft/sec.) and the drying process is complete within 5-10 seconds, producing a product with 96% TS. This drying system may offer the following advantages:

- A well-proven technique for a large variety of products and waste streams
- Minimum risk of fouling and corrosion
- A closed system, thus avoiding air pollution
- A sterile end product.

In the preliminary cost calculations for existing leachate projects with a capacity from 20-45 gpm the operating costs for leachate processing in a combined system featuring:

- *Reverse osmosis* (2 sections) with concentrations from approximately 0.5% to 2.5% dry solids
- *Evaporation* with concentrations from approximately 2.5% to 30% dry solids
- *Drying* from 30% to above 96% dry solids are calculated at 5 cents/gallon of leachate. This amount does not include the cost of discharging the end product. These costs are for Europe estimated at 1 to 2 cents per gallon of leachate.

Solidification/Stabilization Treatment of Lead Battery Site Soils

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INTRODUCTION

One of the most frequently detected metals at uncontrolled hazardous waste sites is lead. A major source of this contaminant is former lead recovery operations such as battery cracking. Lead, like any other metal, cannot be destroyed; it can only be converted to another form and will remain in the environment. Therefore remediation schemes should consider lead recovery processes for reuse such as thermal techniques or acid extraction. Residual lead may still be leachable and poses a threat to groundwater. The remediation scheme must then consider technologies which reduce lead mobility such as solidification/stabilization and vitrification. This paper will focus on the evaluation of stabilizing lead-contaminated soil and debris from battery cracking operations.

Lead recovery from battery cracking operations generally consisted of casing cracking, acid drainage and smelting. Residues include chips of casings (ebonite and polyethylene), metal fragments (lead oxide), lead sulfate sludge and slag. These residuals contaminated soil particles and are also categorized as debris.

Recovery operations should be evaluated before any immobilization process is undertaken. Several problems have been encountered in the evaluation of solidification systems applied to battery sites such as lead particles being isolated (unavailable) in fine casing cracks and lead debris fragments being the same particle size as the cleansed soil and being retained on the same screen.[1,2] These processes are being improved.

The goal of solidification/stabilization processes is the reduction of mobility of heavy metals. This immobilization is accomplished by chemical reaction and encapsulation of the metal by a binding agent such as cement. One of the problems of stabilizing lead battery waste may be that the presence of sulfate or lead interferes with the formation of concrete.[3,4]

DISCUSSION

Several variables will affect the results of the stabilization process evaluation. These variables are the type of leach test utilized, the size of the filter used to separate particulate lead from dissolved lead, the type of binding agent utilized and the size and amount of lead particles in the waste. Several leaching test procedures are available to evaluate stabilization including the EP TOX, TCLP, MEP and ANSI 16.1.

Table 1 presents the results of leach tests on stabilized waste from Lead Battery Site A. Substantial decreases in the leaching of lead were obtained by utilizing cement and kiln dust or cement and fly ash. However, the addition of sodium silicate, a common binding agent, shows little mobility reduction (after accounting for dilution).

Table 2 presents the results of leach tests on stabilized waste from Lead Battery Site B. Several binding agents at various binder to soils ratios were evaluated. The data generally show that lead concentration is a function of pH, which is a function of the binder utilized. The cement and lime fly ash binders are capable of reducing leachate concentrations as long as the proper binder to soil ratio is utilized. Cement kiln dust was not effective at all.

Table 3 presents the results of stabilizing soils from Lead Battery Site C. Three different soil types were stabilized with a constant binder to soil ratio of cement. The data show a substantial decrease in lead mobility as evaluated by the TCLP.

Table 4 contains data from Site B with the stabilized waste sub-

Table 1
Lead Battery Site A Stabilization: TCLP Test Data

Binder	E.P. Toxicity (ppm of Pb)
Raw Waste	478.00
Cement + Kiln Dust	0.08
Cement + Kiln Dust	0.09
Cement + Fly Ash	0.30
Cement + Fly Ash	0.20
Cement + Sodium Silicate	318.00
Cement + Sodium Silicate	307.00

Table 2
Lead Battery Site B Stabilization: TCLP Test Data

Binder	Treated Waste Conc. (ppm)	pH
Cement(10%)	500	11.1
Cement(30%)	<0.05	11.4
Cement(60%)	<0.05	11.6
Cement Kiln Dust(10%)	37-150	12.3
Cement Kiln Dust(30%)	16-94	12.6
Cement Kiln Dust(60%)	48-63	12.6
Lime/Fly Ash(10%)	600-700	11.9
Lime/Fly Ash(30%)	<0.05	12.5
Lime/Fly Ash(60%)	2-3	12.5

Table 3
Lead Battery Site C Stabilization: TCLP Test Data

Binder	TCLP (Mg/l of Pb)	pH
Raw waste	287	3.7
Cement (25%)	<0.5	10.6
Raw waste	210	3.6
Cement (25%)	<0.5	10.7
Raw waste	175	3.6
Cement (25%)	<0.5	10.7

Table 4
Lead Battery Site B Stabilization Data from MEP Test Extraction (kng/L Pb)

Extract	1	2	3	4	5	6	7	8
Sample 1	2.9	2.8	25.1	37.5	33.1	40.3	107.3	103.4
Sample 2	3.0	6.1	8.4	5.9	2.4	14.8	39.0	38.2

jected to the MEP procedure. The MEP procedure is designed to mimic continual exposure to acid rain conditions. The test challenges the buffering capacity of the binding system. No clear trend in the data is evident.

ANSI 16.1 test leaching data from these sites were similar to the other leaching tests in that lead concentrations in the extracts were dependent on pH.

Figure 1 illustrates the dependence of lead concentrations on extract pH. These data were derived from both the TCLP and MEP tests on stabilized waste that originated from a metal salvaging operation that did not involve batteries.

(showing that pH is a major factor in Lead Solubility)
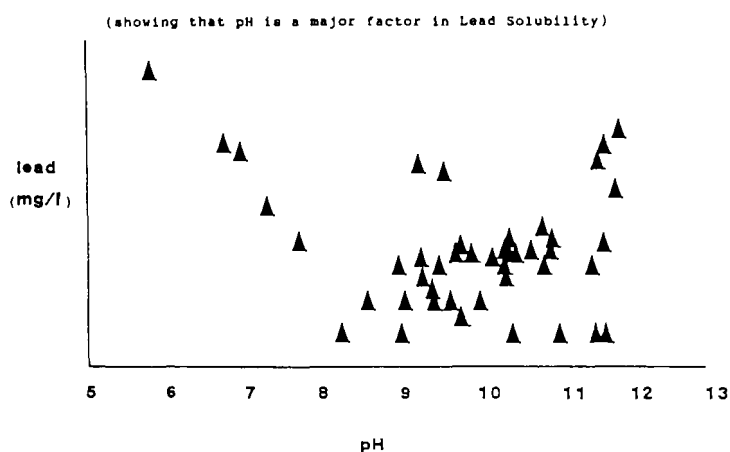
Figure 1
Lead TCLP and MEP Data
(Showing that pH is a major factor in Lead Solubility)

Stabilization Chemistry

The stabilization results from these studies will now be explained chemically. During the solidification/stabilization process of lead with cement, the lead is most likely converted into its most insoluble form, namely lead hydroxide $Pb(OH)_2$ as shown in the following equilibrium equation:

$$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2\ OH^- \tag{1}$$
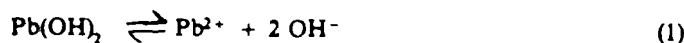
The solubility product constant is then given by the equation:

$$K_{sp} = \frac{[Pb^{2+}]\ [OH^-]^2}{[Pb(OH)_2]} \tag{2}$$

Therefore, K_{sp} is unity since it is a solid.

$$K_{sp} = [Pb^{2+}]\ [OH^-]^2 \tag{3}$$

The literature value for K_{sp} of $Pb(OH)_2$ is 1.2×10^{-15}

Any cement-based binder normally produces a pH of approximately 12 in aqueous solution during mixing with water.

$$\text{Then the } P^{OH} = 14 - pH \tag{4}$$
$$= 14 - 12 = 2$$
$$\text{Hence, } [OH^-] = 0.01 \text{ moles/L}$$

substituting this value in the K_{sp} equation we get:

$$1.2 \times 10^{-15} = [Pb^{2+}]\ [0.01]^2$$
$$\text{Or, } [Pb^{2+}] = \frac{1.2 \times 10^{-15}}{[0.01]^2}$$
$$= 1.2 \times 10^{-11} \text{ moles/L}$$
$$= 1.2 \times 10^{-11} \text{ moles/Kg}$$
$$= 1.2 \times 10^{-11} \times 207.2 \text{ g/Kg}$$
$$= 2.48 \text{ PPT}$$

In essence, only 2.48 ppt of lead can exist in solution (or be environmentally available) at a pH of 12. This calculation clearly reveals that any cement-based binder can immobilize lead readily. On the other hand, when a weak acid-slurry base salt such as

$$Na_2SiO_3 + H_2O \qquad 2NaOH + SiO_2 \tag{5}$$
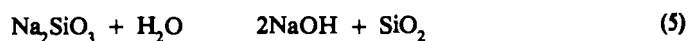
The free NaOH increases the OH^- concentration drastically. This in turn results in the formation of plumbate $[PbO_2]^{2-}$ (6)

$$[Pb(OH_4)]^{2-} \longrightarrow PbO_2^{2-} + 2\ H_2O \tag{7}$$
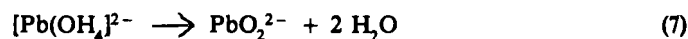
The anionic lead can leach out easily as sodium plumbate which is very soluble in water. The acidity of the leachate in many leaching tests does not impact the pH of the stabilized material.

The dependence of metal solubility on pH as well as the pE of a system is explained in several geochemical textbooks.

One limitation in interpreting metal treatment data is that particulate matter such as colloids may be filtered out before analysis. These colloids can contain metals that may be mobile in a groundwater environment.[5] Small size particulates in drinking water supplies may also be filterable.[6]

CONCLUSIONS

Metal migration from soil and debris from lead battery sites was decreased using various binding agents as evaluated by several leaching tests. The key process variable to control is pH, and one of the key disposal conditions to control is pE. A limitation on data interpretation is particulate lead versus dissolved lead.

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Determination of Ultimate Compliance at an NPL Pump-and-Treat Site

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ABSTRACT

The Western Processing Superfund site is a former industrial waste processing facility located in Kent, Washington, approximately 20 mi south of Seattle. Listed among the 50 most contaminated sites in the nation by U.S. EPA in 1983, an emergency removal and RI/FS identified more than 90 contaminants, predominantly volatile and semivolatile organic compounds and heavy metals in soils, groundwater and surface water.

A Consent Decree for a Phase I surface cleanup was entered in U.S. District Court in August 1984, with more than 200 signatory PRPs. A Consent Decree was entered in U.S. District Court in April 1987 addressing the Phase II subsurface cleanup. The Scope of Work outlines key elements of the remediation and establishes performance criteria for ultimate cleanup and long-term monitoring, including a rigorous 3-year milestone remediation evaluation that was successfully achieved by April 1990.

The 16-acre site is presently undergoing groundwater extraction and treatment, with 200 extraction wells enclosed within a slurry-wall hydraulic barrier that extends from ground surface to more than 40 ft below grade. Extracted groundwater is piped to an on-site treatment plant prior to discharge or infiltration.

Ultimate compliance at the site, as defined in the Consent Decree, revolves around meeting U.S. EPA chronic Ambient Water Quality Criteria (AWQC) in Mill Creek, which bounds the western margin of the site. The Consent Decree requires that the slurry wall be breached after pumping has ceased in order to maintain Mill Creek as a viable location for the evaluation of long-term compliance at the site. However, long-term benefits can be realized by keeping the slurry wall intact after pumping ceases, because it serves as an effective barrier to the transport of contamination toward Mill Creek. Recognizing this, the recent letter from the regulatory agencies overseeing the cleanup to the Court (acknowledging that the consenting defendants have successfully achieved the 3-year compliance milestone) includes a proviso for the development of an alternative means of evaluating ultimate compliance at the site.

Tetra Tech and its subsidiary GeoTrans have been tasked with the development of an alternative means of determining ultimate compliance at the site that will satisfy all involved parties, including methods that can be used to evaluate potential system shutdown scenarios. Quantitative analyses are currently underway to provide constraints on contaminant transport and partitioning mechanisms that will directly effect any evaluation of ultimate compliance at the site. The analyses involve complex interactions of a broad range of contaminants with several media, including contaminant partitioning and transport between subsoils, groundwater and surface water (Mill Creek). Whenever possible, data will also be used to enhance the efficiency of the ongoing

remediation process, including the possible development of enhanced extraction techniques and/or methods for the stabilization/fixation of mobile contaminant constituents.

INTRODUCTION

Western Processing is a former industrial waste processing facility that provided chemical reclamation, recycling and disposal services to more than 400 public and private customers between 1957 and 1983. During its more than 20 years of operation as one of the only approved disposal facilities in the region, Western Processing received wastes from a wide variety of sources. These wastes included fuels, oils, sludges, paints, animal byproducts, brewer's yeast, metal finishing solutions, battery acid and chips, fly ash, cyanide and other waste products. Much of these wastes were reclaimed, recycled, or processed at the site into glue, animal feed supplements, fertilizers, fire retardants, paint pigments, fuels and other saleable products. However accidental releases and spills and the permitted storage of wastes at the site in lined and unlined surface impoundments, aboveground storage tanks, waste piles and other structures, eventually resulted in the contamination of soils, subsoils, surface water and groundwater at the site.

Investigations at the site have identified more than 90 contaminants, primarily volatile and semivolatile organic compounds and heavy metals. The more prevalent contaminants of concern at the site include lead, zinc, cadmium, phenols, toluene, methylene chloride, oxazolidinone (a synthetic fuel component and paint additive) and a variety of chlorinated and nonchlorinated solvents.

Setting

Western Processing is located in an industrialized area within the City of Kent, approximately 20 miles south of Seattle (Fig. 1). The site lies within the Green River valley and is bounded on its western margin by Mill Creek (Fig. 2), which flows in a northerly direction into the Green River, a tributary of the Duwamish River; the Duwamish flows northward, entering Puget Sound at Elliott Bay in an industrialized portion of Seattle.

The Western Processing site is located on flood plain deposits of the Green River that are comprised of complexly interbedded silts and sands. These flood plain deposits overlie similar unconsolidated fine-grained sediments that were deposited in a marine embayment. Together, these deposits house an unconfined alluvial aquifer that extends to a depth exceeding 150 ft below ground surface.

Depth to groundwater in the vicinity of the site varies between 5 and 10 ft below ground surface. Shallow groundwater to a depth of approximately 30-35 ft is in communication with Mill Creek in areas adjacent to the creek; below this level, groundwater moves along a regional gradient in a northwesterly direction at the rate of approximately

100 ft/year. The aquifer reaches its lowest annual levels in the months of August and September, prior to recharge that accompanies the onset of the rainy season, which typically extends from fall through spring. No water supply wells are located in the immediate area.
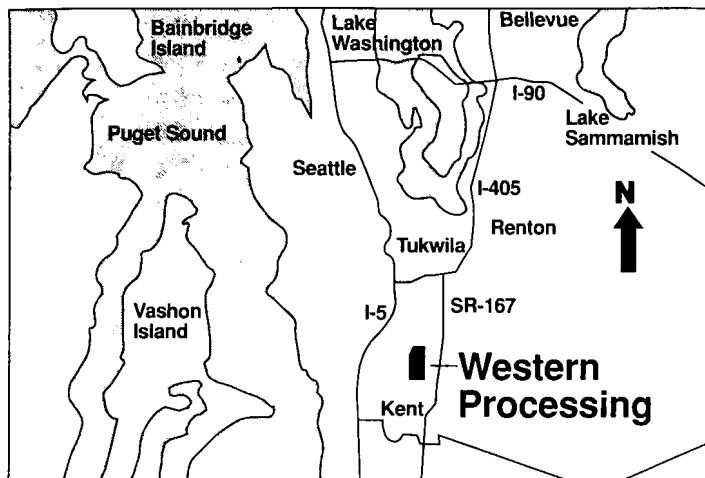
Figure 1
Generalized Location Map
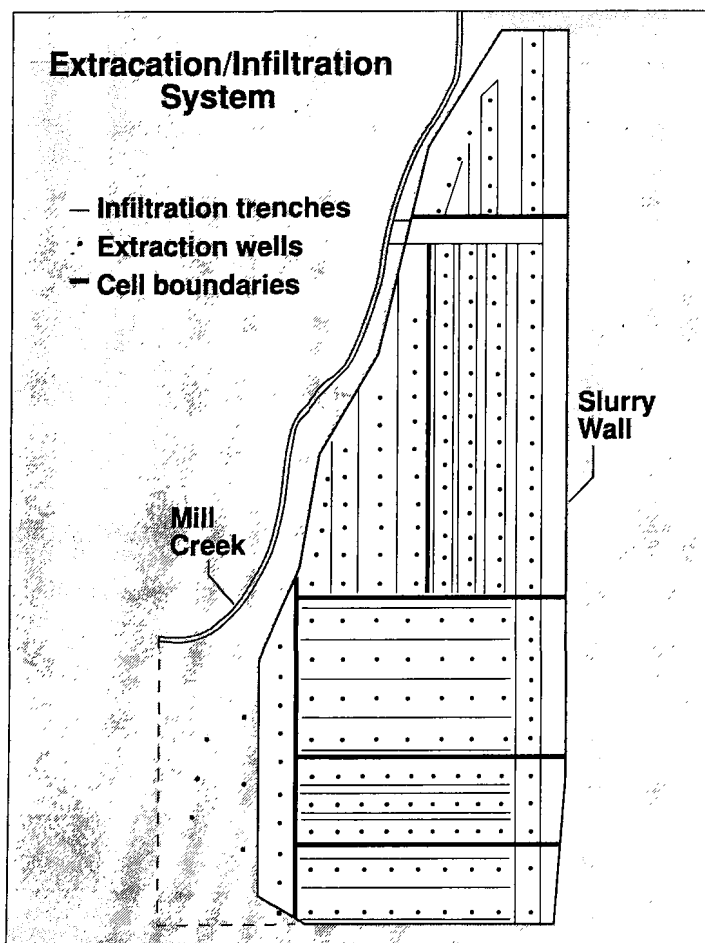
Figure 2
Extraction/Infiltration System Layout and Slurry Wall Trace

REGULATORY AND REMEDIATION HISTORY

Emergency Removal Response

The U.S. EPA closed the site and initiated an emergency removal response in April 1983 to mitigate the threat posed to the public and the environment by the approximately 6,000 drums, 70 bulk storage tanks, 10 surface impoundments, several waste piles and other various structures containing wastes that were present at the site. Drummed wastes included many different acids, bases, solvents, organics, inks and more than 8,000 tons of zinc oxide. Storage tanks containing more than 400,000 gal of liquids, including synfuels of unknown composition, formaldehyde, chlorinated and unchlorinated solvents and other materials were integrity tested and sampled. Surface impoundments for paint sludges, waste solvents, pickling liquor, acid, caustic and cyanide wastes were present, some unlined and others with leaking plastic sheet liners. A large unlined pond containing sludges of varying origin was also present. Waste piles included more than 10,000 tons of fly ash containing heavy metals and 4,000 tons of battery chips.

The Washington State Department of Ecology (WDOE) installed storm water controls to minimize contaminant releases to Mill Creek, which is immediately adjacent to former disposal areas. Hazardous wastes were variously tested and batched for removal, stabilized on-site and shipped off-site for proper disposal over a 75-day period.

Phase I Surface Cleanup

A Consent Decree was entered in U.S. District Court in August 1984, initiating the Phase I surface cleanup at Western Processing. The Phase I cleanup involved the removal of all structures, equipment, tanks, drums and wastes from the surface of the site. More than 2,400 truckloads of various wastes were transferred off-site for treatment or disposal. The site was graded and a stormwater collection and treatment system was installed. A 7,400-gal tank of dioxin-contaminated oily water was treated on-site using a mobile treatment unit that employed a potassium polyethylene glycol chemical process in a low-temperature, low-pressure reaction. The process involved no air emissions or water discharge; a relatively small volume of residual sludge requiring incineration was shipped off-site for treatment. The Phase I cleanup was completed in 1986 after significant delays involving the search for, and application of, the dioxin treatment system.

Phase II Subsurface Cleanup

During implementation of the Phase I surface cleanup, planning for the Phase II subsurface cleanup was undertaken. The Phase II subsurface cleanup planning presented a number of unique challenges, a function of the large number of PRPs; the number, concentration and extent of contaminants in various media at the site; the lack of a well-established experience base regarding large-scale pump-and-treat remediation to draw from; and the resulting absence of an established regulatory history to guide negotiations. Many of the remedial technologies employed at the site were not fully developed or were unproven at the time.

The consenting defendants were organized and led by the Boeing Company, the largest single contributor of wastes to the site. A coordinating committee of Consent Decree signatories (the Trustees) was formed to design a system for cost allocation that attained broad acceptance among the signatory PRPs. This committee was active during the nearly 4 years time that lead to the approval of the Phase II subsurface cleanup plan and remains active in the ongoing remediation. The Phase II cleanup approach was developed by the combined cooperative efforts of the Trustees, U.S. EPA, WDOE and their respective consultants.

The Phase II cleanup was developed and potential remedial alternatives were assessed in accordance with the RI/FS framework outlined in the NCP. The primary elements of the Phase II cleanup were agreed upon and approved by U.S. EPA Region 10, WDOE and, following a public comment and review period, the document was lodged in the form of a Consent Decree with the U.S. District Court on April 10, 1987.

The essential framework outlining the numerous aspects of the cleanup is contained in a Scope of Work included as Attachment B to the Phase II Consent Decree. The Scope of Work establishes critical performance

criteria and standards and outlines the key elements of the project without stipulating the exact design of the subsurface cleanup. The specifics of the Phase II cleanup were established in 30 technical work plans that were subsequently developed to address all aspects of the subsurface cleanup. Each of the work plans underwent separate review and approval by U.S. EPA and WDOE, an iterative process that was ongoing as early work plans were being implemented at the site. This approach allowed the integration of data as it became available, enhancing and refining the quality of the overall remedial approach while allowing cleanup to proceed.

The Scope of Work establishes performance based criteria for the Phase II cleanup, with ultimate compliance revolving around meeting freshwater chronic Ambient Water Quality Criteria (AWQC) in Mill Creek. The following section describes the critical elements of the existing remediation system, which is followed by a brief description of off-site wells and a review of the approaches being taken to evaluate ultimate compliance at the site.

PHASE II REMEDIATION DESIGN AND OPERATION

The Phase II Consent Decree required that a groundwater extraction and treatment system be operated at the site for a minimum of seven years to remedy groundwater contamination beneath the site. In order to achieve this goal, low-permeability wastes present in the subsurface, predominantly fine-grained sludges that originated from surface impoundments, were targeted for removal to permit successful soil flushing.

A drilling, trenching and sampling program was conducted to characterize subsurface contaminants and geology and to define areas requiring removal. Samples were analyzed for hazardous constituents and treatability studies were performed on the subsoils. A specific waste excavation was then conducted prior to the installation of the groundwater extraction system to remove those wastes that would seriously hinder the designed remediation. Over a three month period, a total of 21,900 yd³ of specific waste had been excavated and transported to a U.S. EPA-approved hazardous waste landfill in Arlington, Oregon for disposal. Excavated areas, some extending more than 15 ft below grade, were backfilled with natural permeable materials from both on-site and off-site sources, resulting in subsoil characteristics that would allow successful operation of a soil leaching/flushing system.

Groundwater Extraction/Infiltration/Treatment System

An extraction/infiltration system comprised of more than 200 extraction wells was installed more than a 16-acre area. The extraction wells and infiltration galleries (Fig. 2) were arrayed with respect to subsurface conditions and contaminant concentrations. The extraction cells are arranged in groups comprising seven pumping cells. Within each cell, extraction wells are aligned in rows, with each row separated from adjacent rows by an infiltration gallery. A vacuum pumping system provides draw that can be controlled at several levels: within cells, along a row and at each individual well point. Individual well points are installed to a depth of 30 ft within a casing that is slotted over a 5-ft length and is surrounded by an annular sandpack that includes the screened interval and extends above it approximately 15-20 ft.

Groundwater removal from the extraction wells is piped to an on-site treatment system consisting of two components: (1) a water treatment plant for metals and semivolatile organic compounds removal and (2) an air pollution control unit for VOC removal from the exhaust gas. The water treatment system includes phenol reduction by aqueous oxidation using hydrogen peroxide; heavy metals precipitation/clarification utilizing individual process vessels for pH adjustment, flocculation and clarification; and dewatering of thickened clarifier underflow using a recessed-plate filter press.

Treated groundwater is then pumped to the second component of the treatment process, the air abatement system, where VOCs are removed by hot-air flushing in a stripping tower and are then destroyed in a thermal oxidizer. Fumes from the thermal oxidation unit are cleansed in a wet scrubber prior to discharge to the atmosphere. Effluent water is given a final polish using activated carbon to remove oxizolidinone prior to discharge to a POTW or being pumped into the infiltration galleries located between the rows of well points. The infiltration

galleries consist of perforated pipe surrounded by coarse gravel set in filter-cloth lined trenches.

Slurry Wall

The entire groundwater extraction/infiltration area is surrounded by a slurry wall that extends from ground surface to a depth of 40 to 45 ft below grade. The slurry wall was installed by excavating a trench approximately 30 in. wide and 40-45 ft deep and backfilling with excavated subsoils augmented with bentonite clays and water to form a dense slurry. The slurry wall provides a hydraulic barrier to the lateral movement of contaminated groundwater outward from the extraction/infiltration area, including the entire depth zone of groundwater interaction with Mill Creek. The slurry wall also increases the efficiency of the remediation by preventing the lateral movement of uncontaminated groundwater into the extraction area.

The presence of the slurry wall requires the maintenance of an inward-directed hydraulic gradient along its base to prevent the escape of contaminated groundwater from the extraction area. This is monitored by a piezometer system that includes groundwater measurements obtained from both inboard and outboard of the slurry wall along its entire perimeter (Fig. 3). Piezometers located within the extraction area and at selected locations along the slurry wall trace are completed at different depths to provide the data necessary to calculate vertical hydraulic gradients. These data provide excellent documentation of groundwater behavior at the base of the slurry wall in particular and at the interface between the extraction/infiltration area and the underlying portion of aquifer in general.

Redesign and refitting of the on-site water treatment plant was completed in the fall of 1989, increasing the treatment system capacity from ap!proximately 100 gpm to more than 200 gpm. Strong inward-directed hydraulic gradients have been consistently maintained along the base of the slurry wall since that time, as have upward-directed vertical gradients along the inboard edge of the slurry wall and within the extraction area overall. Downward-directed vertical hydraulic gradients along the outboard edge of the slurry wall have accompanied this trend. The maintenance of beneficial hydraulic gradients at the site is a Consent Decree requirement.

Off-site Wells

In addition to the extraction/infiltration system, four off-site wells are used to capture a VOC-contaminated plume (characterized by cis-1,2-dichloroethene) that extends to the northwest along the regional groundwater gradient (Fig. 3). These wells have a combined pumpage of 40 gpm which is piped directly to the air abatement system, where the VOCs are removed in a dedicated stripping tower prior to discharge or infiltration in the extraction area. The pumping rate from these wells is designed to create overlapping cones of influence to capture the plume; this effect has been documented by aquifer tests.

A series of barrier wells is located west of Mill Creek to prevent off-site migration of contamination (Fig. 3). These wells are present as a contingency in the event that the remediation system cannot prevent contamination from moving off-site; their use has never been required. The barrier wells are presently used as downgradient groundwater monitoring points.

A series of long-term groundwater monitoring wells is located both upgradient and downgradient of the site (Fig. 3). These wells are used to monitor the efficacy of the cleanup and will be points of long-term compliance after groundwater remediation has ceased. Most of these wells are arrayed in clusters of three to four separate completions and are used to monitor multiple depth intervals at the same location. Monitoring well depth intervals in feet below ground surface are: 10-35 ft, 35-70 ft, 70-110 ft and 110-150 ft. The shallow interval corresponds to the zone of interaction of groundwater with Mill Creek; below this level, water travels to the northwest along the regional groundwater gradient as underflow.

The installation of all three of the well systems described above was stipulated in the Consent Decree. A "bank" of several long-term groundwater monitoring wells is held in reserve for future installation at yet

to be prescribed locations to address off-site compliance issues if they arise.

ULTIMATE COMPLIANCE EVALUATION

Geochemical Modeling

The general task assigned to the Tetra Tech/GeoTrans team by the Western Processing Trustees is to estimate the time that the treatment activities must be continued in order to meet the long-term criteria for remediation of groundwater at the site. In order to provide a basis for this estimate, it is necessary to understand the geochemical controls on removal of metals from the subsoils beneath the site, particularly zinc and cadmium. As a first step in this process, water samples were recently collected from selected well points in Cells 5 and 6, the most highly contaminated portions of the area being remediated and are being analyzed to provide information with which to perform geochemical modeling of the groundwater.

These samples are being analyzed for many more inorganic consti-

Well Locations

Slurry Wall

W   Water quality sampling points, Mill Creek, East Drain
M   Monitoring wells
C   Cis-1,2, Dichloroethene extraction wells
B   Barrier wells
P   Piezometers
□   Treatment Plants

Figure 3
Location Map for Long-Term Monitoring Wells,
Piezometers and Off-site Extraction Wells

tuents than have previous samples because of the special needs of geochemical modeling. A list of these parameters is provided in Table 1. Many different redox couples [e.g., Fe(II) and Fe(III), NH_4 and NO_3, Cr(III) and Cr(VI)] are being measured so that the redox state of the water can be determined. It is anticipated that these data will not be consistent, but that, because of kinetic effects, a range of pe values will be computed (pe is the negative log of the electron activity, which is related to Eh). Still, the data will serve as indicators of the approximate redox environment at the site.

Table 1
Inorganic Chemical Parameters for Geochemical
Analysis of Well Point Groundwater Samples

Field Parameters:

    pH, Temperature, Specific Conductance, Hexavalent Chrome

Metals (total and dissolved):

Al	Cr^{+4}	Mn
As	Cu	Mo
Ba	Fe^{+2}	Na
Ca	Fe^{+3}	Ni
Cd	K	Pb
Cr^{+3}	Mg	Zn

Nonmetals (unfiltered):

Alkalinity	Fluoride	Phosphate
Ammonia	Nitrate	Sulphate
Chloride	Nitrite	Sulphide

Total Dissolved Solids

Total Organic Carbon

The analytical data will be used to perform geochemical speciation calculations, using either PHREEQE[1] or MINTEQ.[2] These computer codes calculate the distribution of elements among inorganic species, indicators of the state of saturation of the water with respect to many minerals. Qualitative estimates of the columbic sorptive behavior of metals can subsequently be made based on the charge of the dominant species and on knowledge of the general behavior of common minerals or sorption substrates. Specific sorptive behavior is more difficult to estimate.

Whether precipitation/dissolution reactions are important is commonly estimated based on the value of the Saturation Index (SI) calculated by the model for a number of mineral species. If the SI is approximately 1, then precipitation or dissolution of the indicated mineral may be controlling the water chemistry. Commonly, the rate at which a mineral precipitates or dissolves is too slow to maintain the SI near unity. Because the water sampled had a relatively short contact time (i.e., infiltrated water has a relatively short residence time), the samples are not likely to be saturated (SI less than unity) with respect to, for example, the zinc phases of interest [$Zn(OH)_2$ and $Zn(CO_3)$].

Future steps in this analysis are unclear until the geochemical modeling has been completed and the results analyzed. It may prove beneficial to compare the mass of metals removed against the mass present in the soils before groundwater remediation began, if the preremediation data are adequate. However, because not all of the metals in the subsoil may be mobile, it will not be necessary or possible to obtain 100% removal. The geochemical model also can be used to investigate the feasibility of either increasing or decreasing the mobility of the metals (enhancing metals extraction or causing metals fixation) through adjustment of the chemistry of the infiltration water. If the results are favorable, laboratory testing will be performed to confirm the results.
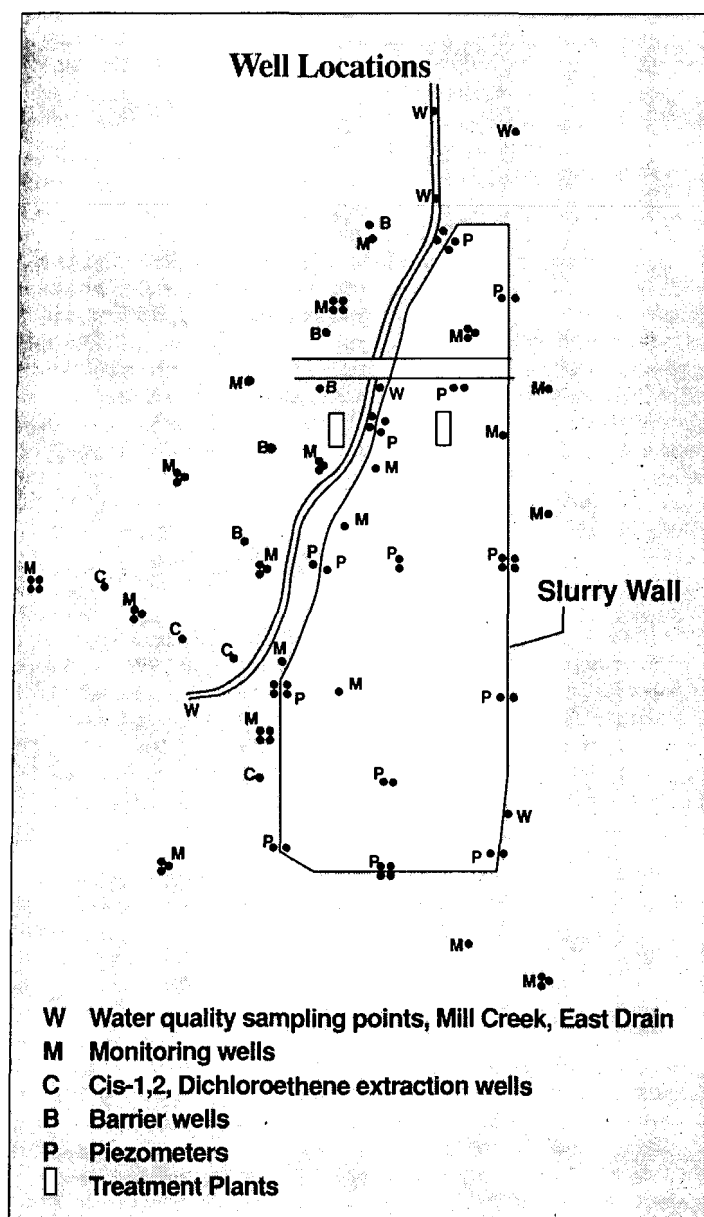
Because of the impact of changes of water chemistry on the treatment plant and perhaps on the pumping systems, changes to the chemistry of infiltration water must be carefully and thoroughly investigated prior to implementation.

The well point sample locations were selected to provide information over a range of concentrations of inorganic constituents and organic compounds. The extraction wells selected for the analysis include well points known to have similar concentrations of metals and a range of concentrations of organic compounds. This will allow the analytical results to be used to determine if significant ligand binding of metals to organic compounds is occurring in the extraction area, a potentially important factor regarding metals transport.

Pertinent Consent Decree Requirements

Ultimate compliance at the site, as detailed in the April 1987 Consent Decree, hinges on: (1) compliance with 1986 fresh water chronic AWQC for Mill Creek waters; and (2) the reduction of VOCs in the contaminant plume that extends off-site to the northwest to a level below 70 ug/L for the cis- and trans-1,2-dichloroethylene isomers. The Consent Decree stipulates a 30-year monitoring period, beginning when groundwater extraction and treatment is terminated, during which the above compliance criterion must be met.

The intent of long-term monitoring is to evaluate possible contaminant rebound effects. The Consent Decree requires that the Trustees submit an application to the agencies overseeing the cleanup (U.S. EPA and WDOE) requesting that the remediation be terminated. This request cannot be made less than 5 years after groundwater extraction and treatment began and must be accompanied by compelling evidence that long-term compliance has been achieved.

A further requirement in the Consent Decree is that the slurry wall be breached following cessation of remediation in order to maintain Mill Creek as a viable measuring point for long-term compliance.

Recent Developments

Four Key Consent Decree elements that had to be achieved at the site within 3 years of the date the Consent Decree was entered (i.e., by April 10, 1990) include:

* The achievement of fresh water chronic AWQC in Mill Creek
* The creation of beneficial groundwater gradients at the base of the slurry wall that encloses the groundwater extraction area
* The establishment of a hydraulic barrier on the regionally downgradient (western) margin of the site to prevent the off-site migration of contamination beneath the Mill Creek groundwater capture zone
* The reduction of contaminant concentrations within the plume of contamination that extends off-site and is characterized by the presence of cis- and trans-1,2-dichloroethylene isomers

U.S. EPA and WDOE (the Governments) submitted a letter to the U.S. District Court dated August 27, 1990 stating that the trustees had successfully achieved the 3 year compliance requirements listed above. This is a significant milestone for the Phase II cleanup, demonstrating the appropriateness of the overall remediation design and the concerted effort made by the Trustees to achieve the stipulated goals.

Included in the letter from the Governments to the Court are provisions for the establishment of the alternative means of demonstrating long-term compliance for the project. The letter further acknowledges that the slurry wall provides a significant barrier to the migration of contamination toward Mill Creek, an obvious short and long-term goal of the remediation effort.

The Tetra Tech/GeoTrans team is presently evaluating a spectrum of potential approaches that will lead to the establishment of an alternative plan for the demonstration of final compliance that is protective of human health and the environment, is cost-effective and which complies with the intent of the NCP cleanup goals, principles and expectations as well as those of the yet-to-be finalized Washington Model Toxics Control Act. The option for alternative establishment of ultimate cleanup criteria is such a recent development that few aspects of such a plan can be stated with surety. One obvious option is the placement of an impermeable cap on the area enclosed by the slurry wall to limit recharge and the hydraulic impetus for contaminant migration into the underlying aquifer. The results of the geochemical speciation modeling detailed in the previous section will provide a basis for further study and evaluation, potentially leading toward enhanced extraction of contaminants prior to in situ immobilization/fixation.

ACKNOWLEDGMENTS

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Heavy Metal-Contaminated Soil Remediation at High Throughput

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ABSTRACT

The technical and operational aspects of the on-site remediation of 100,000 tons of heavy metal-contaminated soil is considered. This treatment project has been completed at a former scrap metal processing yard located at the Port of Los Angeles. The soil was treated at the rate of 100-125 tons/hour using a polysilicate technology in a processing system developed by Solid Treatment Systems Inc. (STS). The efficacy of the treatment is embodied in the transformation of a metal or more commonly the metal oxide into a metasilicate structure such as lead oxide to a form of lead metasilicate. Relatively small quantities of polysilicate and cementitious material are required resulting in a small volume increase after treatment. Further, the process renders a friable soil which can be moved with conventional loading equipment and is suitable for backfilling or other reuse. Although the process is versatile with respect to the nature of its utilization of silicates, the Lopat K20 potassium silicate blend was used for this particular project, where the principal heavy metals of concern were lead, cadmium, copper, zinc, nickel and chromium. Typically, the soluble (STLC) levels of these metals as measured by the California Wet Extraction Test, in the range of several hundred milligrams per liter, were reduced by one to two orders of magnitude by the treatment.

After treatment, the soil, being rendered nonhazardous, was backfilled on the site in compliance with local water board requirements. The unique features of the technology are discussed; the process allows soil to be treated cost-effectively at heretofore unachievable throughput rates. The details and results of this chemical treatment technology are presented, along with a discussion of the relation between total (TTLC) and soluble (STLC) concentrations and their relation to soil treatment.

INTRODUCTION

A heavy metal-contaminated 23.5 acre site involving more than 100,000 tons of soil has been successfully cleaned up using a polysilicate technology. This area, which is part of the Port of Los Angeles, was the site of an extensive metal salvaging operation dealing with a variety of operations which included ship breaking. As a result of these activities, the soil was contaminated with lead, zinc, cadmium, nickel and copper.

In addition to dealing with the heavy metals in the soil, the treatment process had to produce a friable material which could be readily backfilled and compacted on the site. The project schedule imposed a further constraint on the treatment. Basically, material had to be processed at the rate of at least 1000 tons/day in order to meet the project's deadline and avoid the payment of a $2000/day penalty. Thus, in addition to the reliability of the technology, the sequence and performance of unit operations involved in the soil preparation and treatment were a critical part of the overall system.

The mobile nature of the system, owned and operated by Solid Treatment Systems Inc. (STS), allowed it to be erected and operational within 3 working days after arriving on the site. A transportable treatment unit (TTU) permit was obtained from the California Department of Health Services (DHS). An additional permit was required by the Air Resources Board for dust control and operation of the loaders. Because the treated material was to remain on the site, the Water Quality Control Board was required to issue a permit governing the backfilling and subsequent sampling.

Consideration will be given to details of the technology, the processing system and the results of the treatment.

NATURE OF THE TECHNOLOGY

The polysilicate technology used in this project commercialized in 1986 is known as the STS process. The technology provides a reliable, cost-effective mitigation of heavy metals in a solid or semisolid matrix such as soil, residues, ash, baghouse dust, various types of sludges, etc. Several features distinguish this technology from other so-called solidification/stabilization (S/S) processes which are commercially available. The majority of these systems utilize proprietary reagents which are said to form crosslinks with waste components, micro-encapsulate hazardous compounds, absorb contaminants, neutralize constituents, etc. Further, many of these systems are characterized by large (double) volume increases and a final material form which resembles a concrete-like mass.

The STS process is considered to be a chemical treatment technology; that is, not a typical S/S type of process. Three steps are involved in this treatment: (1) the initial formation of a metal metasilicate resulting from the thorough wetting of the material with a polysilicate water blend; (2) the addition of a cementitious material which produces a pozzalonic reaction; and (3) curing or drying. Only small amounts of silicate and cementitious material are required for effective treatment. A previous field evaluation of the technology conducted by the DHS showed that the overall dilution factor was less than ten percent. Typically, one half to 0.75 gallon/ton of silicates and approximately ten percent cementitious material are required. The exact quantities of chemicals are a function of the types of metals and their concentrations. The type of cementitious material determines the required quantity. Curing produces a friable soil-like material which is easily moved and backfilled with conventional earth moving equipment.

The silicates are the critical component of the treatment. An optimum blend can be developed for a particular waste stream. This project used the Lopat K20 silicate blend which is manufactured in two parts; i.e., part A is a blend of three different viscosity potassium silicates and part B contains a catalyzer and dispersing agent.

METHODS AND MATERIALS

The project location was in the Terminal Island District of the Port of Los Angeles, to the rear of Berths 212-215 on the north side of New Dock Street. Basically, the site was a flat or level area consisting of approximately 23.5 acres. According to the analytical results of the initial site characterization, approximately 18 to 24 inches of top soil material would require treatment. Thus, the port engineering surveys estimated that on the order of 60,000 tons of soil would require treatment. In actuality, 106,700 tons of soil were treated in the overall project.

A clean area was prepared on the site for the mobile equipment treatment operations. The contaminated layer was removed in a 300- by 300-foot area, stockpiled in an adjacent location on the site and replaced or backfilled with clean decomposed granite soil. This area provided a working pad for the equipment and the curing of treated material.

The principal elements of the treatment system, shown schematically in Figure 1, consist of the feeder, magnet, screen, pug mill mixing plant and the polysilicate blending unit. These unit operations were operated as an inline continuous system with a throughput of 100 to 125 tons/hour. The material requiring treatment was not typical soil. Because of the prior metal salvaging activities, the material contained a variety of ferrous and nonferrous metals, rocks and stones, pieces of wood and asphalt and other miscellaneous items. The size distribution of these materials spanned several orders of magnitude ranging from less than one inch to several feet. Occasionally, various parts of ships (i.e., riveted and welded beams, parts of anchors, sections of mechanical equipment, etc.) were uncovered in the excavation of the site and found their way into the stockpiled material for treatment. Consequently, the heterogeneous nature of the material dictated the type of preprocessing unit operations prior to mitigating the heavy metals.
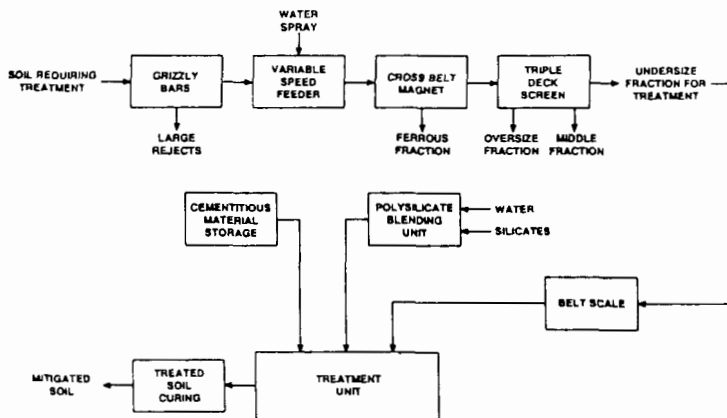
Figure 1
Schematic Diagram of Soil Treatment System

A brief description of the system follows. Soil requiring treatment was taken from the stockpiled material with a front-end loader and fed into the variable speed feeder equipped with a set of grizzly bars to remove large tramp material. Occasionally, metal and other objects would fall through the grizzlies, causing tears in the feeder belt and jams in the feeder, causing excessive equipment maintenance and downtime. This problem was corrected by prescreening the stockpiled material prior to loading into the feed hopper. The prescreen was a mobile unit with a short residence time intended to remove only large objects. After the material exited the feeder, it passed under a cross belt magnet to remove the ferrous fraction. The material then entered the triple deck screen where the large oversize fraction consisting of pieces of concrete, asphalt, wood, etc. was removed on the top deck. After the middle fraction (i.e., smaller-sized rocks, stones, nonferrous metals etc.) were removed, the remaining material was the undersize soil which was suitably conditioned for treatment. A certified belt scale

recorded the feedrate of the material entering the feed hopper on the treatment unit.

The polysilicate additives and mixing process employ two mobile treatment units. The mixing unit consists of two feed hoppers, a twin screw pug mill, a cementitious material storage silo and a discharge conveyor. The silo, capable of storing approximately 50 tons of material, is hydraulically elevated after the unit arrives on the site. Although a diesel engine generator system is mounted on the mixing trailer to provide a self-contained source of power, the demands of the ancillary equipment required the use of a separate mobile system on the site. The polysilicate delivery system is contained on a separate trailer. A 2,000 gallon buffer tank allows the polysilicate-containing water blend to be delivered to a spray nozzle system at the point where the soil enters the pug mill. The polysilicates are added to the buffer tank by means of calibrated metering pumps connected to four, 250 gallon tanks. Polysilicate in fifty-five gallon drums can be directly pumped into these tanks from outside the trailer. Water directly enters the buffer tank from an on-site hydrant.

Appropriate instrumentation allows for the measurement of all water and chemical flow rates entering and exiting the chemical delivery system. Thus, along with the measurement of the soil throughput, a complete mass balance can be performed on the system.

During operation, material requiring treatment enters the rear of the twin screw pug mill. The diluted polysilicate blend is sprayed onto the feed soil. Intensive wetting of the soil with the polysilicates occurs in the first half portion of the mixer. The cementitious material is introduced at the midpoint of the mixer. The feedrate can be adjusted by controlling the variable speed drive on the silo rotary vane feeder. The residence time in the mixer is controlled by the blade angles. For soil, a 22° blade angle is used in the first half of the mixer to enhance retention, (i.e., increase the contact time between the silicates and the material). In the section after the cementitious material is added, the blade angles are set at approximately 45° to enhance mixing and removal of the treated material from the chamber. As the treated material exits the pug mill unit, a radial stacking conveyor piles the material. The process is complete after the material has cured in the stockpiles. The treated stockpiles typically are turned with a front-end loader on a daily basis for several days. Recently, the use of a Bomag unit has simplified the turning and curing of the treated piles.

Although the project was permitted to operate from 6:00 a.m. to 6:00 p.m. 5 days/week, the South Coast Air Quality District imposed the added restriction that all operations including the operation of rolling stock cease by 5:00 pm. Consequently, the effective daily treatment window was approximately ten hours or less depending upon downtime. A period of at least one hour was required for cleanup, maintenance, moving piles, etc. at the end of each shift. Thus, in order to meet the project schedule, a nominal 1000 tons of material/day had to be processed within these time constraints.

Material requiring treatment was arranged in 1000-ton, 30- by 150- by 8-feet high stockpiles on the site adjacent to the clean soil equipment zone. Samples of this material for laboratory analysis of heavy metals were taken as the piles were generated. These data were used to supplement the original site characterization data and provide guidance in establishing the daily treatment protocols. The sampling protocol also involved the collection of samples of untreated and treated material at fifteen minute intervals during operation. These samples formed a daily composite which was split for independent certified laboratory analysis. After receipt of the laboratory report and acceptance by the Port inspectors, the material was backfilled on the site. Additional samples of the in-place material were also taken.

TREATMENT LEVELS

Testing of the contaminated soil for all 17 metals revealed that only five had elevated levels requiring treatment. The range of these metals in terms of both the soluble (STLC) and total (TTLC) concentrations is summarized as follows: (1) lead, STLC—11 to 121 mg/L, TTLC—27 to 1500 mg/kg; (2) zinc, STLC—14 to 320 mg/L, TTLC—242 to 3130 mg/kg; (3) cadmium, STLC—0.1 to 1.9 mg/L, TTLC—2 to 12 mg/kg;

(4) nickel, STLC—0.2 to 7 mg/L, TTLC—30 to 600 mg/kg; and (5) copper, STLC—2 to 96 mg/L, TTLC—70 to 2610 mg/kg. The soluble concentrations were determined by the CAM wet extraction method which involves milling to pass a No. 10 standard sieve and followed by 48 hours of extraction in a sodium citrate solution.

The relationship between the total and soluble concentrations, summarized in Figure 2 shows the respective ranges for each metal. In effect, the treatment process must deal with metals whose concentrations cover a range of four orders of magnitude. It should be noted that the values of lead shown in Figure 2 are plotted as Pb/100 to aid in pattern recognition. Thus, the concentrations of lead are in the same general band as copper and the lower range of zinc.
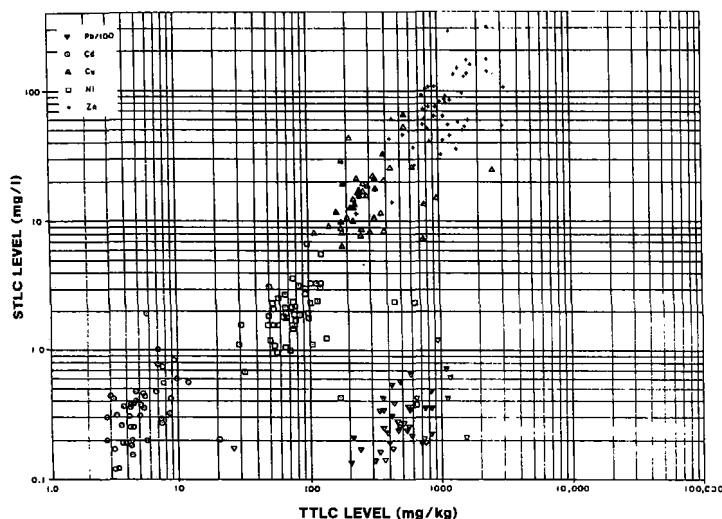
Figure 2
Relation Between Soluble and Total Concentration
Levels in Untreated Soil

The correlation between soluble and total concentrations can be seen in Figure 2. For example, on the average, the soluble concentrations of these metals would be 16 to 47 times less than the total concentrations. In terms of the specific metals, these reductions would be as follows: (1) lead—20.2, (2) zinc—17.5, (3) cadmium—15.9, (4) nickel—47.2 and (5) copper—22.7. It is interesting to note that with the exception of nickel, the soluble concentrations of the other metals are about 20 times less than the total concentrations.

TREATMENT RESULTS

The actual treatment activities began on Oct. 9, 1989 and terminated on Apr. 12, 1990. The treatment of the initial 60,000 tons of material was completed by the contracted schedule date of Jan. 15, 1990. The project period was then extended to treat the additional 47,000 tons of soil. Approximately 16,000 tons of nonhazardous oversize material was removed in the screening operation. With the exception of the ferrous metals, this fraction was disposed of in a Class III landfill.

The quantities of polysilicates and cementitious material were adjusted to coincide with the concentrations of metals in the in feed material. For a combination of logistical, economic and treatability considerations, cement was used as the cementitious material. Throughout the course of the treatment, the addition of cement ranged from 10.14 to 11.08 percent. Even with the wide range of STLC concentrations of the various metals, the usage of polysilicates varied over a relatively narrow band which ranged from 0.513 to 0.59 gallons/ton of soil. The relation of silicate usage as a function of STLC level in the in feed material requiring treatment is given for the five metals, (lead, zinc, cadmium, nickel and copper) in Figures 3 to 7, respectively. In each case, the treatment achieved at least a 99 percent reduction in STLC level. The data suggest a general trend of increasing silicates with STLC level. A particular group of data lie in the range of 0.578 to 0.59

gallon/ton. In this situation, the silicate addition rate was increased in anticipation of high STLC levels in the in feed material. In actuality, the in feed levels were not excessively high, so that the subsequent STLC concentrations in the treated material resulting from the increased silicate usage were all nondetectable.
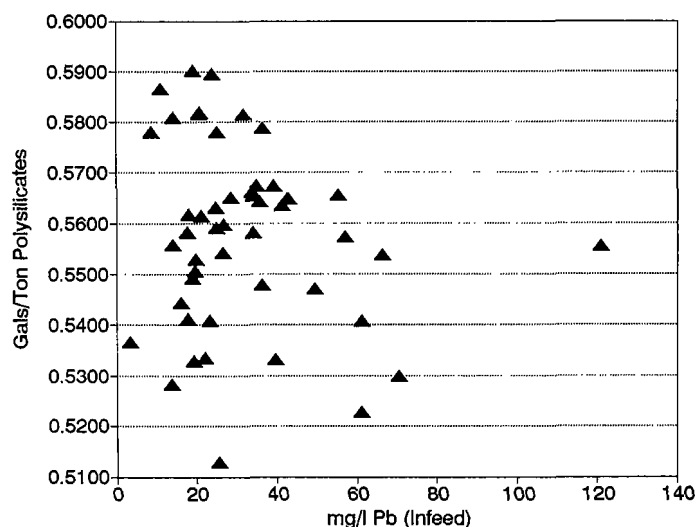
Figure 3
Polysilicate Usage for Lead Treatment
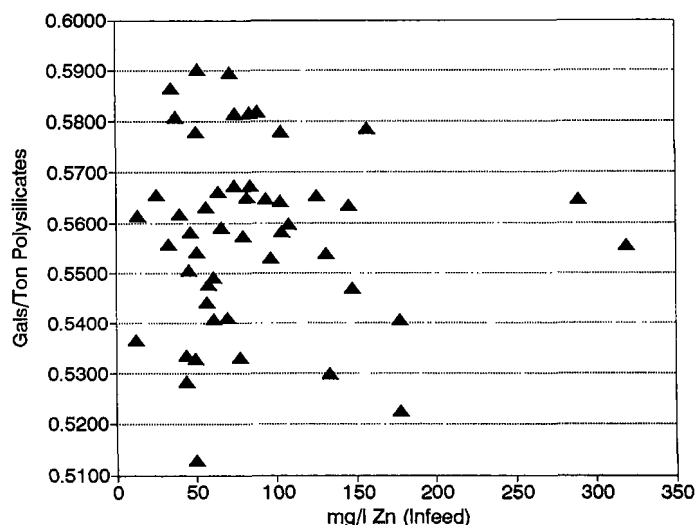
Figure 4
Polysilicate Usage for Zinc Treatment

CONCLUSION

The STS polysilicate technology is an effective and relatively low cost method of treating heavy metal-contaminated materials. Because of its straightforward manner of application, material can be treated at rates exceeding 100 tons/hour, thereby allowing the achievement of very favorable economies of scale. Further, the treatment yields significant reductions in soluble (STLC) levels of metals with minimal increases in volume or weight, (i.e., dilution factors of less than ten percent).

The polysilicate blend and the formation of a metasilicate is a critical element in the treatment technology. As shown in the literature, treatment process using only cementitious materials are unlikely to have long-term metal retention properties. In these cases, certain metals may have an adverse effect on the cementitious matrix which negates their immobilization.
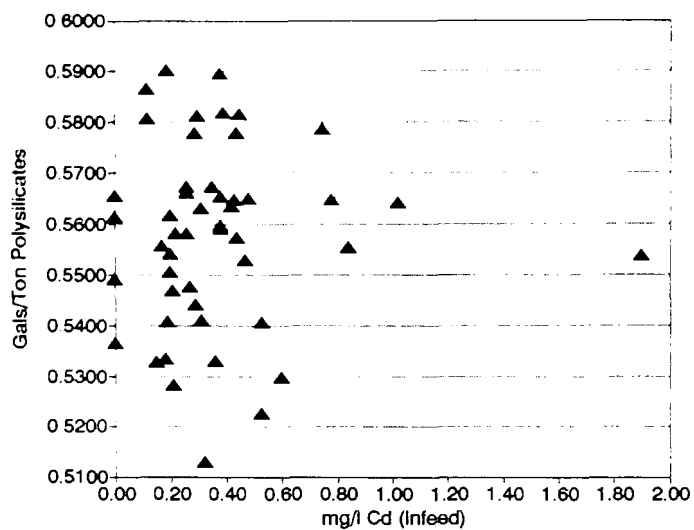
Figure 5
Polysilicate Usage for Cadmium Treatment
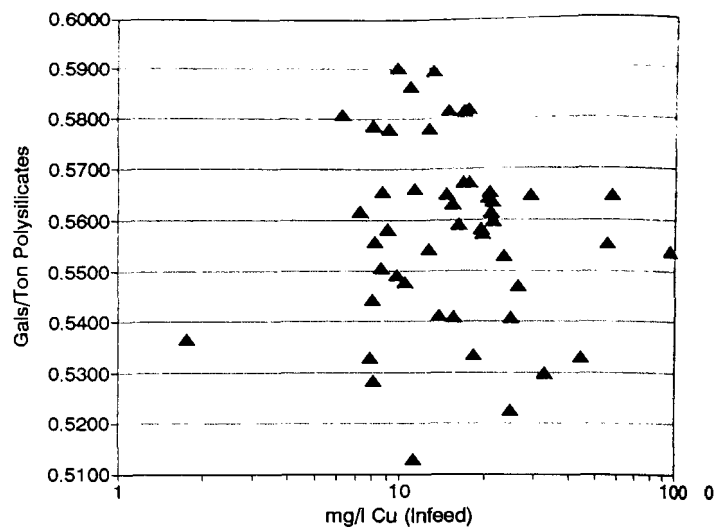
Figure 7
Polysilicate Usage for Copper Treatment
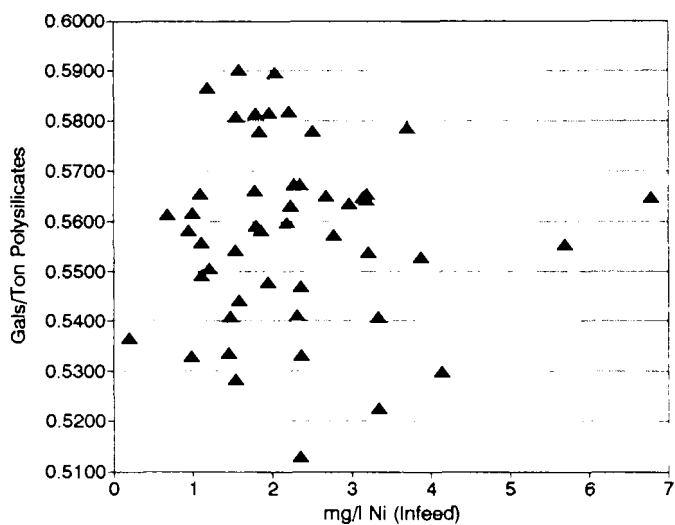
Figure 6
Polysilicate Usage for Nickel Treatment

This technology also has a mitigating effect on the total (TTLC) concentrations of the metals. Typically, the size distribution of the treated material, particularly soil, will be increased or shifted toward larger particle sizes. The mean particle size of the treated material is increased by at least an order of magnitude which greatly reduces the dispersion of total metal concentrations in airborne particulates.

In Situ Treatment: When Does It Apply?

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ABSTRACT

As more and more abandoned hazardous waste sites are investigated, specifications designating in situ remedial activities for soil and groundwater are becoming more common. Advantages of in situ treatment technologies include reduced cost and ease of implementation when compared with intrusive types of remedies. In situ treatment technologies such as soil vapor extraction, bioremediation, soil washing/flushing and air/steam stripping are applicable to many hazardous waste site needs. However, a close examination and evaluation of all factors must be considered prior to consideration of these technologies.

Upon initial appraisal, in situ technologies may appear to possess wide applicability. Unfortunately, in-depth evaluations indicate these techniques cannot be used in all instances and in some cases should not be specified. Differences in geology, cleanup criteria and remedy implementation time constraints may preclude their use. Some of the difficulties with in situ type remedies include; confirmation of compliance and length of time for remedy implementation.

Given the many recommendations for these technologies at remedial actions, the need for some "Rules of Thumb" on using these techniques arises. This paper attempts to set forth guidelines for the applicability of in situ treatment technologies to the remediation of hazardous waste sites.

INTRODUCTION

Recently, the burden of hazardous waste site investigation and cleanup has shifted to the private sector. At the same time, in situ treatment technologies are becoming more popular. In situ treatment technologies are defined by the U.S. EPA as those treatment processes "that can be applied to treat the hazardous constituents of a contaminated environmental medium where they are located and are capable of reducing the risk posed by these contaminants to an acceptable level or completely eliminating that risk."[1]

In general, all of the currently used in situ treatment technologies can be placed into the four general categories listed in Table 1.

Table 1
General Categories for In situ Treatment Technologies

1. Vapor Phase Treatment Technologies
2. Liquid Phase Treatment Technologies
3. Bioremediation
4. Stabilization/Solidification

Virtually all of the in situ techniques currently used fit into one of these classifications. For example, in situ soil vapor extraction (SVE) can be classified as a vapor phase treatment technology. Along these same lines, soil flushing can be classified under this system as a liquid phase treatment technology.

In situ technologies do have many uses. In many cases they can be less costly than intrusive remedial techniques. Unfortunately, they are not useful in all cases. This paper describes many of the in situ technologies in brief detail and generates some general guidelines for their use in the field.

TECHNOLOGIES

There are many different types of in situ treatment technologies that are currently being investigated. Presented below are a few fundamental technologies that are currently being tested and, in some cases, employed on a large scale. By no means is this list complete: it simply serves as beginning point for discussion of the issues considered when specifying their use.

Soil Vapor Extraction

Soil Vapor Extraction (SVE) is a process used to remove VOCs from soil. This technology has very effectively removed fuel from soil (for example, contamination found during removal of underground storage tanks). SVE is a mechanism whereby wells are installed in close proximity to an area contaminated with VOCs. A vacuum is induced on approximately one half of the wells, and the other wells are left open for air induction (Fig. 1). As a vacuum is induced in the interstices of the soil, the VOCs tend to volatilize and are removed with the vapor stream and subsequently can be condensed from the vapor stream for disposal or treatment. SVE can be classified as a Vapor Phase Treatment Technology.
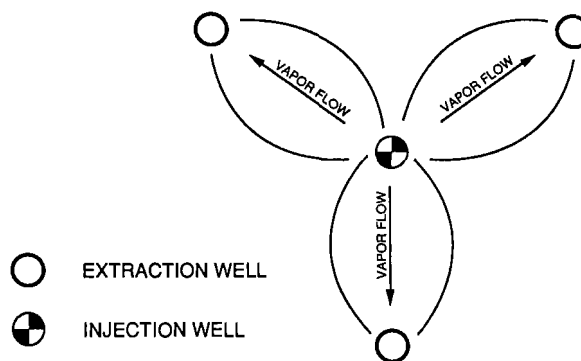
Figure 1
Soil Vapor Extraction

Steam or Air Stripping

Stripping of VOCs from contaminated soil is also a technology that can be used in situ also. This process utilizes basically the same type of setup as SVE, except that injection wells are used in place of induction wells. In this process, steam or hot air is injected into the soil while a small vacuum is concurrently induced at the extraction wells. The steam or hot air heats the soil and increases the vapor pressure of the organic contaminants in the soil. This vaporization of the contaminants separates them from the soil, facilitating removal with the extracted vapor stream. Steam stripping has been more effective than hot air on some higher boiling point semivolatile compounds.[2] Like SVE, Steam/Air stripping can also be classified as a Vapor Phase Extraction Technology.

Soil Washing/Flushing

Soil Washing/Flushing is a Liquid Phase Treatment Technology very similar to steam stripping. Basically, a circulating system is set up in which contaminated groundwater is extracted downgradient of the contaminated area. This water is treated to remove contaminants. The treated water is then recycled to infiltrate back into the contaminated area (Fig. 2). This process is similar to a solvent extraction process. As clean water comes in contact with contaminated soil, there is a contaminant concentration gradient driving contaminants into the water. This gradient induces contaminants to desorb from the soil and move into the liquid phase. This technology can effectively remove inorganic contaminants from the soil and can be improved by adding chelating agents.
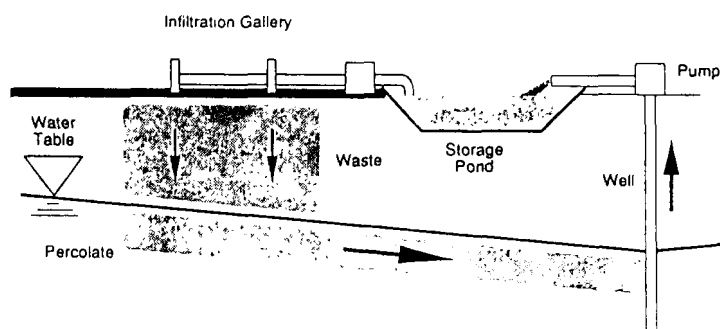
Figure 2
Soil Flushing

Chemical Degradation

Another form of Liquid Phase in situ treatment is chemical degradation. In this process, chemically reactive compounds are injected upgradient of a contaminated area. In theory, as these compounds—which can be oxidizers or reducing agents—come in contact with the contaminated soil, they will react with and render harmless the contaminants. Groundwater usually is extracted downgradient of the site to help maintain proper gradients. This process can be controversial due to public perception that injection of certain chemicals into the subsurface is not acceptable no matter what the outcome. These issues must be carefully investigated prior to commencement of any type of injection of chemical degradation additives.

Bioremediation

In situ bioremediation utilizes the same basic biological degradation process as ex situ bioremediation techniques. In situ bioremediation is perhaps the most common type of in situ treatment now being employed for remediation of hazardous waste sites contaminated with organic wastes. The process is similar to chemical degradation treatment except microorganisms and/or nutrients are added to the liquid injection stream rather than chemical degradation agents. In many cases bioorganisms are stimulated by adding basic nutrients such as oxygen, nitrogen and phosphorus. In other uses of in situ bioremediation, hybrid

organisms are introduced to the injection stream along with the nutrients. Groundwater downgradient of the site is monitored and nutrient levels are compared to initial loadings to determine biological degradation rates.

Stabilization/Solidification

Stabilization and Solidification are processes in which contaminants are immobilized, rendering the waste nonhazardous. This process too, can be accomplished in an in situ manner. The most common system uses a series of hollow, vertical augers to dig into the soil. Stabilization additive mixtures are injected through the augers and blended with the contaminated medium. The augers are transported and stabilization takes place in an overlapping fashion (Fig. 3). This technique can be employed to immobilize contaminants either in soil or groundwater. At the same time the soil is being stabilized, an impermeable groundwater barrier can be built to aid in other parts of full facility remedial action.
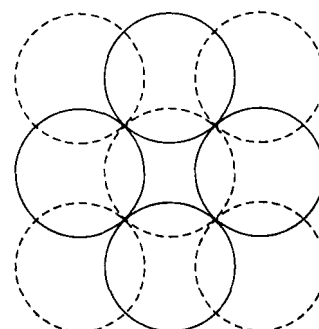
Auger Pattern
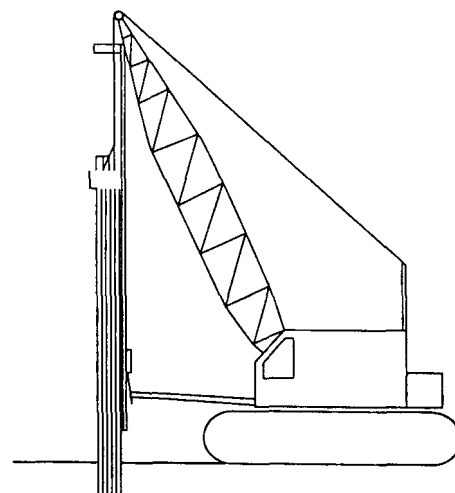
Figure 3
In Situ Stabilization

In situ Vitrification

In situ Vitrification (ISV) is a process that utilizes electricity to melt soil and solid materials into a glass-like inert product. Electrodes are placed into the ground in a box-shaped pattern. A starter path of flaked graphite and glass frit is placed on the surface between the electrodes. As current is applied, the molten path (at approximately 1600°C) progresses from the surface downward (Fig. 4). After the desired melt mass is achieved, the electricity is turned off and clean backfill is used to fill the subsidence volume. As the molten material cools, it takes on the characteristics of Obsidian (Volcanic glass). The solidified mass

has virtually no leachability, has great strength and should last forever.

This brief overview of some of the more popular in situ treatment technologies will aid in later discussions of the principles under which these technologies can and should be applied.
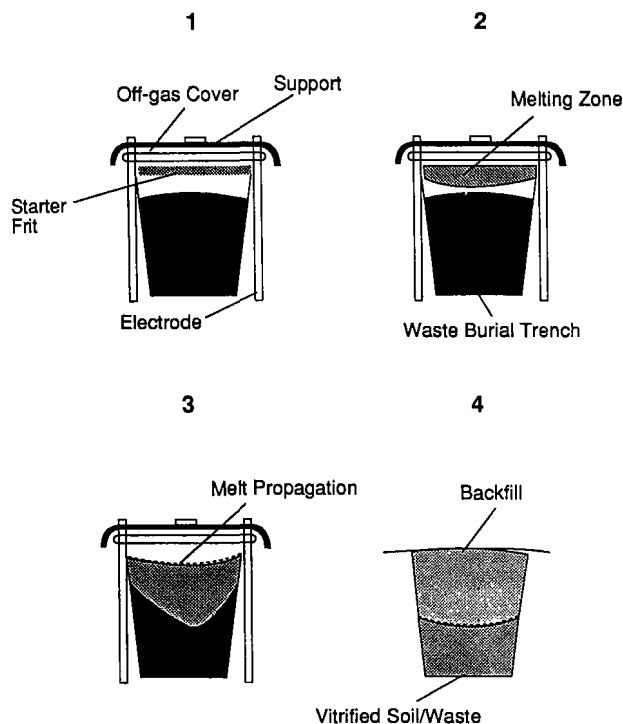
Figure 4
In Situ Vitrification

GUIDELINES FOR USE

With the large amounts of money being spent on remedial actions, there are some important points that must be considered in the specification of in situ remedial measures for hazardous waste sites. These issues must be carefully evaluated in order to insure the success and cost-effectiveness of remedial activities.

The first key issue in dealing with the selection of a remedial technology—not just in situ—is how to confirm the remedial technology will achieve the cleanup standards desired. This is especially true in the use of in situ cleanup technologies.

In an intrusive type of remedial effort, it is much easier to take samples of the treated material and determine if the appropriate cleanup criteria are being achieved. Because in situ remedies basically occur remotely, it is more difficult to take samples; the targeted material is often below the surface and is inaccessible to sampling. Consequently, method of sampling must be devised at the beginning the remedial design to determine how compliance will be monitored. Borings can be taken periodically and the extracted material tested. If frequent borings must be taken, the costs of the overall remedy can increase dramatically.

In some cases, soil cleanup data can be inferred from down-gradient groundwater quality. This method, however, is indirect and may introduce a large error into the data. This point is of great importance—an acceptable method of monitoring compliance must be determined before beginning any cleanup.

It is also important to establish an achievable cleanup standard prior to commencement of the remedy. Many times these cleanup standards are risk-based or are set by a governing agency. Small changes in this standard can have large impacts on final remedy cost.

Third, a projection of the remedy implementation time interval must

be made. This is a difficult task in which many assumptions come are made. In some cases—such as excavation and removal—an intrusive remedy will take a much shorter time period than an in situ remedy. All of the parties involved must have some understanding of the length of time involved in implementing an in situ remedy. In many cases in situ remedies, while cheaper, take a longer time for completion. This time-frame must be considered in the cost/benefit analysis of any remedy.

After reviewing these important general points, there are some in-depth questions to contemplate for specific in situ remedies. For example, in attempting to use a vapor phase in situ treatment technology for the treatment of contaminated soils, clearly, there must be a vapor phase to treat. If the water table of a particular site is too close to the surface, there will be no vadose zone from which to extract vapor. An artificial vadose can be induced using dewatering wells and this has been done very successfully in the past. However, the water table proximity to the surface can still pose a problem if a site has large fluctuations in its water table. In the opposite sense, there can also be a problem if liquid phase treatment is attempted in an area with a very low water table. Consequently, thorough understanding of the site water table characteristics must be obtained prior to investigation of an in situ remedy for the site.

As was mentioned earlier, one of the key considerations in any remedial activity is the estimated length of time for treatment completion. Two variables that will significantly impact the cleanup time for in situ remedies are: (1) permeability of the soil and (2) the magnitude of the groundwater gradient. In the instance of in situ chemical degradation or bioremediation (3) small groundwater gradients will cause nutrients and chemicals to move at a slower pace; thus the cleanup will also occur at a slower pace. This problem also occurs with vapor movement in low permeability soils such as clay. Vapor phase remedies will take longer in this material. Fractures in a geological unit may "short circuit" the flow creating preferential flow channels, bypassing much of the contamination and creating a compliance assurance problem. Nonhomogeneity of soil may cause localized differences in permeability as well. Groundwater gradients can be controlled by pumping and there are ways of increasing permeability, but these modifications all add costs to the final remedy. All of these points lead to one conclusion; in any in situ type remedy there must be a consistently reliable method to reach the contaminants with liquid, vapor, bioorganisms or stabilization agents in a reasonable period of time.

CONCLUSION

In situ treatment technologies have many issues that must be considered prior to their use (Table 2). Initially, these technologies may appear to possess wide applicability. Unfortunately, they cannot be used in all instances and in some cases should not be specified. Differences in geology, cleanup criteria and available time for remedy implementation may preclude their use. Some of the difficulties with in situ type remedies include: (1) confirmation of compliance and (2) length of time required for remedy implementation.

Table 2
Summary of Issues to Consider for In Situ Remedy Selection

1. How will compliance of the remedy with specified goals be monitored?
2. What are the cleanup criteria?
3. What is the estimated time for remedy implementation and completion?
4. Is movement of the water along the groundwater table gradient fully understood?
5. What is the magnitude of the groundwater gradient?
6. What are the permeability characteristics of the soils in the contaminated zone?

Although not applicable to all remedial situations, in situ remedies definitely do have a place. Many successful in situ remediations projects have been completed. These remedies have been successful because planners have carefully considered the six points listed above and applied them to the hazardous waste sites' specific geological and hydrogeological characteristics while keeping in mind cleanup criteria, compliance confirmation and time constraints imposed. Investigation and understanding of these points will lead to many more effective in situ remedies in the future.

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Evaluation of Treatability Studies at the Petro-Chemical Systems Superfund Site

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ABSTRACT

Lockwood, Andrews & Newnam, Inc. (LAN) has been contracted by the Texas Water Commission to conduct an RI/FS for the Petro-Chemical Systems Superfund Site in Liberty County, Texas. A portion of this work includes Treatability Studies on the contaminated material from the site. The Treatability Studies are required to demonstrate the effectiveness of selected treatment technologies on clay soils containing volatiles, semivolatiles and heavy metals.

The Petro-Chemical Systems site is a 312-acre tract of land located in primarily rural Liberty County, Texas. The site received various chemical wastes in the early 1970s and was placed on the NPL in 1984. Subsequent investigation has revealed dumping activities in three areas of the site and contaminant concentration for heavy metals to 500 ppm, semivolatile hydrocarbons to 4000 ppm and volatile hydrocarbons to 1000 ppm.

Removal of volatile and semivolatile contaminants in the clay soils by a solvent extraction technique will be investigated. Chemical and microbial evaluation, as well as laboratory simulations, will be conducted during this study. The bioremediation treatability study will also attempt to determine the contribution to contaminant removal associated with degradation vs. volatilization. High concentrations of chromium and lead are localized at the site. Inhibition of bioremediation by heavy metals will also be evaluated.

The treatability studies will attempt to determine operating conditions, process requirements, power requirements and chemical requirements. Estimates of treatment costs and treatment schedule will also be determined.

The paper will discuss the process used to select the treatability studies, the results of both treatability studies and their impact on the remediation at the site.

INTRODUCTION

The Petro-Chemical Systems site is a 312 acre tract of land located approximately 65 mi east of Houston, Texas (Fig. 1). The site is approximately 7 mi north of Interstate 10 and 15 mi southeast of Liberty along Farm to Market Road (FM) 563 (Fig. 2). Frontier Park Road provides access to the site from FM 563.

Unpermitted waste disposal operations at the site may have started in the late 1960s. Disposal of waste oils is documented from 1971 when an application for a commercial disposal permit in the name of Petro-Chemical Systems, Inc. was granted by the Texas Water Quality Board. Waste oils were apparently deposited in pits throughout the site and spread on Frontier Park Road as a dust abatement measure.

Opposition to the disposal activity developed, and legal action resulted in the permit being revoked in 1974. The site was then subdivided into 5-to 15-acre tracts and sold for residential development. Five families currently live on these tracts.

Attention brought by local residents in the early 1980s resulted in the site being placed on the NPL. In 1985, the Texas Water Commission contracted with Lockwood Andrews & Newnam, Inc. (LAN) to perform a Remedial Investigation and Feasibility Study on the site. The first task consisted of performing a focused RI/FS on Frontier Park Road, the access road for the site which had been contaminated with waste oils. The road was remediated and the contaminated soil was stored in a RCRA vault on-site pending selection of a remedy for the entire site. The RI/FS for the remaining site was completed in 1990.

REMEDIAL INVESTIGATION RESULTS

The primary contaminates found on-site were volatile and semivolatile organics, chromium and lead. Indicator chemicals were selected during the Risk Assessment and were used throughout the RI to define the extent of contamination and to estimate the volume of contaminated material on site. The indicator chemicals were:

- Benzene
- Ethylbenzene
- Xylene
- Naphthalene
- Benzo (a) pyrene
- Lead

TREATABILITY STUDIES

Two technologies were selected to evaluate remediating the contaminated soils. These were bioremediation and solvent extraction.
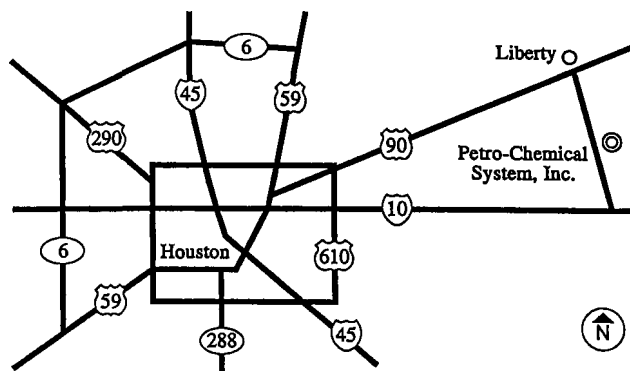
Figure 1
Site Location Map
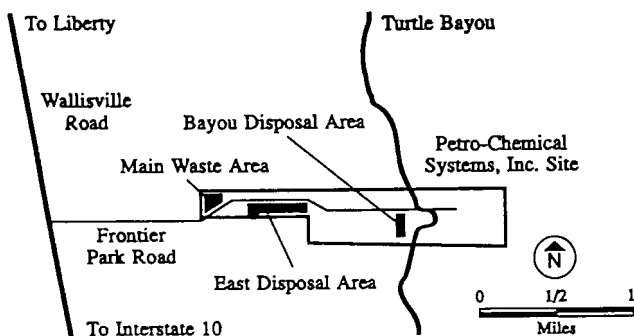
Figure 2
Site Vicinity Map

BIOREMEDIATION

Bioremediation of the contaminated soils was simulated by Harding Lawson Associates, a member of the RI/FS team. Prior to commencing the actual laboratory simulation, chemical and microbiological evaluations of the soil were performed. Of prime interest is the ratio of hydrocarbon degrading microorganisms to total microorganisms. This ratio ranged from 12% to 26% and is considered a suitable subpopulation with which to start the test. A soil chemistry profile was conducted to determine nutrient requirements for the treatment process. The chemistry profile indicated that ammonia and phosphorous were the limiting nutrients and required supplementation in a form readily available to the microorganisms. The soil pH was determined to be too low and had to be adjusted with lime.

Treatment Simulation

A laboratory-scale treatment system was constructed to simulate conditions under which the bioremediation process would be implemented in the field. The treatment system (Fig. 3) consisted of a polyethylene-lined treatment bed within an air-tight glove bag enclosure. Air that was pretreated through a carbon trap was supplied to the enclosed treatment unit at a rate between 20 to 40 ft³/hr. Exhaust air leaving the treatment system was filtered through three individual 100 gram carbon traps in series to capture volatile compounds that were released during the treatment process. Nutrient supplementation, mechanical aeration and soil sampling procedures were performed within the treatment system via a pair of side arms with gloves attached to the enclosure. Soil samples were removed from the system via a sampling port.

A composite soil sample weighing approximately 120 lbs was placed into the laboratory-scale treatment system to a depth of approximately 12 inches. Base line parameters, which include BTEX, PNAs, chromium and lead, were measured for the soil. During a six week treatment period, the soil was amended with a nutrient formulation on a weekly basis and mechanically aerated three times per week to provide oxygen for microbial metabolism. Additionally, weekly soil samples were obtained and analyzed for BTEX and microbial populations. Following

Figure 3
Biological Treatment

the treatment period, soil samples were obtained and analyzed for the same base line parameters as previously described.

Study Results

The initial concentration of BTEX in soil was reduced approximately 99.8% (Table 1) during the treatment period. Additionally, the hydrocarbon-utilizing microbial population increased four orders of magnitude indicating that soil conditions conducive to biological metabolism of the hydrocarbons were present during the treatment period. The calculated half-life for BTEX during the treatment period was approximately 5.0 days. The initial concentration of PNAs in the soil was reduced approximately 94% during the treatment period (Table 2). The calculated half-life for PNA during the treatment period was approximately 8.3 days. These data indicate that biological treatment is effective in significantly reducing the concentrations of BTEX and PNAs in soils at the Petro-Chemical Systems site.

Table 1
Biodegradation of BTEX Compounds Petro-Chemical Systems

| Compound | Treatment Period in Weeks | | | | | | | Percent Removal |
	0	1	2	3	4	5	6	
	Concentration in ug/kg							
Benzene	450	121	100	NT	<28	<13	<7	98.5
Toluene	2,300	227	415	NT	<42	<20	<7	99.7
Ethylbenzene	2,400	1,400	102	NT	<42	<20	<7	99.7
Xylenes	8,500	5,000	1,350	NT	200	<40	8	99.9
Total BTEX	13,650	6,748	1,967	NT	312	93	29	99.8

NT - Not Tested

Table 2
Biodegradation of Polynuclear Aromatic Compounds

Compound	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Removal
Naphthalene	130	2.9	98.2
2-methylnaphthalene	61	1.2	98.0
Acenaphthylene	22	1.1	95.0
Acenaphthene	10.1	0.7	93.0
Fluorene	2.3	0.8	61.0
Phenanthrene	33	2.3	93.0
Anthracene	4.2	.7	83.0
Fluoranthene	4.8	1.1	77.0
Pyrene	10.5	3.9	63.0
Total PNA	277.3	15.4	94.0

Petro-Chemical Systems

Activated carbon from the exhaust carbon canisters was extracted with carbon disulfide and the resulting extract was analyzed for BTEX. BTEX compounds volatilized and absorbed to the carbon traps during the period amounted to approximately 3% of the total mass of BTEX present in the soil.

Conceptual Design

The results of a bioremediation treatability study indicate that biological treatment is a technically feasible and effective method for reducing BTEX and PNA concentrations in soils at the Petro-Chemical Systems site. Although the actual design of the full-scale system will be based on site-specific factors, a brief description and conceptual design of a full-scale bioremediation treatment system is presented below.

Soil that requires treatment would be excavated and placed in the treatment facility. A conceptual design of the biotreatment facility is presented in Figures 4 and 5. The biotreatment facility will be an enclosed, above-grade, lined treatment bed capable of treating approximately 2,000 yd³ of soil. It is estimated that the biotreatment will extend over an area of approximately 1.5 acres. The biotreatment facility
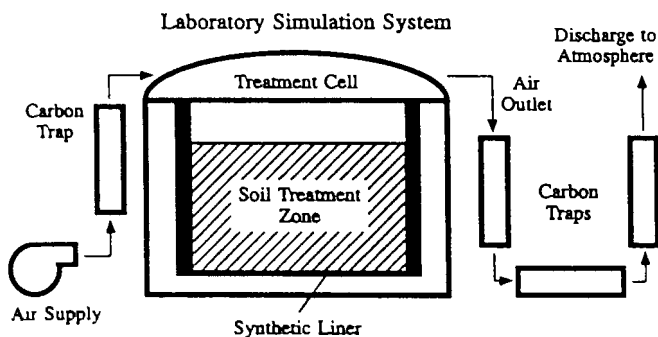
will also be equipped with air emissions control system including a vapor phase carbon unit to remove any VOCs that are released during the treatment process.
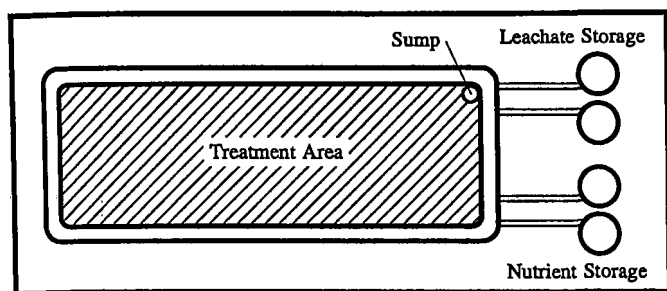
Figure 4
Bioremediation Conceptual Layout
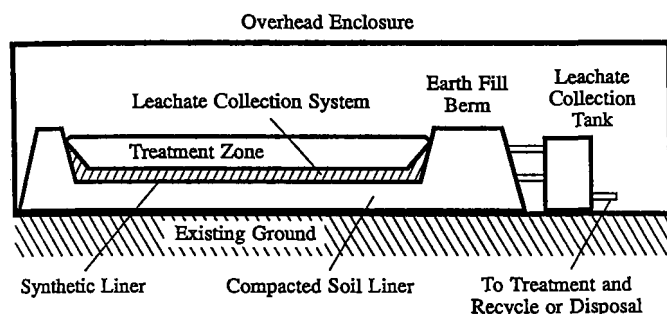
Figure 5
Typical Bioremediation Section
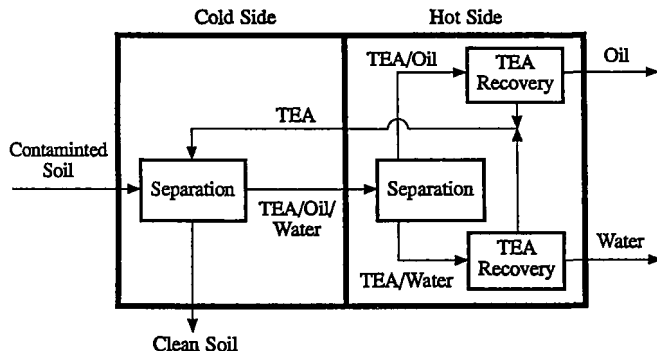
Figure 6
B.E.S.T.® Process Flow Diagram

Before beginning the treatment process, homogenization of the soil into a uniform consistency may be necessary. Following soil homogenization, base line soil samples would be collected to ascertain organic chemical concentration, microbial population, soil pH and moisture. The nutrient formulation would be applied at an estimated dose of 1.5 to 3.0 gallons/yd³. The nutrient formulation may be applied through several mobile sprinkler nozzles placed within the treatment area. It is estimated that two to four nutrient applications would be performed during the treatment period.

The soil would be mechanically aerated with a tractor-mounted rototiller or discing equipment. The frequency of aeration is estimated to be three times per week during the treatment period. The treatment period for each soil unit volume (2,000 yd³) is estimated to be 8 to 12 weeks. The treatment period is based on the results of the bioremediation laboratory simulation and operating experience with similar pro-

jects. Generally, for projects of this type, the soil treatment cost is estimated to be $84 to $130/yd³.

SOLVENT EXTRACTION

The solvent extraction treatability study was conducted by Resource Conservation Company using their B.E.S.T.ᴿ process. This process uses triethylamine (TEA) to separate sludges, soils and sediments into their oil, water and solid fractions. The physical properties of TEA are ideal for this purpose. TEA is a powerful solvent for organic compounds and has unique water miscibility properties. The key to the success of amine extraction is the property of inverse miscibility. This unique property allows TEA to solvate oil and water simultaneously, resulting in very high extraction efficiency of organic contaminants.

At temperatures below 60°F, TEA is perfectly miscible with water. Above this temperature, TEA and water are only partially miscible. This physical property can be used by the realization that cold TEA can simultaneously solvate oil and water. In the B.E.S.T.ᴿ system, this principle is exploited by performing the extractions in the temperature region where the solvent is miscible with both oil and water, creating a single-phase extraction medium.

Once the extraction of the sample is complete, soil particulates are removed by either gravity settling or centrifugation. The cold, single-phase solution of TEA, water and oil is then heated to 130°F. Heat drives the solution into the temperature region where TEA and water are only partially miscible. The TEA/oil fraction is then easily separated from the water fraction by decanting off the water.

Bench Scale Study

Soil samples were collected from site locations selected on the basis of the first phase RI data. The samples were shipped on ice in four one-liter containers. The samples were kept cold until the initiation of the test.

Initial examination of the sample indicated a soil pH of 3.1. Due to the basic nature of TEA, the pH of the feed for the process must be controlled to a level of 10 or higher. It was determined by titration that 21 mL/kg of 50% caustic soda (NaOH) of feedstock would be required to adjust the pH to the required range.

Based on this information, a prechilled, 600 gm portion of the soil sample was pH adjusted by adding 13 mL of 50% caustic soda at the same time that three liters of chilled TEA were added. Mixing was performed by an air-driven prop mixer in an open top beaker.

As expected, the solvent became colored, indicating that oil extraction was taking place. Mixing time was extended from the standard 30 minutes period to 42 minutes to ensure that all the sample was adequately mixed with the TEA. After mixing ceased, heavy particles immediately settled to the bottom of the beaker. Fine particulates did not readily settle to the bottom of the beaker indicating that gravity settling alone would not be sufficient to remove all the particulates from the extraction mixture. As a consequence, centrifugation was used to remove the particulates between each extraction stage.

The cold centrate recovered from centrifugation was decanted from the particulate solids at this point and retained for further processing. The remaining solids were placed back into the extraction flask in preparation for the next two extraction stages.

Two more stages were performed for a total of three extraction stages. The recovered soils from the centrifugation of the previous stage were mixed with the same amount of TEA, 3.0 liters, for the second and third stages. No additional caustic was added. After 30 minutes of mixing, centrifugation was performed as before. After the third stage centrifugation was completed, the solids were dried.

The centrate recovered from the first extraction stage was separated into its aqueous and organic components. The TEA/Oil/Water mixture was heated to approximately 140°F to effect the separation of the two phases. The hot centrate was permitted to stand and separate for 30 minutes in a four-liter separatory funnel immersed in a hot water bath.

Separation of the organic and aqueous phases was immediate, with no rag formation. After the 30-minute standing period, the aqueous phase was decanted off the bottom of the organic phase and retained

for further treatment. The organic phase was then ready for the TEA Recovery/Oil Stripping process.

Only the centrate from the first extraction stage had a significant amount of water in solution; therefore, only the centrate from the first extraction stage was decanted.

Analysis showed the organic fraction contained only 2% fugitive water, which is the minimum achievable concentration in a pure triethylamine/water system. The concentration of fugitive triethylamine in the aqueous fraction was also low, namely, 2.8%.

Recovery of product oil was accomplished in three steps. First, the bulk of the TEA was removed by simple distillation. Second, the residual TEA was stripped from the oil by steam distillation. Third, the oil was heated to the further reduce the residual levels of TEA and water. No foaming was observed during the above operation and no TEA odor was apparent in the oil at the completion of the steam stripping step.

Due to the extremely low oil content of the feedstock, very little oil was recovered. The amount of oil recovered was not sufficient to perform any laboratory analysis.

Removal of triethylamine from the decant water was accomplished by heating the water on a hotplate, while insuring an elevated pH was maintained. The elevated pH was necessary to insure that the majority of the triethylamine was in the volatile molecular form. Additional caustic was required, 0.4 mL/L 50% NaOH decant water, to maintain the elevated pH. No foaming was observed during the stripping.

Study Results

Prior to starting the test, an initial sample was analyzed to provide a base line for comparison. Sample characteristics are shown in Table 3.

Table 3
Feed Compositional Analysis

Oil	0.99%
Water	9.0%
Solids	70.0%
Ash	65.0%
Cyanide	0.54 ppm

The remaining laboratory results are presented in Tables 4 through 6. The tables show the initial and final concentration for each analyte with the calculated percent removal.

Table 4
Volatile Organic Compounds

ANALYTE	RESULT, MG/KG		
	INITIAL	FINAL	% REMOVAL
Methylene Chloride	14	0.06	99 6
Acetone	<28	3.2	88.6
2-Butanone	<42	1.9	95.5
Benzene	<5.6	0.016	99.7
2-Hexanone	6.5	0.022	99.7
Toluene	13	0 032	99.8
Ethylbenzene	15	0.008	99.9
Styrene	35	0.024	99.9
Xylene	43	0.053	99.9

In selecting a chemical extraction method, we were concerned with metals treatment and ultimate on-site disposal of the residual solids. To address this concern, we requested that a leachate test, EP Toxicity, be run on the residual solids to give us a feel for the expected final characteristics of these solids. Table 6 gives the initial and final total metals analysis by Method TCL 6010-7000 and the EP Toxicity concentration of the eight targeted metals.

Summary

The contaminated soil sample from the Petro-Chemical Systems

Table 5
Semivolatile Compounds

ANALYTE	RESULTS, MG/KG	
	INITIAL	FINAL
Phenol	4.9	BND
Naphthalene	240	BND
2-Methylnaphthalene	95.0	BND
Acenaphthene	21.0	BND
Dibenzofuran	2.4	BND
Fluorene	43.0	BND
Phenanthrene	60.0	BND
Anthracene	11.0	BND
Fluoranthene	7.1	BND
Pyrene	13.0	BND
Benzo(a)Anthracene	2.2	BND
bis(2-Ethylhexyl)Phthalate	2.1	BND
Chrysene	2.1	BND

BND - Denotes below detection limits

Table 6
Metals Analysis and EP Toxicity

METAL	INITIAL MG/KG	FINAL MG/KG	EP TOXICITY MG/L
Aluminum	57,000	64,000	
Antimony	53	43	
Arsenic	3.1	3.6	0.004
Barium	120	130	0.11
Beryllium	1.7	2.1	
Cadmium	7.1	8.8	<0.02
Calcium	1,700	2,800	
Chromium	46	73	<0.05
Cobalt	5.1	7.1	
Copper	9.8	15	
Iron	27,000	42,000	
Lead	51	88	<0.1
Magnesium	2,200	3,200	
Manganese	60	110	
Mercury	0.013	0.027	<0.1
Nickel	16	15	
Potassium	3,600	3,000	
Selenium	0.42	0.55	<0.001
Silver	1.3	2.0	
Sodium	310	11,000	
Thallium	<3	<2	
Zinc	45	63	
Vanadium	71	110	

Superfund Site was suitable for processing with the B.E.S.T.[R] solvent extraction process. There were no significant problems observed during testing of the samples and consequently, full-scale processing should be straightforward. Key observations concerning the test results include the following:

- The oil was chemically compatible with triethylamine.
- The oil in the sample was readily extracted from the soil. The soil and grease residual in the product solids was 470 ppm, compared to 9,900 ppm in the feedstock, yielding a 95% extraction efficiency in three extraction stages.
- All semivolatile compounds were below detection limits in the treated solids. However, two volatile compounds, acetone and 2-butanone (MEK), were quantified above 1 ppm in the product solids. Thus the treatment objective of 1 ppm or less volatile organic compounds in the treated soil was not achieved.
- The product solids readily passed the EP Toxicity Leaching test for metals.
- The separation of TEA/oil from water by heating and gravity decantation was very effective in that it was immediate and minimal concentrations of fugitive water and TEA/oil remained in the decant TEA/oil and decant water fractions, respectively.

- The untreated product water contained 41 mg/L oil and grease and also contained very low concentrations of metals. Both oil and grease content and heavy metals content could be further reduced by post-treatment if desired.

Conceptual Design

The contaminated soil could be treated in a 110 yd³/day B.E.S.T.ᴿ transportable processing unit. The unit would operate 24-hours per day during the processing period with an average utilization rate of 80%.

The estimated unit cost for this treatment system is $160-$210/yd³.

CONCLUSIONS

Both of the technologies studied can successfully treat the contaminated soils at the Petro Chemical Systems Site. The bioremediation alternative may have a cost advantage over the solvent extraction technology; however, confirmation of this preliminary conclusion will be based on a more detailed economic comparison.

Design Modifications to Improve Granular Activated Carbon Treatment System Performance

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ABSTRACT

Improvements were recommended and designed for the South Tacoma Channel Groundwater Treatment System. The treatment system was implemented to assist with remedial cleanup activities at this NPL site in Tacoma, Washington. The existing treatment system utilizes liquid-phase, granular activated carbon (GAC) treating 150 gpm of groundwater to remove volatile chlorinated hydrocarbons. Current GAC performance for contaminant breakthrough and competitive adsorption was accurately simulated with a plug-flow pore and surface diffusion model for multicomponent, fixed-bed mixtures. The model was also used to estimate GAC performance at higher influent loading rates, which would occur if a new proposed groundwater extraction well were added to the system in the future.

The recommended design improvements included the addition of an air stripping process at the end of the GAC system to remove vinyl chloride. The air stripping tower was designed to remove only vinyl chloride, which is weakly adsorbed and quickly displaced from the GAC by other competing organics, resulting in high overall carbon usage rates. An analysis of air stripping design was performed with a computer model based on a two-resistance approach using Onda correlations. The modified treatment system configuration of GAC combined with air stripping, as simulated by computer models, was shown to be capable of surpassing performance requirements for air and water discharge. An economic evaluation showed that the modifications could pay for themselves in approximately two years based on savings associated with carbon replacement if more stringent vinyl chloride discharge standards were adopted in the future.

INTRODUCTION

The South Tacoma Channel Well 12A site is located in Tacoma, Washington, within the Commencement Bay drainage area. Well 12A is part of an alluvial well field providing a supplemental potable water source for the City of Tacoma. Chlorinated hydrocarbon compounds have been detected in the groundwater withdrawn from Well 12A at concentrations high enough to preclude its use in the water system without first receiving treatment to remove contaminants. To cleanup the aquifer, a groundwater extraction and GAC treatment system was installed at the contaminant source location in 1988. The treatment system consists of two GAC adsorbers operated in series. The overall objectives of the extraction and treatment system are to remove and treat groundwater contaminants at their sources and to restore the quality of the aquifer to acceptable drinking water standards.

The GAC treatment system, which has operated continuously since 1988, is capable of reducing influent VOC concentrations to below standard detection levels available by GC/MS analysis for all compounds except vinyl chloride. Vinyl chloride is weakly adsorbed onto GAC and

quickly displaced by other, more strongly adsorbing organic compounds. The displacement of vinyl chloride routinely produces an effluent vinyl chloride concentration from the treatment system that is higher than the influent concentration. To address the issue of vinyl chloride, the U.S. EPA tasked Black & Veatch to evaluate the technical and economic feasibility of applying air stripping treatment to the existing GAC system to reduce the effluent levels of vinyl chloride. Although vinyl chloride is not effectively removed by GAC, it has properties of high volatility and low molecular weight that make it very suitable for removal by air stripping.

For purposes of the evaluation, the following discharge goals and operating criteria were proposed by the U.S. EPA and the Washington State Department of Ecology:

- No displacement standard. This discharge goal requires that effluent vinyl chloride concentrations be no greater than the average influent concentration.
- Carbon replacement in the lead bed based on 300 $\mu g/L$ breakthrough of 1,2-dichloroethene (1,2-DCE) in the lead bed effluent. This operating criterion allows full breakthrough and displacement of vinyl chloride in the effluent but maintains all other contaminants below detection levels by using 1,2-DCE as a precursor.

For comparison, the evaluation also investigated the feasibility and cost of meeting a discharge goal of 2 $\mu g/L$, which is the drinking water maximum contaminant level (MCL) for vinyl chloride. In addition, the evaluation considered the impact of adding another extraction well to the system, which would increase the influent hydraulic and contaminant loading rates.

The current treatment requirements for vinyl chloride are based on meeting U.S. EPA Marine Water Quality Criterion of 525 $\mu g/L$. The existing GAC system can meet this standard even with the displacement of vinyl chloride. However, if a no displacement standard were adopted in the future, the operating costs of the system would increase substantially because of the very high carbon usage rates required to remove vinyl chloride. Therefore, significant cost savings would be achieved by modifying the system with an air stripping tower to selectively remove vinyl chloride.

DESCRIPTION OF EXISTING GAC TREATMENT SYSTEM AND OPERATING PERFORMANCE

The operating performance of the GAC treatment system is summarized in Table 1. As shown in the table, all VOCs are routinely removed to below detection limits by GAC, with the exception of vinyl chloride. Treated effluent is discharged through a storm drain into Puget Sound. The current discharge standards, which are based on U.S. EPA Marine Water Quality Criteria, are continuously met for all compounds including vinyl chloride which has a standard of 525 $\mu g/L$.

Table 1
Operating Performance of Existing GAC System

Parameter	Influent		Effluent	
	Average	Range	Average	Range
Volatile Organic Compounds (ug/l)				
Vinyl Chloride	28.8	22-39	27.5	1.6-54
Trans 1,2-DCE	337	230-520	1.1U	
Cis 1,2-DCE	222	130-430	1.2U	
Trichloroethene	1000	580-1400	0.8U	
1,1,2-Trichloroethane	25.2	12-43	0.3U	
Tetrachloroethene	62.5	31-110	0.6U	
1,1,2,2-Tetrachloroethane	2780	1500-3900	0.6U	
Toluene	24	7.9-41	0.6U	
pH	6.7	5.2-7.5	6.7	5.2-7.5
TOC (mg/l)	6.3	0.9-21	0.34	0.1-0.8
Monthly Flow (Mgal)	5.9	5.0-7.2		

U = Compound was analyzed for but not detected at the given detection limit.

The existing treatment process consists of two carbon adsorption vessels with identical dimensions: 10 feet in diameter and approximately twelve feet high. Each vessel contains approximately 20,000 lbs. of 12 by 40 standard sieve GAC, which is used in a pressurized, downflow operational mode. The maximum flow capacity of the system is rated at 500 gpm. The flowrate is presently limited to 150 gpm because of hydraulic restraints of the groundwater well extraction system. This production rate is the maximum that currently can be sustained without pumping the well dry. At 150 gpm, the empty bed contact time (EBACT) within each adsorber is 36 minutes.

During normal operation, the vessels are operated in a series configuration. Exhaustion of the activated carbon in the lead bed is based on reaching a concentration of 300 μg/L of combined cis- and trans-1,2-dichloroethene (1,2-DCE) in the effluent from the lead vessel. 1,2-DCE is the second-weakest adsorbing component and is used as a precursor to the breakthrough of other contaminants. When the 1,2,-DCE concentration has approximately reached this breakthrough level, the lead bed is taken out of service, and the spent carbon is replaced with fresh carbon. After the carbon is replaced in the first vessel, the valve sequence is manually changed, and the bed is returned to service as the second bed in series.

At 150 gpm, the treatment system operates at only 30% of its maximum hydraulic loading capacity. The U.S. EPA tentatively plans to install a new extraction well directly below the primary source of groundwater contamination. The purpose of the new well will be to speed up groundwater remediation by extracting groundwater having the highest contamination concentration. If installed, the new well would add approximately 150 gpm to the system, for a total flowrate of approximately 300 gpm. It is expected that the new well will contain the same VOC contaminants that the system currently processes, but at roughly 10 times higher concentration.

For purposes of the air stripping process evaluation, the maximum emission allowance for vinyl chloride was set at 1 lb/day. This value was based on the local air pollution control standards for Tacoma-Pierce County, which were in effect at the time of this study.

DESCRIPTION OF PROCESS MODELS

The mathematical models used to simulate GAC performance and to assist with design of the air stripping treatment process are complex, and a full description would require a separate technical paper. Therefore, this paper will present only a brief description of the models with references to the literature for a more complete description and theoretical basis.

Air Stripping Process Model

The computer model used to perform the air stripping analysis is based on a two-resistance approach using Onda correlations to determine liquid) and gas-phase mass transfer coefficients. The model considers both liquid-phase and gas-phase resistance to mass transfer and has been found to offer significant improvement over single-phase models in predicting volatilization of trace VOCs in the air stripping process.

The rate of mass transfer across an air-water interface in the stripping process is controlled by the sum of resistances in the liquid and gas-phase boundary layers. Assuming that Henry's Law describes the chemical equilibrium conditions between the air and water phases (a valid assumption for low concentrations of VOCs in groundwater) the overall rate constant is given by:[1]

$$K_L a = [(1/k_L a) + (1/k_G a \, H_c)]^{-1} \qquad (1)$$

in which K_L is the overall mass transfer coefficient (m/sec), k_L and k_g are the mass transfer coefficients for the liquid and gas phases (m/sec), a is the specific interfacial area of packing m^2/m^3 and H$_c$ is the Henry's Law constant (dimensionless). The product of $K_L a$ is equivalent to the first order, transfer rate constant. Values for k_L, k_G and a (area) were determined by correlations developed by Onda et al.[2]

By incorporating the overall transfer rate constant into mass balance equations based on influent and desired effluent contaminant concentrations, important design parameters such as packing height and air-to-water ratio were determined for the air stripping process.

GAC Process Model

The computer program used to perform the GAC analysis was developed by John C. Crittenden at Michigan Technological University and is commonly referred to in engineering literature as the plug-flow pore and surface diffusion model (PFPSDM).[3]

The PFPSDM is used to predict effluent concentration profiles and carbon usage rates for multicomponent mixtures treated by a fixed-bed GAC adsorber. The model considers mass transfer resistances due to both pore and surface diffusion. Once contaminant molecules have diffused from the bulk solution to the outside surface of the adsorbent grain, they then diffuse to the inside of the porous adsorbent because of the high internal surface area of the adsorbent. The internal transfer step can proceed in the liquid-filled pores, which is referred to as pore diffusion, or along the walls of the pores as adsorbed molecules, which is referred to as surface diffusion. Although most adsorbents used to remove organic compounds from water have very heterogeneous and porous structures, the PFPSDM assumes that the adsorbent grain is a spherical particle of homogeneous structure such that the solid-phase contaminant concentration, adsorbent density and surface depend only on the radial location in the particle.

The assumptions incorporated into the PFPSDM are as follows:

- The liquid-phase flux may be described by a linear driving force
- Local equilibrium exists throughout the adsorbent phase
- The adsorption equilibria may be described by the Freundlich isotherm equations and ideal adsorbed solution theory
- The intraparticle mass flux is given by both surface and pore diffusion
- There are no solute-solute interactions in the diffusion process
- Solute transport in the axial direction is by advective flow
- The effects of radial dispersion are negligible

To make predictive calculations with the PFPSDM, the following five parameters must be determined for each contaminant: Freundlich capacity parameter K_f; Freundlich intensity parameter, 1/n; film transfer coefficient; surface diffusion coefficient; and pore diffusion coefficient.

The program solves a system of simultaneous partial differential equations by converting them to a system of ordinary differential equations using the orthogonal collocation method then integrating by the Dgear method. The PFPSDM program accurately predicts the competitive adsorption effects in multicomponent mixtures and can be used to determine the elution order and effluent breakthrough profiles of contaminants and the highest effluent concentrations due to displacement from competitive adsorption.

EVALUATION PROCEDURES FOR GAC

The Freundlich isotherm constants used in the process model were reduced to account for a reduction in GAC adsorption capacity because of fouling by influent total organic carbon (TOC). The adverse effect of TOC loading on the performance of the GAC treatment system is due to the significant differences in adsorption behavior between trace VOCs and natural organic matter (measured as TOC). Within an adsorption vessel, the chlorinated hydrocarbons build up in a well-defined mass transfer zone, which migrates slowly through the carbon bed with increased running time. The large humic molecules that comprise the majority of TOC constituents have slow adsorption kinetics, which leads to a rapid migration velocity and a long mass transfer zone. This, in turn, yields a fast breakthrough of TOC in the effluent of adsorption vessels designed specifically for trace VOC removal. The effect of this TOC preloading is a substantial reduction of carbon adsorption capacity over time. For modeling the existing treatment system, TOC preloading reduced the Freundlich constants to approximately 70% of the adsorption capacity of virgin carbon. The value for each adjusted Freundlich constant is shown in Table 2.

Figure 1
Displacement of Vinyl Chloride
Predicted vs Actual

Figure 2
Breakthrough of 1,2-DCE
Predicted vs Actual

Table 2
Existing Treatment System GAC Modeling Parameters

Parameter	Influent Concentration (ug/l)	Freundlich Constant (um/g)$^{1/n}$ (1/um)	Freundlich Exponent (dimension-less)
Volatile Organic Compounds			
Vinyl Chloride	28.8	5.6	0.72
Trans-1,2-DCE	337	29.7	0.59
Cis-1,2-DCE	222	34.6	0.59
Trichloroethene	1,000	150.5	0.45
1,1,2-Trichloroethane	25.2	83.3	0.49
Tetrachloroethene	62.5	367.5	0.40
1,1,2,2-Tetrachloroethane	2,780	306.0	0.36
Toluene	24	285.3	0.40
TOC (mg/l)	6		
Water Temperature C	12		
Average Monthly Flow, Mgal	5.2		

The results of the modeling predictions are compared with the observed monitoring data for the treatment system for displacement of vinyl chloride in Figure 1 and breakthrough of 1,2-DCE in Figure 2. As indicated in the figures, the modeling results agree very closely with the actual treatment system performance observed at the site. The increased vinyl chloride concentration in the treated effluent is due to competitive displacement occurring in the carbon beds between compounds of different adsorption strength. The competitive displacement or desorption process occurring within the carbon beds at the Well 12A treatment system can be described as an interaction between the compounds vinyl chloride and 1,2-DCE. Both of these VOCs are being fed simultaneously to the treatment system and 1,2-DCE has a higher adsorption affinity and migrates more slowly than the vinyl chloride as these compounds move through the carbon beds. Consequently, the weakly adsorbing component (vinyl chloride) migrates through the bed faster than the more strongly adsorbing component and saturates the bed as if it were present as a single component. This phenomenon leads to a solid-phase concentration for the vinyl chloride in the deeper part of the bed that exceeds the solid-phase concentration that results when 1,2-DCE is also present. Accordingly, the weakly adsorbing component is displaced by 1,2-DCE in a manner in which the displaced concentration exceeds the influent concentration.

Under the current operating conditions and discharge standards, the most efficient utilization of carbon can be attained by rotating the carbon bed sequence upon depletion and by allowing the lead adsorber to saturate completely with 1,2-DCE before replacement. Bed satura-

tion is achieved for a given contaminant when the bed effluent concentration becomes equivalent to the influent concentration. Because the discharge standard (1.85 μg/L) for cis- or tans-1,2-DCE is only slightly above the analytical detection level, concentrations of this compound must remain below detection levels in the effluent at all times. The adsorption capacity and breakthrough data obtained with the PFPSDM model indicate that, for both the current and potential future treatment system operating conditions, the lead vessel can be saturated with 1,2-DCE without 1,2-DCE or any other VOCs (with the exception of vinyl chloride) being detected in the effluent from the second vessel. Furthermore, there is a minimum time period of approximately one month between 1,2-DCE saturation of the lead carbon bed and the beginning of 1,2-DCE breakthrough of the second carbon bed. This time period should provide a sufficient safety factor to ensure that carbon replacement in the lead vessel will occur before 1,2-DCE is detected in the system's discharge.
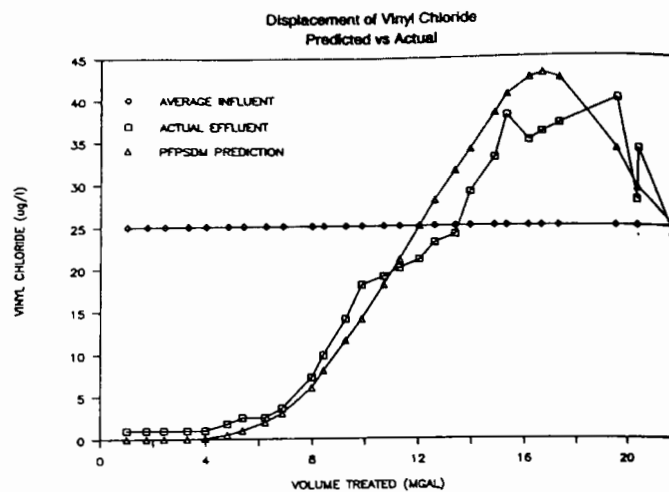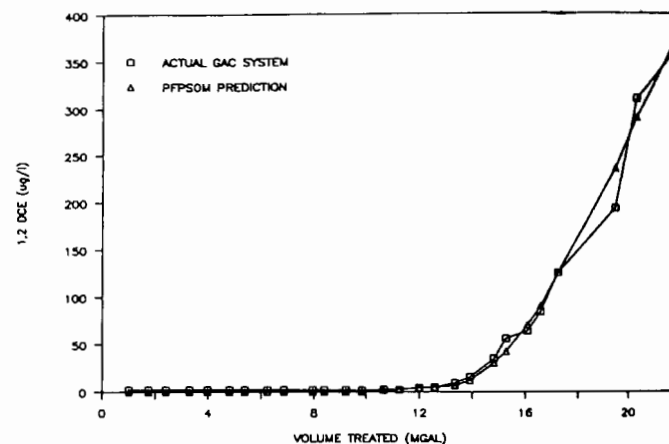
EVALUATION AND DESIGN PROCEDURES FOR THE AIR STRIPPING PROCESS

Optimum Configuration

The alternative configurations that were reviewed for placing an air stripping tower in the treatment process included:

- After the groundwater extraction well and before the carbon adsorp-

tion vessels
- Between the first and second carbon adsorption vessels
- At the end of the GAC process after the second carbon adsorption vessel

The capital cost of either of the first two configurations would exceed the cost of the third alternative because a new pumping station would be needed to pump effluent from the air stripping tower through the downstream carbon adsorption vessel(s). The first alternative would also air strip other VOCs besides vinyl chloride, resulting in VOC emissions in excess of the local standard of 1 lb/day for total chlorinated hydrocarbons. The second alternative, locating an air stripping tower between the first and second carbon adsorption vessels, could be operated in a manner that would eliminate excess VOC emissions by allowing only vinyl chloride removal. However, the operating criteria necessary to achieve this goal would adversely impact the treatment system's cost-effectiveness because the first carbon bed would require replacement as soon as 1,2-DCE was detected in the air stripping tower's influent.

Placement of an air stripping tower located after the second carbon adsorption vessel (the third alternative) was chosen for further detailed evaluation. Only vinyl chloride is removed by the air stripping tower in this alternative and carbon usage in the lead vessel is maximized by completely saturating the carbon in the lead vessel with 1,2-DCE.

Design Criteria

Design criteria for the air stripping tower were evaluated and selected using the previously described air stripping computer model. The design of the air stripping tower was based on the most conservative parameters projected for the treatment system, including addition of the new groundwater extraction well. The treatment objective was based on meeting the most stringent discharge goal of 2 μg/L of vinyl chloride. This goal would require removing 99.33% of the vinyl chloride displaced from the GAC system. Based on the displacement concentration projected by the GAC model, a maximum vinyl chloride concentration of approximately 300 μg/L could be present in the effluent from the carbon adsorption vessels. Removing at least 99.33% would also result in air emissions consistent with the local air pollution control standard of 1 lb/day for total chlorinated hydrocarbons.

The modeling analysis showed that a minimum height of packing material required to achieve 99.33% removal of vinyl chloride would be approximately 18 feet for a tower 5 feet in diameter and an air-to-water ratio of 30. Figure 3 shows the relationship between packing height and air-to-water ratio. At an air-to-water ratio between 20 and 30, the curve starts to flatten out and packing height decreases little for further increases in the air-to-water ratio. The packing height approaches an asymptote at high air-to-water ratios because the liquid loading decreases, which in turn decreases the overall mass transfer coefficient
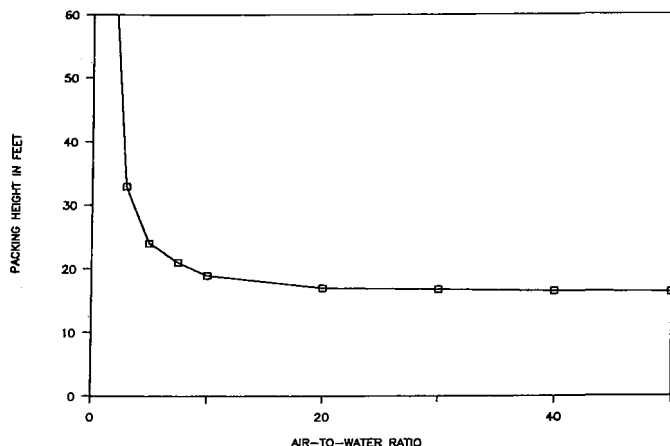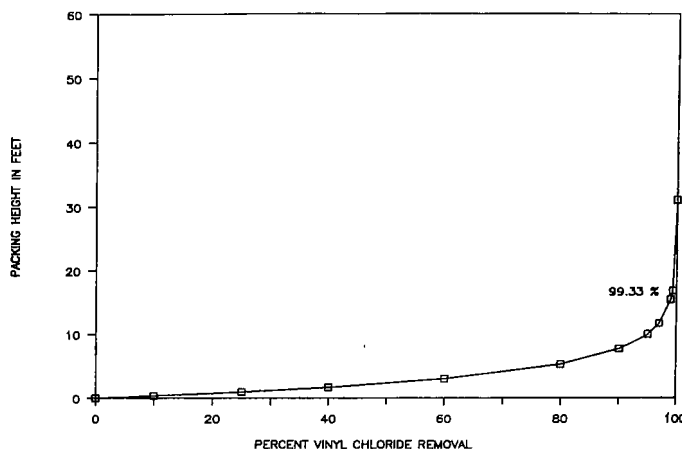
Figure 4
Relationship Between Packing Height and Percent Removal
(Air-to-Water Ratio = 30)

in Equation 1. Although the gas-phase loading and, thus, gas-phase mass transfer is increased, the overall mass transfer coefficient is reduced because most of the mass transfer resistance is in the liquid phase. Figure 4 shows the packing height versus percent vinyl chloride removal for a 5-foot-diameter tower and an air-to-water ratio of 30. The figure indicates that the packing height increases rapidly as percent removal increases beyond the required removal rate of 99.33%.

Table 3 summarizes the design criteria developed for the air stripping treatment system. The air stripping process was designed to meet the lowest discharge goal of 2 μg/L. However, the system could meet other less stringent goals, such as a no displacement standard for vinyl chloride, if the air-to-water ratio were lowered.

Table 3
Air stripping Tower Design Criteria

Design Parameter	Design Value
Minimum Vinyl Chloride Removal Efficiency, percent	99.33
Vinyl Chloride Concentration, ug/l	300
Water Flow, gpm	300
Air Flow, cfm	1200
Air-to-Water Ratio	30
Blower Requirement, hp	5.0
Tower Geometry	
Effective Packing Height, ft	18
Height of Main Section, ft	28
Diameter of Main Section, ft	5
Minimum Water Temperature, F	50
Minimum Air Temperature, F	32
Henry's Constant, dimensionless	0.63
Specific Surface Area of Packing, ft^{-1}	46

COST ANALYSIS

Carbon Usage Rates

The impact of alternative discharge goals on the annual carbon usage rates and carbon replacement costs for the existing treatment system are indicated in Table 4. The predicted carbon usage rates and resulting costs were based on treatment system breakthrough performance as estimated by the PFPSDM GAC model for meeting each of the different discharge goals. The carbon usage rate indicated in the table for

Figure 3
Relationship Between Packing Height and A/W Ratio
(93.33% Vinyl Chloride Removal)

meeting the current discharge standard of 525 µg/L vinyl chloride assumes optimum carbon utilization by allowing the lead bed to fully saturate with 1,2-DCE before replacement. Based on the analysis, adoption of a no displacement standard for vinyl chloride, compared to the current 525 µg/L discharge standard, would increase carbon replacement costs by $70,000/yr. For comparison, Table 4 also lists carbon replacement costs for achieving a discharge goal of 2 µg/L vinyl chloride. The table shows carbon replacement costs under the current operating criterion of 300 µg/L of 1,2-DCE from the lead bed effluent.

Table 4
Impact of Alternative Discharge Criteria
on Annual Carbon Replacement Costs

Conditions	Discharge Criteria VC (ug/l)	Carbon Usage Rate (lbs/1000 gal)	Annual Carbon Replacement Cost* ($)
Existing Conditions With 1 Extraction Well			
Marine Discharge Standard	525	0.77	66,000
No Displacement Standard	28.8	1.59	136,000
300 ug/l 1,2-DCE (Lead Bed)	>30	0.85	73,000
Safe Drinking Water Act MCL	2	1.75	150,000
Future Conditions With 2 Extraction Wells			
Marine Discharge Standard	525	0.98	168,000
No Displacement Standard	158	1.75	299,000
300 ug/l 1,2-DCE (Lead Bed)	>30	1.35	231,000
Safe Drinking Water Act MCL	2	1.92	329,000

*Based on actual carbon replacement cost of $1.37 per pound. Cost calculation assumes a total flow of 62.4 million gallons with one extraction well and 124.8 gallons with two extraction wells.

Based on the accuracy of the GAC computer model in simulating the performance of the existing treatment system, process modeling was performed to evaluate the performance of the treatment system in the event that a new groundwater extraction well was installed. As a basis for comparison, it was assumed that the new extraction well would add 150 gpm to the existing influent and contain 10 times the current concentration of each VOC and TOC. The modeling analysis used an approach similar to the method described for the existing treatment system except that, because of the higher VOC loading rates and corresponding increased carbon usage rates, the TOC preloading effects were slightly reduced and, therefore, the Freundlich constants were estimated to be 80% of the adsorption capacity predicted by virgin carbon. Based on the vinyl chloride and 1,2-DCE breakthrough curves predicted by the PFPSDM model for the future treatment system with higher loading, the impact of alternative discharge goals on the carbon replacement costs were evaluated. Table 4 indicates the projected carbon usage rates and annual carbon costs for meeting each of the alternative discharge goals in the event that a new groundwater extraction well was added to the treatment system. The results indicate that adoption of a no displacement standard would increase carbon replacement costs by $131,000/yr.

Air Stripping Treatment Costs

Total construction costs for the air stripping tower were estimated to be $122,000. These costs include the air stripping tower, foundation, installation, startup and testing, contingencies and engineering. The cost for the air stripping tower and associated equipment were estimated to be $50,000, which includes the tower structure, 18 feet of packing material, the blower, electrical controls and all necessary piping. Annual operation and maintenance (O&M) costs including power consumption of the blower were estimated to be $3,000/yr.

Present Worth Analysis

A present worth analysis was conducted to determine the benefits,

Table 5
Economic Analysis
Existing Treatment System

	No Action Alternative	Air Stripping Tower Alternative				
Year	Carbon Costs* ($)	Air Stripping Tower ($)	Carbon Costs** ($)	Additional O&M ($)	Total Costs ($)	Net Savings ($)
0		122,000				(122,000)
1	136,000		66,000	3,000	69,000	(55,000)
2	140,080		67,980	3,090	71,070	14,010
3	144,282		70,019	3,183	73,202	85,090
4	148,611		72,120	3,278	75,398	158,303
5	153,069		74,284	3,377	77,660	233,712
6	157,661		76,512	3,478	79,990	311,383
7	162,391		78,807	3,582	82,390	391,385
8	167,263		81,172	3,690	84,861	473,787
9	172,281		83,607	3,800	87,407	558,660
10	177,449		86,115	3,914	90,029	646,080
11	182,773		88,698	4,032	92,730	736,122
12	188,256		91,359	4,153	95,512	828,866
13	193,903		94,100	4,277	98,378	924,392
14	199,721		96,923	4,406	101,329	1,022,784
15	205,712		99,831	4,538	104,369	1,124,127
***	1,384,109	122,000	671,700	30,532	702,232	3,250,697

Assumptions: Inflation = 3%, Discount Rate = 8%

*Based on costs presented in Table 4 for 28.8 ug/l vinyl chloride discharge standard.

**Based on costs presented in Table 4 for 525 ug/l vinyl chloride discharge standard.

***Net present value.

if any, of installing an air stripping tower to remove vinyl chloride from the GAC treatment system's effluent. The analysis was based on the design criteria developed for both the existing treatment system and the future treatment system, which includes a new groundwater extraction well. As a basis for comparison, a no action alternative was developed that considers the cost requirements for meeting a lower discharge standard with the existing GAC system. The no action alternative's carbon replacement costs were based on the carbon usage rates estimated as necessary to meet the discharge requirements that would result from the adoption of a no displacement standard.

The no action alternative's costs were then compared to the costs associated with meeting the same discharge standard by adding an air stripping tower at the end of the existing GAC treatment system. For the analyses, carbon replacement costs and O&M costs were escalated annually over the life of the project at a 3% rate of inflation. A discount rate of 8% was assumed for the present worth calculations. The present worth analysis for the current treatment system operating with one extraction well is summarized in Table 5. The net savings indicated in the table are based on three primary considerations:

- The economic analysis uses the no action alternative's carbon replacement costs and associated 28.8 µg/L vinyl chloride discharge standard as the basis for comparison. Carbon usage rates are based on values given in Table 4 for meeting the 28.8 µg/L standard.
- An air stripping tower is included to achieve the 28.8 µg/L vinyl chloride effluent limitation. Capital and O&M costs for addition of the air stripping tower are based on the costs developed in the previous subsection.
- The carbon usage rates associated with the modified treatment system with air stripping are based on values given in Table 4 for meeting the 525 µg/L discharge standard for vinyl chloride.

The results of the present worth analysis show that the modifications associated with adding an air stripping unit would pay for themselves

within two years based on cost savings associated with carbon replacement. For the first 15 years, the present worth of the net savings of air stripping vinyl chloride over continued carbon treatment exceeds $3.3 million.

A second present worth analysis was conducted for the case of a future treatment system operating with two extraction wells. The same no action alternative used as a basis for comparison in the first present worth analysis was also used in the second analysis. The carbon replacement costs were based on the values shown in Table 4 for operation with two extraction wells. The air stripping system was designed to handle either high- or low- influent loading conditions. Therefore, the costs associated with adding the air stripping unit were the same as those used in the first analysis. Because of the higher influent loading conditions and reduced capacity of the GAC, the second present worth analysis indicated an even shorter payback period of one year and a 15-year present worth net savings in excess of $7 million.

CONCLUSIONS

The PFPSDF model can be used as an accurate predictor of full-scale GAC performance under the conditions of multicomponent competitive interactions observed at the Well 12A treatment system. The modified treatment system configuration of GAC followed by air stripping, as simulated by computer models, was shown to be capable of meeting existing discharge requirements for air and each proposed discharge goal for water. By applying air stripping treatment at the end of the GAC system to selectively remove vinyl chloride, more efficient carbon utilization may be achieved by allowing 1,2-DCE to saturate the lead adsorber. If more stringent water discharge standards for vinyl chloride were adopted in the future, such as a no displacement standard, significant carbon replacement cost savings could be achieved by modifying the existing GAC system with an air stripping tower.

The displacement and early breakthrough of certain organic contaminants is not uncommon with GAC treatment. The design and analysis procedures described in this paper can be applied similarly to other water treatment systems employing GAC.

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Key Mixed Waste Regulatory and Policy Issues

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INTRODUCTION

This paper contains a discussion of the key regulatory and policy issues regarding mixed waste (waste containing both radioactive and nonradioactive hazardous chemical constituents). This includes a brief discussion of relevant NRC and U.S. EPA regulatory and policy requirements. The key regulatory and policy issues addressed in this paper are: (1) NRC-U.S. EPA regulatory consistency, (2) the land disposal ban effect and (3) Federal-State regulatory complexity. It concludes with some key observations and recommendations.

BACKGROUND

According to the U.S. EPA, there are approximately 30 Department of Energy (DOE) installations that generate mixed waste and approximately 26,000 Nuclear Regulatory Commission (NRC) licensees [see 54 FR 48372, 48492 (Nov. 22, 1989)]. The U.S. EPA states that 13 of the 30 DOE installations generate the majority of the mixed waste containing high-level, low-level and transuranic radioactive waste.

The NRC licensee mixed waste generators include hospitals, universities and nuclear power plants. The radioactive waste in this mixed waste consists largely of low-level radionuclides. The principal nonradioactive hazardous constituents include solvents, lead, chromium and other hazardous elements generated by the biomedical and nuclear power industries. The U.S. EPA estimates that commercially generated mixed waste represents approximately 2-3% of the low-level radioactive waste generated annually.

The U.S. EPA notes that there are inadequate government or industrial facilities licensed by both the NRC and the U.S. EPA to dispose of mixed waste. According to the U.S. EPA, most mixed waste is being managed by either recycling (mixed waste containing lead, for example) or incineration (scintillation cocktails containing solvents, for example). Most mixed waste is stored by generators under hazardous waste storage permits.

MIXED WASTE REGULATION AND POLICY

Commercially generated mixed waste is subject to federal regulation by NRC (radioactive waste constituents) and U.S. EPA (hazardous waste constituents) or states federally delegated or exercising independent, regulatory authority.[1] DOE generated mixed waste is subject to self-regulation regarding the radioactive waste constituents and U.S. EPA or state regulations regarding the hazardous waste constituents.[2]

NRC regulates the management of radioactive waste under the AEA, Nuclear Waste Policy Act (high-level waste) (NWPA) (42 USC sec. 10101-10226) and Low-Level Radioactive Waste Policy Act (LLRWPA) (low-level waste) (42 USC sec. 2021b-2121d) and implementing regulations. This paper concentrates on low-level mixed waste. NRC low-level waste regulations govern generation, treatment, storage, disposal

(10 CFR Parts 20, 30, 40, 50, 61 and 70) and transportation (10 CFR Parts 20, 71 and 73).

Under NRC regulations, the on-site treatment and storage of low-level radioactive waste is authorized as part of nuclear reactor and radioactive materials possession licenses. Both nuclear reactor and radioactive materials possession licensees are subject to various regulatory requirements regarding, among other things, on-site and off-site radiological exposure limits, operating procedures, environmental reviews and facility and equipment tests and inspections [see 10 CFR sec. 50.34 and 50.34a (reactor) and 10 CFR Parts 30, 40 and 70 (materials)]. The on-site disposal of low-level radioactive waste, such as incineration, requires additional authorization (see 10 CFR sec. 20.302). The off-site disposal of low-level radioactive waste requires an NRC license for the disposal facility operator (see 10 CFR Part 61). Low-level radioactive waste facility licensees are subject to various regulatory requirements regarding, among other things, waste classification siting, design, radiological performance objectives, environmental monitoring, closure and post-closure (see 10 CFR Part 61).

U.S. EPA regulates the management of hazardous waste under the Solid Waste Disposal Act, as amended by the RCRA (42 USC sec. 6901-6991k), and implementing regulations. These implementing regulations govern hazardous waste generation (40 CFR Part 262), transportation (40 CFR Part 263), treatment, storage and disposal (TSD) and cleanup and compensation (10 CFR Parts 264, 265 and 270). Hazardous waste includes U.S. EPA-listed waste (40 CFR Part 261) or waste that exhibits one or more of the following characteristics: ignitability, corrosivity, reactivity or toxicity. Characteristic waste can be determined either on the basis of known properties or testing (see 40 CFR sec. 261.3 and 261.20). RCRA cannot be applied in a manner inconsistent with the AEA. (see 42 USC 6906).

Under RCRA and regulations, bulk or containerized liquid hazardous waste, free liquids containing hazardous waste, specified concentrations of certain listed hazardous waste (including solvents and dioxins), "California list" waste and other listed and characteristic hazardous waste are prohibited from land disposal unless the U.S. EPA determines that such prohibition is unnecessary in order to protect human health and the environment [see 42 USC sec. 6924(c)-(g)]. An application for such a determination by an interested party must demonstrate, to a reasonable degree of certainty, that there will be no migration of hazardous constituents from the disposal unit or injection zone as long as the waste remains hazardous [see 42 USC sec. 6925(d)]. The land disposal ban extends to landfills, surface impoundments, waste pits, injection wells, land treatment facilities, salt dome formations and underground mines or caves [see 42 USC sec. 6924(k)]. Land banned waste can only be stored for the purpose of resource recovery, treatment or disposal [see 42 USC sec. 6924(j)].

Minimum technological requirements exist for new and interim status landfills or surface impoundments and new incinerators [see 42 USC sec. 6924(o)]. Interim status mixed waste disposal facilities are those in existence on July 3, 1986 and for which a partial (part A) permit application was submitted by March 23, 1989 [see 53 FR 37045 (September 13, 1988)].

Minimum technological requirements for landfills and surface impoundments include double liners, leachate collection systems and groundwater monitoring [see 42 USC sec. 6924(o) and 40 CFR sec. 264.221 (surface impoundments), sec. 264.301 (landfills) and sec. 264.97 (groundwater monitoring)]. Requirements for incinerators include compliance with minimum destruction and removal efficiency standards. Double liners and a leachate collection system are not required if the TSD operator can demonstrate that alternative design and operating practices, together with location characteristics, will prevent the migration of any hazardous constituents into the groundwater or surface waste as effectively as liners and leachate collection system [see 42 USC sec. 6924(o)(2)]. New TSD facility location standards, including criteria for identifying areas of vulnerable hydrogeology, are pending [see 42 USC sec. 6924(o)(7)].

Under RCRA regulations, hazardous waste can be stored on-site for 90 days without an interim status or full-scale TSD permit (see 40 CFR sec. 262.34). TSD permitees are subject to various regulatory requirements regarding, among other things, waste analysis, siting, design, manifesting, equipment and facility inspections, groundwater monitoring, corrective action, closure and post-closure procedures.

The NRC and the U.S. EPA have issued three policy memoranda describing their positions on commercial mixed waste definition, disposal facility siting and disposal facility design. The first memorandum defines mixed waste as waste that meets the definition of low-level waste under the LLRWPA and contains hazardous waste that is either a U.S. EPA-listed waste or characteristic waste.[3] The memorandum presents a method for generators to use in identifying characteristic mixed waste. The memorandum stated further that, if a generator normally segregates radioactive and hazardous waste, there is no need to assume that hazardous waste has inadvertently mixed with radioactive waste so as to form mixed waste or to inspect each container or receptacle to ensure that inadvertent mixing has not occurred.

The second policy memorandum identifies 11 siting criteria deemed acceptable for the selection of a mixed waste disposal site pending issuance of U.S. EPA's new location standards.[4]

The third policy memorandum presents a conceptual design approach that meets the U.S. EPA's minimum technology requirements for liners and leachate collection systems and NRC requirements for minimization of contact of waste and water while also assuring long-term stability and avoidance of long-term maintenance which are required by both agencies.[5] The policy states that, depending on the particular type of conceptual design selected by an NRC licensee, the U.S. EPA may permit variances to the double liner and leachate collection system requirement.

In a September 1988 the U.S. EPA mixed waste policy statement, the U.S. EPA indicated that the NRC and the U.S. EPA were exploring the possibility of issuing a joint licensing-permitting policy [see 53 FR 37045 (September 23, 1988)].

In a January 19, 1990, letter from NRC Chairman Carr to Congressman Udall, NRC indicated that consideration is being given to the issuance of guidance documents on waste characterization, inspection and storage. It states that the waste characterization guidance will address occupational exposures during sampling and testing. The sampling and testing guidance will provide NRC regional, NRC agreement states, U.S. EPA regional and U.S. EPA-authorized state inspectors with background information on mixed waste licensing and permitting, inspection planning and coordination, cross-training and conduct of mixed waste inspections. The storage guidance will combine the NRC radioactive waste storage recommendations with U.S. EPA storage requirements.

KEY MIXED WASTE REGULATORY AND POLICY ISSUES

NRC-U.S. EPA Regulatory Consistency

Under RCRA section 1006, RCRA cannot be applied in a manner inconsistent with the AEA. The September 1988 U.S. EPA mixed waste policy statement contained a commitment by the U.S. EPA to minimize the impact of RCRA regulation of mixed waste by developing a strategy for the least burdensome dual regulation of mixed waste. The U.S. EPA indicated that, where NRC and U.S. EPA regulations were duplicative, compliance with NRC regulation might achieve a level of environmental protection commensurate with that of U.S. EPA regulations and that, in such instances, it would accept information submitted in an NRC waste disposal license application when processing a U.S. EPA mixed waste permit application.

The U.S. EPA stated that a U.S. EPA and NRC staff review found no inconsistences in the agencies' respective regulations although U.S. EPA regulations were more prescriptive in some instances and differed in stringency. The U.S. EPA requested that any cases of actual inconsistency be brought to its attention for future rulemaking or policy consideration.[6] The 1990 NRC letter of Congressman Udall also stated that the NRC knew of no AEA-RCRA regulatory inconsistencies.

The January 1987 version of the NRC-U.S. EPA joint policy memorandum on mixed waste definition and identification provided that a RCRA-AEA regulatory inconsistency would exist in a situation where satisfying both sets of regulations would increase the radiation hazard, would be technically infeasible or would violate national security interest. It stated that variances from the RCRA requirements could be granted to generators, transporters and facilities that treat, store or dispose of mixed waste. The 1987 policy stated that NRC licensees could petition for variances from a RCRA requirement when they believe the application of such requirement would be inconsistent with the AEA. The policy did not identify any NRC regulatory process or procedure for considering inconsistency variance petitions. There is no discussion in the policy of how U.S. EPA permittees could obtain an inconsistency determination. It is not clear whether the NRC licensee variance petition is to be submitted to the NRC and/or the U.S. EPA. The inference appears to be that NRC decides inconsistency variance petitions for NRC licensees. The 1987 policy stated, for example, that NRC licensees should discuss any inconsistency with NRC prior to submitting a variance petition. If this interpretation is correct, it raises a jurisdictional question since the U.S. EPA, not the NRC, has RCRA implementation responsibility.

RCRA section 1006 is not discussed in the October 1989 final version of this policy memorandum. It is, thus, unclear whether the 1987 passage continues to represent the NRC or the U.S. EPA position on section 1006.

The September 1988 U.S. EPA mixed waste policy statement sheds some additional light on the meaning of the term inconsistency from the U.S. EPA viewpoint. The U.S. EPA stated that differing or more stringent regulations do not necessarily constitute inconsistent regulations. At the same time, it noted that dual regulation could result in instances where compliance with both sets of regulations may be both undesirable and infeasible. It is not clear whether the U.S. EPA would regard such an instance as one of regulatory inconsistency. In the written materials for the U.S. EPA mixed waste training course given to familiarize U.S. EPA mixed waste permit reviewers and inspectors with mixed waste issues, it is provided that an inconsistency exists when compliance with one set of regulations would cause noncompliance with the other.[7]

In my opinion, there are no substantive NRC-U.S. EPA regulatory inconsistencies per se although differences exist. With regard to mixed waste generators, a primary difference is that a RCRA permit is required for the treatment or storage of mixed waste which would not otherwise be required for the treatment or storage of radioactive waste by an NRC materials or reactor licensee. NRC regulations permit on-site treatment or storage by NRC licensees without further regulatory approvals. The

on-site treatment or storage of mixed waste subjects NRC licensees to a wholly new permitting scheme and regulatory authorities with which they are unfamiliar. In addition, since there are no off-site treatment or disposal facilities, generators must obtain some form of regulatory relief in order to overcome mixed waste storage and land disposal restrictions. These are discussed later.

Additionally, mixed waste characterization and analysis requirements arguably conflict with the NRC requirements to maintain occupational radiation exposure as low as reasonably achievable (ALARA) and remain a potential dissimilarity at least until the promised NRC-U.S. EPA policy guidance on the subject is issued.

With regard to mixed waste disposal facility operators, in my opinion, there are five major regulatory dissimilarities. First, since the NRC relies heavily on natural site features to control the migration of hazardous constituents, existing NRC siting regulations are more detailed than existing U.S. EPA siting regulations. However, the joint NRC-U.S. EPA siting guidance alters this and reduces any adverse impact from this fact. New U.S. EPA siting regulations are pending with an indeterminate impact at this writing.

Second, NRC regulations provide general design criteria which, along with siting, operation and closure measures, must permit the site to meet performance objectives regarding radiological exposure, prevention of inadvertent intrusion and post-closure site stability, as well as minimize wastewater contact and assure long-term stability and post-closure maintenance. NRC design details can be developed during the licensing process. U.S. EPA regulations (as required by RCRA) contain prescriptive design requirements for a double liner and leachate collection system. However, as already noted, RCRA permits a party to recommend an alternative facility design upon a demonstration of equivalent disposal facility performance. This also is addressed in the NRC-U.S. EPA design guidance document.

The third dissimilarity is in the area of groundwater monitoring. U.S. EPA regulations are far more prescriptive and extensive than NRC regulations in this area. Both NRC and U.S. EPA regulations require monitoring during site operation and the post-closure surveillance periods. Under NRC regulations, monitoring must be capable of detecting radiological releases before they reach the site boundary. Monitoring plan details are not specified and are left for development in individual license applications. U.S. EPA groundwater monitoring regulations, on the other hand, are quite detailed and include specific requirements for well locations, construction, sampling and data handling.

The fourth dissimilarity is in the area of sampling and inspections. U.S. EPA regulations require sites to be inspected weekly and after storms to detect any evidence of deterioration or malfunction of the run-on and run-off systems, proper functioning of the wind dispersal control system and the presence of leachate in the leachate collection system. NRC has no specific inspection regulations. Any such license requirements would be developed as part of the operating plan for individual applications. The potential for additional occupational radiation exposure exists from the U.S. EPA inspection requirement. This subject has already been touched upon.

The fifth and final dissimilarity of note is in the area of post-closure. NRC regulations require 5-year post-closure observation and maintenance by the licensee unless site-specific conditions necessitate a shorter or longer period. Following the required transfer of the site to a federal or state entity, an institutional control period of at least 100 years is required, which includes site monitoring and surveillance and limited custodial care. U.S. EPA regulations do not require transfer to a government agency and require a 30 year period of post-closure care by the permittee, which includes monitoring, reporting and maintenance. Accordingly, the institutional care period required by NRC is longer than required by the U.S. EPA and different bodies (the federal or state government for the NRC and the permittee for the U.S. EPA) are responsible for activities during this period. Both NRC and U.S. EPA regulations, however, provide that shorter or longer post-closure periods can be established on a case-by-case basis depending on site-specific conditions.

In summary, and despite the noted dissimilarities, statutory and regulatory means exist to obtain relief from any or all of the noted requirements on a case-by-case basis. For example, as already noted, RCRA prohibits inconsistent RCRA and AEA application. How a party can obtain such a determination, as also noted, is not clear. NRC licensees can also seek to obtain a regulatory exemption from a given NRC requirement upon a certain specified showing [see 10 CFR 30.11, 40.14, 70.14 (materials licensees), 50.12 (reactor licensees), 61.6 (disposal facility licensees)]. Although there is no comparable U.S. EPA regulation, the U.S. EPA has the inherent authority to grant relief from its own regulations. Both agencies are also on record as committed to eliminate consistencies if present and to otherwise harmonize the two sets of regulations. The results of ongoing discussions regarding future guidance documents should reveal the sincerity of this commitment and its achievability.

Land Disposal Ban Effect

As noted above, the RCRA land ban and associated storage restriction precludes the storage of untreated mixed waste. Since there is virtually no national mixed waste treatment capability and no mixed waste disposal capability, there is no alternative but to store mixed waste indefinitely. But such storage is prohibited, thus exposing generators to U.S. EPA or state enforcement action. There are 4 options for obtaining regulatory relief from the RCRA land disposal and storage ban: (1) no-migration petition, (2) national capacity variance, (3) case-by-case extension and (4) treatment variance.

The no-migration petition option was discussed earlier. A national capacity variance may be granted by the U.S. EPA when it determines that there is insufficient treatment or recovery capacity for a particular waste type. During the period a capacity variance is in place, land banned waste can only be land disposed in a facility that meets the RCRA minimum technology requirements (namely, a double liner and leachate collection system). Most mixed waste is characteristic hazardous waste for which a national capacity variance has been proposed by the U.S. EPA in its 1989 proposed rulemaking containing proposed treatment standards and prohibition effective dates for all characteristic hazardous waste and some listed waste (the third-third rule) [see 54 FR 48372 (Nov. 22, 1989)].

A case-by-case extension may be granted by the U.S. EPA upon a demonstration that a binding contractual commitment exists to construct or otherwise provide alternative capacity and the capacity cannot be available by the effective date because of circumstances beyond the petitioner's control (see 40 CFR sec. 268.5). During an extension period, land banned waste can only be disposed of in facilities meeting the minimum technology requirements. A treatment variance may be granted by the U.S. EPA by rulemaking on a generic or site-specific basis. A variance petition must demonstrate that: (1) because the physical or chemical properties of the waste differ significantly from the waste evaluated by the U.S. EPA in establishing the treatment standard, the waste cannot be treated to the level or by the method specified by the treatment standard or (2) that such standard or method is inappropriate for the waste. A site-specific treatment variance may be granted but it has no generic application to wastes at other sites (see 40 CFR sec. 260.20).

Varied Federal-State Regulation

The complexity and rigors of federal mixed waste regulation is compounded by the fact that some states exercise some or all NRC or U.S. EPA mixed regulatory authority and may additionally have hazardous waste laws that are more stringent than RCRA. NRC agreements state radioactive waste laws cannot be more stringent than NRC requirements. Thus, compliance with NRC and U.S. EPA mixed waste regulatory requirements may not be enough and regulated parties are subject to the interpretation and application of State laws with which they may have less familiarity and for which there may be less compliance guidance and consistency.

CONCLUSION

The NRC and the U.S. EPA take the view that there are no NRC-U.S. EPA regulatory inconsistencies relative to mixed waste regulation. Both agencies appear committed to address such inconsistencies brought to their attention. The process for resolving regulatory inconsistencies is unclear. Some existing and prospective NRC-U.S. EPA policy statements could eliminate real or perceived regulatory inconsistencies. In order to effectively eliminate real or perceived regulatory inconsistencies, it would be preferable to vest one agency or the other with exclusive or primary jurisdiction over mixed waste. Accomplishing this designation could require a legislative change. No such legislation is pending.

The RCRA hazardous waste land ban and storage restrictions place mixed waste generators in a quandary. Untreated mixed waste may not be stored or disposed of. There are inadequate mixed waste treatment and disposal facilities. Although some covered waste is not land banned until May 1992 under the third-third rule national capacity variance, the situation may not be much different then. Thus, mixed waste generators must obtain some form of regulatory relief or face potential regulatory enforcement action.

The fact that some states exercise NRC mixed waste regulatory authority, that some state exercise the U.S. EPA mixed waste regulatory authority, that some states exercise the U.S. EPA hazardous waste but not mixed waste regulatory authority and that some states exercise independent hazardous waste regulatory authority not derived from RCRA, creates a potential patchwork of mixed waste regulatory programs at the state level. State radioactive waste regulatory policies may differ from NRC radioactive waste regulatory policies. Therefore, the degree to which a particular state exercises delegated federal mixed waste regulatory authority or its own state regulatory authority will dictate how certain mixed waste regulatory requirements are interpreted and applied. Thus, the mixed waste generator must be aware of the regulatory policies in the state in which it operates. It cannot rely solely on federal regulatory policies which may or may not have been adopted by the state.

FOOTNOTES

1. See 42 USC sec. 2224 (NRC agreement states) and 42 USC sec. 6926 (U.S. EPA-authorized states). State hazardous waste regulation may exist independent of EPA delegation. State radioactive waste regulations may exist independent of NRC delegation.

2. The Atomic Energy Act (AEA) (42 USC sec. 2011-2296) and DOE Act (42 USC sec. 7101-7375) authorize DOE to govern its own nuclear activities through the issuance of orders to protect public health, life and property, which could include standards controlling the design, location and operation of facilities associated with these activities. See 42 USC sec. 2201(i) (3). Doe nuclear activities include nuclear weapons production, uranium enrichment and nuclear research.

   DOE low-level radioactive waste management policy is contained in DOE Order 5280.2A and includes provisions on waste form acceptance criteria, site selection criteria, design criteria, operating procedures (including training, environmental monitoring, testing, site access and emergency planning) and closure and post-closure (including periodic surveillance and maintenance provisions). DOE hazardous and mixed waste management policy is contained in DOE Order 5400.3 and essentially invokes applicable U.S. EPA and state requirements.

3. See Memorandum to NRC Licensees (Jan. 8, 1987, as revised, Oct. 4, 1989).

4. See Memorandum to States and Low Level Waste Compacts (Mar. 13, 1987).

5. See Memorandum to States, Compacts and Licensees (Aug. 3, 1987).

6. The author has not seen the responses to this notice. However, a nuclear industry trade association has published a report comparing NRC and U.S. EPA mixed waste regulations and the impact of dual regulation on nuclear reactor and low-level radioactive waste disposal facility licensees. See "The Management of Mixed Low-Level Radioactive Waste in the Nuclear Power Industry," Nuclear management and Resources Council (January 1990).

7. See U.S. EPA Office of Solid Waste "Mixed Waste Training Course: 1989/1990" summary outline at page 12.

Remediation of Solvent Contaminated Soils by Aeration

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ABSTRACT

A bench-scale box test was performed to evaluate the feasibility of rototilling to remediate excavated soils contaminated with tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA). Two soils containing different concentrations of the target analytes were tested. PCE in Soil A decreased from 25,000 μg/kg to 5,053 μg/kg within the first 24 hours (an 80% decrease of the initial concentration) and to 834 μg/kg after 407 hours. PCE in Soil B decreased from 8,881 μg/kg to 500 μg/kg (a 94% loss) after 96 hours. The initial TCE concentration in Soil A was 1,100 μg/kg, decreasing to 30 μg/kg after 408 hours. The initial TCE concentration in Soil B was 1,573 μg/kg decreasing to 37 μg/kg (a 98% loss) after 192 hours. The maximum PCE concentrations in the off-gas were 1.5 ng/mL and 0.8 ng/mL above Soils A and B respectively, during the first 24 hours of exposure. Subsequent air samples all were below 0.1 ng/mL (the detection limit). Concentrations of TCE in the air above the soils were below the detection limit (> 0.1 ng/mL) throughout the experiment. Maximum 1,1,1-TCA air concentrations were 0.14 ng/mL during the first 24 hours in Box A.

INTRODUCTION

Chlorinated industrial solvents, e.g., tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA), are among the most common contaminants found at hazardous and industrial waste sites.[5] Remediation of soils contaminated with these compounds using techniques such as solidification/stabilization, incineration, soil vapor extraction, soil flushing or in situ biodegradation are expensive and time-consuming alternatives.[2,8] This contamination problem, requires a simple and effective remedy; one such alternative is enhanced solvent volatilization by excavation and rototilling.

A major concern with this option is the ensuing media transfer of contaminants from the soil to the urban atmosphere. However, once exposed to ultraviolet radiation, these compounds readily photolyze in the atmosphere (e.g., TCE $t_{1/2}$ = 5.2 days[3]); while in the troposphere, the unsaturated double bond is highly reactive, rapidly degrading to HCl, CO, CO_2 and carboxylic acid with a rate constant of $3x10^{12}cm^3/$ sec for TCE and $1.3x10^{12}cm^3$/sec for PCE.[11] Consequently, volatilization followed by degradation of the chlorinated compound in the atmosphere and troposphere appears to be a simple, safe and effective remedial option for soils contaminated with chlorinated solvents.

This study was designed to evaluate the efficacy of a proposed aeration technique (excavating, rototilling and exposing contaminated soils to the atmosphere) in terms of the concentrations of solvents released into the atmosphere under ambient atmospheric conditions and the time required to volatilize a significant (<90%) proportion of the contaminants. To quantify removal rates of PCE, TCE and 1,1,1-TCA from

the contaminated soils, a bench-scale aeration test was performed in an experimental environment similar to the anticipated field conditions. Another facet of the investigation was to calculate the maximum mass of PCE, TCE and 1,1,1-TCA potentially released to the atmosphere over the course of the experiment.

This study was undertaken to provide practical data on solvent volatility from contaminated soils. Although the physical characteristics of the three target compounds are well known, to date there has been little investigation into their volatility from soils and water surfaces. The only research that has been reported[12] focused on the release of PCE from soil immediately following application. No work appears to have been undertaken using soil that has been contaminated with PCE for several years.

MATERIALS AND METHODS

The aeration test apparatus consisted of two wooden boxes (60 cm long, 30 cm wide and 15 cm deep) lined with aluminum foil to prevent contaminant loss to the wood. Two rectangular openings were cut at each end, one a portal for a shaded pole fan and the other for an exit vent. The fan was used to provide a constant 10 km/hr breeze over the soil (characteristic of average wind speed conditions at the site) monitored at each box exit using a hand-held anamometer.

Two clay rich test soils were evaluated with Soil A containing >100 mg/kg VOCs and Soil B containing 10 to 20 mg/kg VOCs. After sampling, the soils were shipped to the laboratory on ice in coolers and maintained at 4 °C until the start of the experiment. Each box was filled with uncompacted soil to a depth of 30 cm, broken into clods 2.5 to 4 cm in diameter. These conditions were thought to be representative of a realistic depth and the likely size fraction resulting from rototilling the soil. Samples from each box were then taken in order to establish initial soil conditions. After sampling, the boxes were closed and placed in a ventilation hood. The box fans were turned on and air samples were collected immediately. Every 24 hours the entire soil column was overturned and soil samples were collected after rototilling.

The greatest variable in the soils was the moisture content of the clods, determined using ASTM D2216-80,[1] so this factor was incorporated into the sampling strategy. After the soil had been tilled, four clods, apparently representing the range of moisture observed in the soil at the time of sampling, were selected from each box. The clods were aggregated and the blended soil was analyzed. Due to the volatile nature of the compounds of interest, processing was performed quickly and the composited samples were placed in a glass vial containing as little head space as possible. To evaluate solvent diffusion out of the clods, the interior and exterior (rind) of Soil A clods were sampled on four occasions. These samples were collected by removing and compositing the exterior one centimeter from each of three clods. Moisture, PCE

and TCE were measured in both rind and interior samples.

Each representative sample weighed approximately 80 grams. Of this amount, 30 grams were used for moisture analysis, 30 grams were split into three 10-gram aliquots for chemical analyses and the rest was discarded. At the time of sampling, the relative humidity, wind speed and temperature of the air in the box were recorded.

Air sampling commenced immediately after the soils were placed in the boxes. Air samples were obtained using a 5-mL syringe through the exit port at hourly intervals for the first 4 hours and then again after 30 hours. The fan on Box A was turned off overnight after the second day and the box was sealed tightly in order to test the buildup of gas over Soil A. Subsequently, air samples were collected before the fan was turned on, 15 minutes after and again after rototilling. To characterize air quality over Soil B, three samples were collected over a 1.5-hour period on the first day and over a 1.5-hour period on the second day. Between samples, the syringes used to collect the samples were flushed 10 times with air.

Three separate 5-gram aliquots of soil were extracted in reagent grade methanol following U.S. EPA method 5030, the extracts were analyzed separately and the results averaged or the extracts combined and analyzed together or the soil splits were combined prior to extraction. The extracts were analyzed for PCE, TCE and 1,1,1-TCA using a Purge and Trap/Temperature Programmable Gas Chromatograph with a Hall detector in the halogen specific mode (following U.S. EPA method 8010a).

Quality assurance for the measurement of halogenated compounds was monitored four ways: by relative percent difference (RPD) of duplicate analyses, by soil spiking, by adding blanks and by introducing of a surrogate compound. To ensure analytical replicability, one duplicate sample was run from Soil A each day. For soils, the acceptable RPD limit is +/-35%.[10] With the exception of one TCE data point at a low soil concentration, the duplicate extractions all met this criterion.

A blank was run to test for: (1) cross contamination of soils during the extraction step, (2) contaminants in the methanol extractant, (3) contaminants on the glassware and (4) other contamination introduced during analysis. No contamination was detected in any blank over the course of the bench test. Each day a split of blended Soil B was spiked with a 1-mL mixture of the halogenated compounds of interest to determine a percent recovery for each analyte. The spike concentration decreased with time to reflect the decreasing soil analyte concentration in the unspiked soil. The spike recovery range for all analytes fell between 60-140%, also meeting the criteria established by the U.S EPA.[10]

To ensure that the purge/trap extraction mechanism and the Hall Detector were working properly, 100 ng of dichlorobromomethane were added to each extract and the percent recovery of the surrogate was calculated. The acceptable surrogate recovery range for soil methods is 75-125%.[10] The percent recovery of surrogate from these samples ranged from 82 to 110% and averaged 95%.

RESULTS AND DISCUSSION

Both soils were clay rich ranging in color from dark brown when moist to light brown when dry. The soil dried into clods that were very difficult to break. Soil moisture averaged 18% at the start of the experiment, decreasing to 2% after 7 days (Fig. 1). Percent moisture values for rinds and interior samples fell below bulk percent moisture values for both soils, although the rind and interior values measured after 24 hours lie within a similar percentage range. These data are indicative of the heterogeneity of the soil clods in contrast with the more homogenized sample used for the bulk soil test.

The highest analyte concentrations determined were PCE, followed by TCE and 1,1,1 TCA. Concentrations decreased most rapidly within the first 24 hours, approaching an asymptote after approximately 150 hours. The initial PCE concentration in Soil A was 25,000 μg/kg, decreasing to 5053 μg/kg within 24 hours; a loss of 80% of the initial concentration (Fig. 2). The PCE concentration decreased to 3330 μg/kg (an 87% decrease) after 48 hours and to 1000 μg/kg after 192 hours (a 96% decrease).

In Box B, the initial PCE concentration was 8880 μg/kg (Fig. 2),

decreasing to 6290 μg/kg after 24 hours (a 29% decrease), to 2410 μg/kg after 48 hours (a 73% decrease) and to 500 μg/kg after 192 hours (a 94% decrease). For both the rind and interior PCE analyses, the rind concentration was less than the average clod concentration, which was less than the interior PCE concentration. These data suggest that a diffusive mechanism controlled release of PCE from the interior of the clod (Fig. 2).
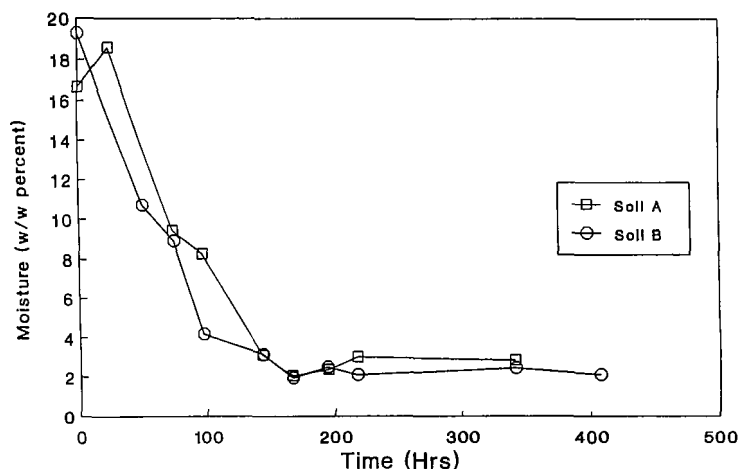
Figure 1
Soil Moisture Content
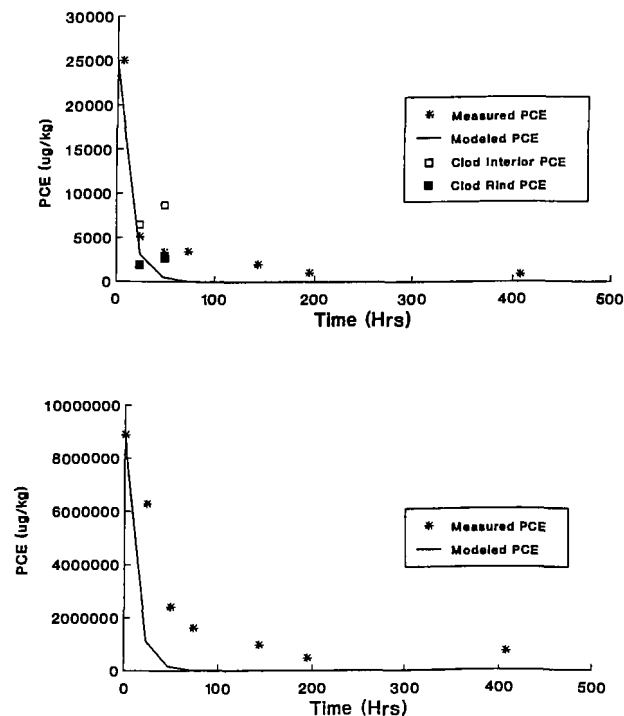
Figure 2
Concentration of PCE in Soils A and B

TCE in Soil A was initially 1100 μg/kg (Fig. 3) decreasing to 144 μg/kg after 24 hours (an 87% decrease) and to 25 μg/kg after 192 hours (a 98% loss). In Soil B, the initial concentration of TCE (1573 μg/kg) was higher than Soil A. An 84% loss of TCE (to 250 μg/kg) was measured in the first 24 hours. After 192 hours, the concentration had decreased to 25 μg/kg (a 98% loss).
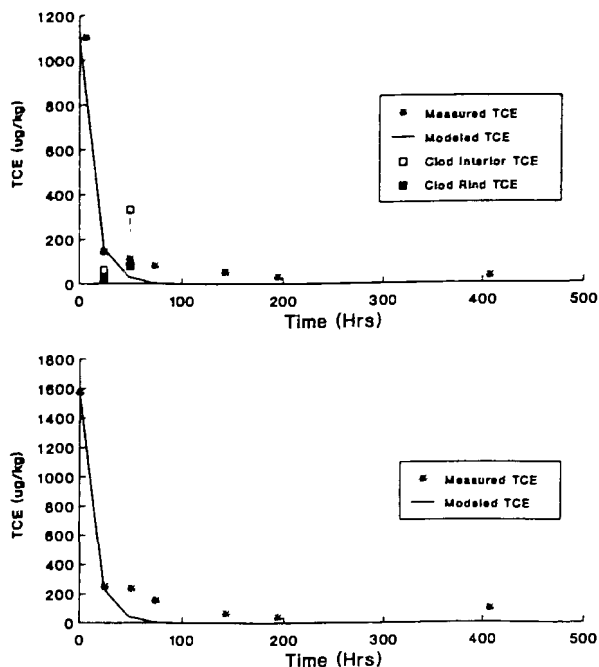
Figure 3
Concentration of TCE in Soils A and B

Soil A) to 8.1% (TCA in Soil B). PCE had the highest refractory fraction of the total mass, consistent with its high K_{ow}. Research by Zytner et al.[12] demonstrated that the volatilization rate of pure PCE after a recent soil application is 4 to 5 times slower than PCE dissolved in water, indicating that the volatilization rate of PCE from soil also depends on the form in which PCE enters the unsaturated zone. In addition, Petersen et al.[6] found that TCE partition coefficients were higher for dry soils than for moist soils, while Smith et al.[7] in a field study at Picatinny Arsenal, New Jersey, also demonstrated that TCE sorption was highly dependent on the soil humidity.

Both rind and interior samples taken after 24 hours contained less TCE than the bulk sample soils. Soil A clods collected after 48 hours, however, spanned the bulk concentration (Fig. 3).

1,1,1-TCA in Soil A behaved in a similar fashion to both TCE and PCE, decreasing from 793 μg/kg to 211 μg/kg (a 73% loss) after 24 hours and to 47 μg/kg (a 94% loss) after 194 hours. A similar concentration of 1,1,1-TCA (883 μg/kg) was found in Soil B. The evaporative rate loss was similar; 87% after 24 hours and 96% after 194 hours.

The initial PCE in Soil A air was 1.5 ng/mL and 0.8 ng/mL in Soil B air. Air samples taken 24 hours after initial rototilling measured less than 0.1 ng/mL (the detection limit) for both boxes. The fans were then turned off for 12 hours to allow a build-up of gas. An air sample was collected before the fans were turned on (PCE = 4.0 ng/mL) and fifteen minutes after the fan was turned on, at which time a concentration of < 0.1 ng/mL PCE was measured. No TCE concentrations above detection limits (0.1 ng/mL) were measured at any time. Initial 1,1,1-TCA soil gas concentrations were 0.14 ng/mL in Box A and < 0.1 ng/mL in Box B. The 24 hour air sample was below the detection limit (0.1 ng/mL). After gas accumulated over the 12 hour period, 1,1,1-TCA was 0.18 ng/mL, but was below the detection limit 15 minutes after the fan was turned on.

Calculation of the mass flux of solvents from the soil to the atmosphere on a daily basis demonstrates that the bulk of PCE, TCE and 1,1,1-TCA is released over the first 24 hours (Table 1), after which the solvent flux decreased substantially.

The initial rapid loss of volatiles followed by a slow, longer term decline in solvent concentrations suggests a dual release mechanism. The initial rapid decrease in soil concentrations probably corresponds to evaporation of interstitial water containing high solvent concentrations, a "labile" fraction. Solvents in this fraction would be lost to the atmosphere at a rate governed by the vapor phase concentration and the gaseous diffusion. These parameters are well-known from Henry's Law constant and the diffusivity coefficient, so it is not surprising that PRZM accurately simulated the initial volatilization rate.

The more tightly bound "refractory" fraction comprises only a small percent of the total solvent mass, but is responsible for the asymptotic behavior of the soil concentration curve after the labile fraction has volatilized. This refractory solvent content ranged from 2.7% (TCE in

All these investigations support the labile/refractory hypothesis advanced here. The practical effect of the dual volatilization mechanisms on the simulated soil concentrations is to overestimate solvent degassing, hence underestimating residual soil concentrations after volatilization of the labile solvent fraction. However, it is important to note that the refractory solvent fraction is invariably less than 10% of the total concentration, so that the error introduced in the simulations is not great.

Table 1
Loss of Solvents From Soils A and B

	PCE		TCE		1,1,1-TCA	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Soil A	1.30	0.16	0.06	0.01	0.04	0.003
Soil B	0.46	0.07	0.08	0.01	0.05	0.004

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The Challenge of Treating Contaminated Superfund Soil

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ABSTRACT

The purpose of this paper is to provide an analysis of the effectiveness of treatment technologies for contaminated soil and debris in response to the recommendation in the 1989 U.S. Environmental Protection Agency Superfund Management Review to "carefully evaluate the impact of RCRA land ban and other rules on the use of alternative technologies." This analysis provides support to Regional decisions to employ treatability variances for complying with the RCRA Land Disposal Restrictions as applicable or relevant and appropriate requirements (ARARs) for Superfund actions involving contaminated soil and debris.

INTRODUCTION

The 1989 Superfund Management Review (also known as the 90-Day Study) by the U.S. Environmental Protection Agency acknowledged that Superfund response actions may not be able to meet treatment standards based on "best demonstrated available technology" (BDAT) under the Land Disposal Restrictions (LDRs). This regulation may limit the potential treatment technologies available for Superfund cleanups, with technologies such as soil washing, stabilization and biological treatment being precluded because they may not meet the highest level of performance required by LDRs. In contrast, the 90-Day Study encouraged the greater use of innovative technologies and urged the reduction of nontechnical barriers, such as regulatory and policy constraints, that inhibit the use of treatment technologies, while preserving the intent and spirit of applicable RCRA regulations.

Office of Solid Waste and Emergency Response (OSWER) program offices recognized the potential limitation on treatment technologies for Superfund actions and developed a process to use LDR treatability variances for soil and debris. Guidance was issued to the Regions through the Superfund LDR Guide 6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," (OSWER Directive 9347.3-06FS) in July 1989 and revised in September 1990.[3] Superfund LDR Guide 6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," (OSWER Directive 9347.3-07FS) was issued in December 1989 and revised in September 1990.[4] These guides describe the treatability variance process, include alternate treatment levels to be obtained under treatability variances and identify treatment technologies which have achieved the recommended levels. OSWER recognizes that the use of treatability variances represents an interim approach and is currently in the process of acquiring additional data for developing a regulation on treatment standards for contaminated soil and debris.

On November 30, 1989, the Office of Emergency and Remedial Response (OERR) issued a memorandum on the "Analysis of Treatability Data for Soil and Debris: Evaluation of Land Ban Impact on Use of Superfund Treatment Technologies," (OSWER Directive 9380.3-04).[2] This memorandum was in response to the concern in the Superfund Management Review regarding limitations to the use of alternative technologies at Superfund sites: it included an analysis summarizing the effectiveness of treatment technologies applied to soils and other environmental wastes. The memorandum provides support for decisions by the Regions to use treatability variances, when appropriate. The analysis identifies some of the key technical considerations to be evaluated in obtaining a treatability variance when there is a reasonable doubt that a technology operated at full-scale cannot consistently meet the BDAT treatment standards for the soil and debris to be treated.

ANALYSIS OF TREATMENT EFFECTIVENESS

An extensive effort was undertaken during 1987 and 1988 to collect data on the treatment of soil, sludge, debris and related environmental media. The results from several hundred studies were collected and reviewed. All applicable treatment information from 67 studies was extracted, loaded into a data base and analyzed to determine the effectiveness of technologies to treat different chemical groups (Summary of Treatment Technology Effectiveness for Contaminated Soil, U.S. EPA, EPA/540/2-89/053).[1]

Although some of the data on which the analysis is based have limited quality assurance information, the data, nevertheless, do indicate potential effectiveness (at least 90% to 99% reduction of concentration or mobility of hazardous constituents) of treatment technologies to treat Superfund wastes. Some reductions in organic concentrations or organic mobility of more volatile compounds may actually represent the removal of those compounds as a direct result of volatilization. Technologies where this is most likely to occur include dechlorination, bioremediation, soil washing or immobilization, and consideration of appropriate emission controls is required. Percentage removal reductions (removal efficiencies) are not always a good measure of effectiveness, especially when high concentrations remain in the residuals. Some of the performance observations are based upon a relatively small number of data points and may not extrapolate well to the broad array of soils requiring treatment.

Based on this analysis, a number of technologies commonly used in the Superfund program provide substantial reduction in mobility and toxicity of wastes as required in Section 121 of the Superfund Amendments and Reauthorization Act (SARA) of 1986. For example:

- Thermal destruction has been proven effective on all organic compounds, usually accomplishing well over 99% reduction of organics.
- Although the data indicate that PCBs, dioxins, furans and other aromatic compounds have been dechlorinated to approximately 80%, more recent data indicate that removal efficiencies may approach 99.9%.
- Bioremediation successfully treats many halogenated aliphatic compounds, nonhalogenated aromatics, heterocyclics and other polar compounds with removal efficiencies in excess of 99%.
- Removal efficiencies for low temperature thermal desorption have been demonstrated with averages up to 99% for nonpolar halogenated aromatics and with treatment often exceeding 90% for other polar organics.
- Soil washing data on organic compounds indicate average removal efficiencies of approximately 90% for polar nonhalogenated organics and 99% for halogenated aromatics, with treatment often exceeding 90% for polynuclear aromatics. The chemical extraction process, with optimized solvent selection, has demonstrated removal efficiencies often exceeding 90% for volatile and nonvolatile metals.
- Immobilization processes, while not actually destroying the organic compounds, reduce the mobility of contaminants an average of 99% for polynuclear aromatic compounds. Immobilization may not effectively stabilize some organic compounds, such as volatile organics, and the long-term effectiveness of immobilization of organics is under evaluation. Immobilization can achieve average reductions in mobility of 93% for volatile metals, with reductions in mobility often exceeding 90% for nonvolatile metals.

A more detailed summary of the data follows, extracted from the "Summary of Treatment Technology Effectiveness for Contaminated Soil."

TECHNOLOGY LIMITATIONS TO BE CONSIDERED

The data available suggest that the treatment of soil and debris with organic contamination by technologies other than thermal destruction will not consistently achieve BDAT standards. Therefore, other technologies should be used for those wastes only if approved under a treatability variance.

The residual concentrations in contaminated soil treated by technologies other than thermal destruction are highly dependent upon the concentrations in the untreated soil. Therefore, when evaluating technologies other than thermal destruction, the ability of those technologies to treat high concentrations of organics should be considered.

Site conditions and characteristics must be carefully considered when designing and operating materials handling, pretreatment and treatment requirements. High variability in contaminant concentrations of untreated soil may have an adverse effect on the ability to achieve treatment levels using technologies other than thermal destruction. Consideration should be given to the need for blending wastes. In selecting technologies for contaminated soils and sludges, the number and types of contaminants must be carefully screened, and, in some cases, different technologies may be necessary for soils and sludges.

UNIQUE CONSIDERATIONS OF SOIL TREATMENT

The complex nature of solid waste matrices, such as contaminated soil from a Superfund site, severely complicates the treatment process. Soil is a nonhomogeneous living medium and the proportion of clay, organic matter, silt, sand, debris and other constituents can affect the treatability of a contaminated soil. In addition, the distribution of contaminants often is also nonhomogeneous and is dependent on patterns of contaminant deposition and transport. Collectively, these conditions make the treatment of contaminated

soil a formidable technical challenge. Discussions of some important considerations relevant to the selection of soil treatment processes follow.

A critical element in soil treatment is materials handling. Special approaches to waste transfer throughout the treatment system are particularly important for solids and viscous sludges where traditional conveyance methods are frequently ineffective. Slugs of material or debris tend to jam treatment equipment, resulting in breakage, downtime and the potential for uncontrolled releases to the environment. Materials handling equipment should be tested on the waste as part of any treatability testing program. Experiments should be conducted on an untreated waste as well as on any intermediate mixtures exhibiting changes in viscosity, particle size, density, etc.

The preprocessing of waste to maximize homogeneity and modify the waste characteristics is important to successful treatment technology operation. Any treatment technology will operate most efficiently and cost effectively when it is designed and utilized to treat a homogeneous waste with a narrow range of physical/chemical characteristics. If contaminant types and concentrations, waste viscosity, BTU content, moisture content, acidity, alkalinity, etc. vary widely, control of the system can be difficult and costly to maintain. Many of these waste characteristics can be modified and improved with appropriate preprocessing.

In addition, the most effective technology performance is achieved when the soil particle size is small and the maximum amount of surface area is exposed. This condition facilitates intimate contact between the contaminant sorption sites and the driving force of the technology (i.e., microorganism, solvent, warm air, etc.). The key to achieving this contact, and subsequent contaminant destruction, transfer to another medium or bonding, is often achieved only through significant preprocessing.

Materials handling and preprocessing technologies with potential application for soil are currently in use in the construction, agriculture and mining industries. All of these industries routinely handle large quantities of soil or rock. The use of technologies from these industries should be considered during all soil remediation activities. Materials handling and preprocessing techniques should also be incorporated in treatability testing programs. The results of such tests will better define the range of waste characteristics which the actual treatment technology will have to address.

CONCLUSIONS REGARDING SOIL TREATMENT TECHNOLOGY EFFECTIVENESS

Contaminated soils can be treated through three basic mechanisms: (1) destruction of the contaminants through chemical alteration to a less toxic compound (e.g., thermal destruction, dechlorination and bioremediation); (2) physical transfer of the contaminants to another waste stream for subsequent treatment or recovery (e.g., low temperature thermal desorption and chemical extraction and soil washing); and (3) permanent bonding of the contaminants within a stabilized matrix to prevent future leaching (e.g., immobilization). In general, the destruction technologies effectively reduce the toxicity of many organic contaminants. The physical transfer technologies reduce the toxicity and often the volume of selected organic and inorganic contaminants. While the bonding technologies most effectively reduce the mobility and, therefore, the toxicity of inorganic contaminants, some increasing effectiveness is being demonstrated on selected organic contaminants as well. Figure 1 presents a summary of these basic conceptual conclusions. A more detailed discussion follows.

The technologies that have been widely demonstrated on soils are thermal destruction for organic contaminants and immobilization for inorganic contaminants. While these two technologies may be highly effective in treating particular classes of compounds, neither provides an ideal solution to complex mixtures of organic and inorganic contaminants which are common at Superfund sites. The inherent difficulty in treating contaminants in a soil matrix, where

waste conveyance and mixing are in themselves complicated unit operations, contributes to the need to find special solutions. Other issues, such as landfill capacity and cost, cross-media impacts and natural resource conservation, also support the need to develop and use alternative and innovative treatment technologies for contaminated soil.

Contaminant	Technology		
	Physical Transfer or Recovery	Destruction	Stabilization
Volatile Organics	●	●	✖
Semi-Volatile Organics	◒	●	◒
Metals	◒	✖	●

● Demonstrated Effectiveness　　✖ Not Effective, Not Advised

◒ Potential Effectiveness
(More Data Required)

Figure 1
Soil Treatment Effectiveness - Conceptual Approach

Because of the U.S. EPA's ultimate goal of developing LDRs for contaminated soil and debris, this study evaluates a number of treatment options that are applicable to excavated soils. In situ soil techniques, such as some types of bioremediation, soil vapor extraction, in situ immobilization and combined groundwater and vadose zone soil treatment were not included in the scope of this evaluation. In situ techniques should also be considered when researching remediation measures for a contaminated soil problem. When in situ technologies are used at Superfund sites, the LDRs may not be applicable because the waste has not been excavated and subsequently "placed" in a landfill or other RCRA unit.

Based upon the data collected and evaluated by OERR from more than 200 soil treatment tests, conclusions were developed regarding the effectiveness of six soil treatment technology groups on each of 11 contaminant treatability groups. For destruction and physical transfer technologies applied to organic contaminants, the removal efficiency was analyzed. This evaluation factor was replaced by the reduction in mobility for immobilization for organics and inorganics, and for chemical extraction and soil washing of inorganics.

In Figure 2, "Predicted Treatment Effectiveness for Contaminated Soil," summary information is provided for each of 11 contaminant treatability groups and six treatment technology categories. For each treatability group, the effectiveness of various technologies is evaluated using the following ratings:
- Demonstrated Effectiveness: A significant percentage of the data, at least 20%, is from pilot- or full-scale operations, the average removal efficiency for all of the data exceeds 90% and there are at least 10 data pairs.
- Potential Effectiveness: The average removal efficiency for all of the data exceeds 70%.
- No Expected Effectiveness: The average removal efficiency for all of the data is less than 70% and no interference is expected to this process as a result of this group.
- No Expected Effectiveness: Potential adverse effects to the environment or the treatment process may occur. For example, high concentrations of metals may interfere with biological treatment.

In some cases, a different rating was selected when additional qualitative information and engineering judgment warranted. Two ratings were selected if the compounds within a treatability group were so variable that a range of conclusions could be drawn for a particular technology.

Figure 2
Predicted Treatment Effectiveness for Contaminated Soil

Thermal Destruction (See Figure 3)

Principle of Operation
- Thermal destruction uses high temperatures to incinerate and destroy hazardous wastes, usually by converting the contaminants to carbon dioxide, water and other combustion products in the presence of oxygen.

Effectiveness on Organics
- This technology has been proven effective on all organic compounds, usually accomplishing well over 99% removal.
- Thermal destruction technologies are equally effective on halogenated, nonhalogenated, nitrated, aliphatic, aromatic and polynuclear compounds.
- Incineration of nitrated compounds such as trinitrotoluene (TNT) may generate large quantities of nitrous oxides.

Effectiveness on Inorganics
- Thermal destruction is not an effective technology for treating soils contaminated with high concentrations of some metals.
- High concentrations of volatile metal compounds (lead) present a significant emissions problem which cannot be effectively contained by conventional scrubbers or electrostatic precipitators due to the small particle size of metal-containing particulates.
- Nonvolatile metals (copper) tend to remain in the soil when exposed to thermal destruction; however, they may slag and foul the equipment.

Dechlorination (See Figure 4)

Principle of Operation
- Dechlorination is a destruction process that uses a chemical reaction to replace chlorine atoms in the chlorinated aromatic molecules with an ether or hydroxyl group. This reaction converts the more toxic compounds into less toxic, more water-soluble products. The transformation of contaminants within the soil produces compounds that are more readily removed from the soil. An evaluation of the end products is necessary to determine whether further treatment is required.

Effectiveness on Organics
- PCBs, dioxins, furans and other aromatic compounds (such as pentachlorophenol) have been dechlorinated to approximately

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % REMOVALS		GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	32 PAIRS 6 % BENCH 94 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 590 TREATED 0.024	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology works very well at optimum operating conditions on a variety of initial concentrations. • Brominated compounds will inhibit flame propagation. • High levels of acid gases produced in the presence of oxygen will attack the refractory walls and exposed metal surfaces.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECUSORS (W02)	161 PAIRS 3 % BENCH 83 % PILOT 14 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,100 TREATED 0.055	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology works very well at optimum operating conditions on a variety of initial concentrations. • High levels of acid gases produced in the presence of oxygen will attack the refractory walls and exposed metal surfaces.
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	81 PAIRS 92 % BENCH 2 % PILOT 6 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 550 TREATED 0.70	AVERAGE REMOVAL EFFICIENCY 96 %	• This technology works well at optimum operating conditions on a variety of initial concentrations. • Oxides of nitrogen and sulfur can create potential serious cross media impacts if not removed from gas emissions. • High concentrations of acid gases produced in the presence of oxygen will attack the refractory walls and exposed metal surfaces.
HALOGENATED ALIPHATIC COMPOUNDS (W04)	92 PAIRS 21 % BENCH 79 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 41 TREATED 0.016	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology works well at optimum operating conditions on a variety of initial concentrations. • If this is the only treatability group present, low temperature thermal desorption may be more cost effective. • High levels of acid gases produced in the presence of oxygen will attack the refractory walls and exposed metal surfaces.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	116 PAIRS 67 % BENCH 33 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 790 TREATED 17	AVERAGE REMOVAL EFFICIENCY 99 %	• This technology works well at optimum operating conditions on a variety of initial concentrations.
NITRATED COMPOUNDS (W06)	142 PAIRS 73 % BENCH 27 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 98,000 TREATED 200	AVERAGE REMOVAL EFFICIENCY 99 %	• This technology works well at optimum operating conditions on a variety of initial concentrations. • High amounts of nitrous gases may be released into the atmosphere if not controlled by a nitrous oxide burner.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	42 PAIRS 7 % BENCH 88 % PILOT 5 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 740 TREATED 0.077	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology works very well at optimum operating conditions on a variety of initial concentrations. • Low temperature thermal desorption may be more cost effective.
POLYNUCLEAR AROMATICS (W08)	24 PAIRS 33 % BENCH 59 % PILOT 8 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,200 TREATED 0.32	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology works very well at optimum operating conditions on a variety of initial concentrations.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	34 PAIRS 35 % BENCH 65 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 690 TREATED 0.28	AVERAGE REMOVAL EFFICIENCY 98 %	• This technology works well at optimum operating conditions on a variety of initial concentrations.
NON-VOLATILE METALS (W10)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• The physical and/or chemical characteristics of the constituents of this treatability group indicate that this technology would not be effective. • Pyrolysis and infrared thermal destruction of wastes with metal concentrations over 500 ppm may possibly reduce the mobility of these metals by binding the metals into the solid residue.
VOLATILE METALS (W11)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• This technology is not recommended if the waste contains high concentrations of volatile metals, due to potential volatilization of these metals with subsequent cross media impacts. • Pyrolysis and infrared thermal destruction may reduce the mobility of these metals by binding the metals into the solid residue.

Figure 3
Final Conclusions by Treatment Technology - Thermal Destruction

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % REMOVALS		GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	8 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 190 TREATED 1.6	AVERAGE REMOVAL EFFICIENCY 98 %	• Data were for chlorobenzene only. These data suggest that this technology is potentially effective in certain situations.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	31 PAIRS 97 % BENCH 3 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 180 TREATED 1.6	AVERAGE REMOVAL EFFICIENCY 83 %	• This technology is potentially effective, especially for sandy soils. • Data on sludges show better removal due to more uniform distribution of contaminants and better reagent contact. • Lower initial concentrations give lower removal efficiencies. • Moisture content over 4 to 7% deactivates the NaPEG reagent. • Particle size and soil matrix affect reagent penetration and process effectiveness. • Recent data indicate that greater than 99% of PCBs and furans can be destroyed (des Rosiers, 1988).
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	8 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 98 TREATED 2.4	AVERAGE REMOVAL EFFICIENCY 98 %	• Data were for pentachlorophenol only. These data suggest that this technology is potentially effective in certain situations. • Recent data indicate that greater than 99% of contaminants can be destroyed (des Rosiers, 1988).
HALOGENATED ALIPHATIC COMPOUNDS (W04)	16 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 330 TREATED 0.44	AVERAGE REMOVAL EFFICIENCY 98 %	• These data suggest that this technology is potentially effective in certain situations. • Some halogenated aliphatics react with the APEG reagents to form explosive compounds, especially in the presence of heavy metals. The potential for this to occur should be evaluated in the laboratory before dechlorination treatment is selected. • The high removal efficiency may be the result of volatilization or the APEG process acting as a soil washing process.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• Data were not available for this treatability group. Data for compounds with similar physical and chemical characteristics suggest that this technology is potentially effective in certain situations. Treatability studies will be needed to confirm the technology's effectiveness.
NITRATED COMPOUNDS (W06)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• Data were not available available for this treatability group. • The physical and/or chemical characteristics of the constituents of this treatability group indicate that this technology would not be effective.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	24 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 2,200 TREATED 23	AVERAGE REMOVAL EFFICIENCY 99 %	• The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective. • The high removal efficiency may be the result of volatilization or the APEG process acting as a soil washing process.
POLYNUCLEAR AROMATICS (W08)	5 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 3,600 TREATED 180	AVERAGE REMOVAL EFFICIENCY 91 %	• The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective. • The high removal efficiency may be the result of volatilization or the APEG process acting as a soil washing process.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	16 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,700 TREATED 30	AVERAGE REMOVAL EFFICIENCY 96 %	• The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective. • The high removal efficiency may be the result of volatilization or the APEG process acting as a soil washing process.
NON-VOLATILE METALS (W10)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective.
VOLATILE METALS (W11)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective.

Figure 4
Final Conclusions by Treatment Technology - Dechlorination

80% removal, with more recent data indicating that removal efficiencies may approach 99.9%.
- Other limited laboratory data suggest potential applicability to other halogenated compounds including straight-chain aliphatics (such as 1,2-dichloroethane). The removal indicated by the data may be due in part to volatilization.
- Although no data were available for halogenated cyclic aliphatics (such as dieldrin), it is expected that dechlorination will be effective on these compounds as well.
- When nonhalogenated compounds are subjected to this process, volatilization may occur.

Effectiveness on Inorganics
- Dechlorination is not effective on metals, and high concentrations of reactive metals (such as aluminum), under very alkaline conditions, hinder the dechlorination process.

Bioremediation (See Figure 5)

Principle of Operation
- Bioremediation is a destruction process that uses soil microorganisms including bacteria, fungi and yeasts to chemically degrade organic contaminants.

Effectiveness on Organics
- Bioremediation appears to successfully treat many halogenated aliphatic compounds (1,1-dichloroethane), nonhalogenated aromatics (benzene), heterocyclics (pyridine) and other polar compounds (phenol) with removal efficiencies in excess of 99%; however, the high removal implied by the available data may be a result of volatilization in addition to bioremediation.
- More complex halogenated (4-4'DDT), nitrated (triazine) and polynuclear aromatic (phenanthrene) compounds exhibited lower removal efficiencies, ranging from approximately 50% to 87%.
- Polyhalogenated compounds may be toxic to many microorganisms.

Effectiveness on Inorganics
- Bioremediation is not effective on metals.
- Metal salts may be inhibitory or toxic to many microorganisms.

Low Temperature Thermal Desorption (See Figure 6)

Principle of Operation
- Low temperature thermal desorption is a physical transfer process that uses air, heat and/or mechanical agitation to volatilize contaminants into a gas stream, where the contaminants are then subjected to further treatment. The degree of volatility of the compound rather than the type of substituted group is the limiting factor in this process.

Effectiveness on Organics
- Removal efficiencies have been demonstrated by these units at bench, pilot and full scales, ranging from approximately 65% for polynuclear aromatics (naphthalene) to 82% for other polar organics (acetone) and 99% for nonpolar halogenated aromatics (chlorobenzene).

Effectiveness on Inorganics
- Low temperature thermal desorption is not effective on metals.
- Only mercury has the potential to be volatilized at the operating temperatures of this technology.

Chemical Extraction and Soil Washing (See Figure 7)

Principle of Operation
- Chemical extraction and soil washing are physical transfer processes in which contaminants are disassociated from the soil, becoming dissolved or suspended in a liquid solvent. This liquid waste stream then undergoes subsequent treatment to remove the contaminants and the solvent is recycled, if possible.
- Soil washing uses water as the solvent to separate the clay particles, which contain the majority of the contaminants, from the sand fraction.
- Chemical extraction processes use a solvent which separates the contaminants from the soil particles and dissolves the contaminant in the solvent.

Effectiveness on Organics
- The majority of the available soil washing data on organic compounds indicates removal efficiencies of approximately 90% for polar nonhalogenated organics (phenol) to 99% for halogenated aromatics (chlorobenzene), with lower values of approximately 71% for PCBs to 82% for polynuclear aromatics (anthracene).
- The reported effectiveness for treatment of these compounds could be due in part to volatilization for compounds with higher vapor pressures (such as acetone).
- This process is least effective for some of the less volatile and less water soluble aromatic compounds.

Effectiveness on Inorganics
- The chemical extraction process, with optimized solvent selection, has demonstrated removal efficiencies of 85% to 89% for volatile metals (lead) and nonvolatile metals (copper), respectively.

Immobilization (See Figure 8)

Principle of Operation
- Immobilization processes reduce the mobility of contaminants by stabilizing them within the soil matrix without causing significant contaminant destruction or transfer to another medium.
- Volatile organic compounds will often volatilize during treatment, therefore an effort should be made to drive off these compounds in conjunction with an emission control system.

Effectiveness on Organics
- Reductions in mobility for organics range from 61% for halogenated phenols (pentachlorophenol) to 99% for polynuclear aromatic compounds (anthracene).
- Immobilization is also effective (84% reduction) on halogenated aliphatics (1,2-dichloroethane).
- Some organic mobility reductions of the more volatile compounds may actually be removals as a direct result of volatilization during the exothermic mixing process and throughout the curing period.
- The immobilization of organics is currently under investigation, including an evaluation of the applicability of analytical protocols (EP, TCLP and total analysis) for predicting long-term effectiveness of immobilization of organics. The preliminary available data indicate that significant bonding takes place between some organic contaminants and certain organophilic species in the binding matrix; however, immobilization may not effectively stabilize some organic compounds, such as volatile organics.

Effectiveness on Inorganics
- Immobilization can accomplish reductions in mobility of 81% for nonvolatile metals (nickel) to 93% for volatile metals (lead).

REGULATORY IMPLEMENTATION

The data indicate potential limitations of technologies that are used to treat Superfund wastes when attempting to meet existing BDAT standards for industrial process wastes. Superfund LDR Guide 6A outlines the treatability variance process for Superfund soil and debris and identifies alternate treatability variance levels. The levels in LDR Guide 6A (Figures 9 and 10) should be followed, when appropriate, until OSWER completes a regulation with treatment standards for contaminated soil and debris. The limitations on technologies identified here should be taken into account when evaluating, selecting, designing and implementing Superfund response actions.

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % REMOVALS		GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	68 PAIRS 95 % BENCH 5 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 2.9 TREATED 0.79	AVERAGE REMOVAL EFFICIENCY 53 %	• This technology is not effective for all contaminants in this class; however, there is potential for effectiveness for low initial concentrations with further development. • The presence of these contaminants at low concentrations is not expected to interfere with the treatment of applicable wastes. • The effectiveness of this technology may be different than the data imply, because the initial concentrations in these tests were so low.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	1 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 2,000 TREATED 0.12	AVERAGE REMOVAL EFFICIENCY 99 %	• The lone data pair is PCBs. • Ongoing research suggests that this technology may be potentially effective for this group.
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	3 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 83 TREATED 17	AVERAGE REMOVAL EFFICIENCY 74 %	• This technology is potentially effective for low initial concentrations. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organics adversely affect the treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Bioremediation has low costs relative to other technologies.
HALOGENATED ALIPHATIC COMPOUNDS (W04)	27 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 23 TREATED 0.027	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective for low initial concentrations. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organics adversely affect the treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Removal may actually represent volatilization during preprocessing and treatment.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• Data were not available for this treatability group. Data for compounds with similar physical and chemical characteristics suggest that this technology may be potentially effective in certain situations with low initial concentrations.
NITRATED COMPOUNDS (W06)	22 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 13,000 TREATED 1,400	AVERAGE REMOVAL EFFICIENCY 82 %	• This technology is potentially effective on these contaminants, especially at low concentrations. • Some of the available data for this treatability group were based on very high initial concentrations; however consideration should be given to the ability of the technology to treat high initial concentrations. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organics adversely affect the treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Bioremediation has low costs relative to other technologies.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	54 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 220 TREATED 0.025	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective for low initial concentrations. • The high removal indicated by the data may actually represent volatilization during preprocessing and treatment. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organic compounds adversely affect treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Bioremediation has low costs relative to other technologies.
POLYNUCLEAR AROMATICS (W08)	37 PAIRS 19 % BENCH 81 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 120 TREATED 3.8	AVERAGE REMOVAL EFFICIENCY 87 %	• This technology is potentially effective for low initial concentrations. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organic compounds adversely affect treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Bioremediation has low costs relative to other technologies.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	22 PAIRS 0 % BENCH 100 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 64 TREATED 0.32	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective for low initial concentrations. • Bioremediation requires uniformly mixed media with small particle sizes. • Toxic compounds such as cyanides, arsenic, heavy metals, and some organic compounds adversely affect treatment. • Preprocessing includes mixing and nutrient and organism addition. • Bioremediation is a slow process. • Bioremediation has low costs relative to other technologies. • Removal may actually represent volatilization during preprocessing and treatment.
NON-VOLATILE METALS (W10)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• High concentrations of heavy metals may adversely affect particular organisms. • The physical and/or chemical characteristics of the constituents of this treatability group suggest that the technology would not be effective.
VOLATILE METALS (W11)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• High concentrations of heavy metals may adversely affect particular organisms. • The physical and/or chemical characteristics of the constituents of this treatability group suggest that the technology would not be effective.

Figure 5
Final Conclusions by Treatment Technology - Bioremediation

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % REMOVALS		GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	29 PAIRS 48 % BENCH 4 % PILOT 48 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 130 TREATED 0.07	AVERAGE REMOVAL EFFICIENCY 99 %	• Although this technology was not expected to perform well on this treatability group, the data from studies which utilized higher operating temperatures and longer residence times indicate that many of the compounds in this group may be treated by this technology with potential effectiveness. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled. • This technology has demonstrated effectiveness on some of the more volatile contaminants in this group, and it is potentially effective on the remaining contaminants.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECUSORS (W02)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• No data were available. • The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	14 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 260 TREATED 67	AVERAGE REMOVAL EFFICIENCY 72 %	• Although the data suggest that this technology is not as effective with this treatability group, the technology, if operated at higher temperatures and residence times, may successfully treat many of the compounds in this group. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
HALOGENATED ALIPHATIC COMPOUNDS (W04)	132 PAIRS 27 % BENCH 50 % PILOT 23 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 590 TREATED 18	AVERAGE REMOVAL EFFICIENCY 94 %	• This technology works well on this treatability group. • Removal efficiencies are not as high with soils having extremely elevated concentrations. A longer residence time may remedy this situation. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• No data were available for this treatability group. • The physical and/or chemical characteristics of the constituents of this treatability group suggest that this technology would not be effective. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
NITRATED COMPOUNDS (W06)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• No data were available for this treatability group. • The physical and/or chemical characteristics of the constituents of this treatability group indicate that this technology would not be effective. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	111 PAIRS 37 % BENCH 39 % PILOT 24 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 920 TREATED 1.7	AVERAGE REMOVAL EFFICIENCY 96 %	• This technology works well on this treatability group. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
POLYNUCLEAR AROMATICS (W08)	52 PAIRS 27 % BENCH 60 % PILOT 13 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,400 TREATED 130	AVERAGE REMOVAL EFFICIENCY 65 %	• This technology is not generally effective as a treatment for this group, but individual compounds may be treated effectively at higher operating temperatures and longer residence times. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	34 PAIRS 82 % BENCH 6 % PILOT 12 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,900 TREATED 170	AVERAGE REMOVAL EFFICIENCY 82 %	• This technology is potentially effective on some contaminants in this group. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
NON-VOLATILE METALS (W10)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• The physical and/or chemical characteristics of the constituents of this treatability group indicate that this technology would not be effective. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.
VOLATILE METALS (W11)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• The physical and/or chemical characteristics of the constituents of this treatability group indicate that this technology would not be effective. • This technology is not recommended for the treatment of waste mixtures which contain high concentrations of metallic and/or organic forms of mercury, unless emissions are controlled.

Figure 6
Final Conclusions by Treatment Technology -
Low Temperature Thermal Desorption

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % REMOVALS		GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	20 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 170 TREATED 0.30	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective on these contaminants but all data are from bench scale. • Surfactants may adhere to the soil and reduce soil permeability. • Possible volatile emission losses may occur during treatment.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECURSORS (W02)	22 PAIRS 82 % BENCH 4 % PILOT 14 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 9,900 TREATED 4,000	AVERAGE REMOVAL EFFICIENCY 71 %	• This technology is potentially effective on these contaminants with further development. • Some of the available data for this treatability group were based on very high initial concentrations; however consideration should be given to the ability of the technology to treat high initial concentrations. • The presence of oil in the matrix enhances removal. • The removal efficiency decreases as the percent of clays and clayey silts increases. • Surfactants may adhere to the soil and reduce soil permeability.
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	20 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 87 TREATED 18	AVERAGE REMOVAL EFFICIENCY 72 %	• Data were from pentachlorophenol only. • This technology is potentially effective on these contaminants, especially for treating sandy soils. • Surfactants may adhere to the soil and reduce soil permeability.
HALOGENATED ALIPHATIC COMPOUNDS (W04)	40 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 290 TREATED 0.22	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective on these contaminants, but all data are from bench scale. • This technology may be more applicable to sandy soils. • Surfactants may adhere to the soil and reduce soil permeability. • Volatile emissions may occur during treatment.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 0 TREATED 0	AVERAGE REMOVAL EFFICIENCY 0 %	• Data were not available for this treatability group. Data for compounds with similar physical and chemical characteristics suggest that this technology is potentially effective in certain situations. • Surfactants may adhere to the soil and reduce soil permeability.
NITRATED COMPOUNDS (W06)	3 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 6,900 TREATED 4.7	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective on these contaminants. However, data are limited and testing was conducted at bench scale.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	55 PAIRS 98 % BENCH 0 % PILOT 2 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,700 TREATED 3.8	AVERAGE REMOVAL EFFICIENCY >99 %	• This technology is potentially effective on these contaminants but nearly all data are from bench scale. • Volatile emissions may occur during treatment. • Surfactants may adhere to the soil and reduce soil permeability.
POLYNUCLEAR AROMATICS (W08)	24 PAIRS 71 % BENCH 0 % PILOT 29 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 1,600 TREATED 380	AVERAGE REMOVAL EFFICIENCY 82 %	• This technology is potentially effective on these contaminants with further development. • Some of the available data for this treatability group were based on very high initial concentrations; however, consideration should be given to the ability of the technology to treat high initial concentrations. • Surfactants may adhere to the soil and reduce soil permeability.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	58 PAIRS 95 % BENCH 0 % PILOT 5 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 70,000 TREATED 15,000	AVERAGE REMOVAL EFFICIENCY 91 %	• This technology is potentially effective on these contaminants. • Some of the available data for this treatability group were based on very high initial concentrations; however, consideration should be given to the ability of the technology to treat high initial concentrations. • Treatment effectiveness should be evaluated on a case-by-case basis. • Surfactants may adhere to the soil and reduce soil permeability. • Volatile emissions may occur during treatment.
NON-VOLATILE METALS (W10)	34 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 34 TREATED 1.1	AVERAGE MOBILITY REDUCTION 89 %	• This technology is potentially effective on these contaminants. • Water and H_2SO_4 at a pH of 1.0 and a 3:1 molar ratio of EDTA at a pH of 12.0 can both achieve good levels of extraction. • Iron (1-2%) may cause solvent regeneration problems.
VOLATILE METALS (W11)	54 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) UNTREATED 71 TREATED 10	AVERAGE MOBILITY REDUCTION 85 %	• This technology is potentially effective on these contaminants, especially for sandy soils. • Silty and clayey soils are not as effectively treated. • Arsenic may be difficult to extract due to low solubility.

Figure 7
Final Conclusions by Treatment Technology -
Chemical Extraction and Soil Washing

TREATABILITY GROUP	NUMBER AND SCALE OF AVAILABLE DATA	AVERAGE CONCENTRATIONS (ppm) AND % AVG. MOBILITY REDUCTION	GENERAL OBSERVATIONS
NON-POLAR HALOGENATED AROMATICS (W01)	4 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 3.1 — 83 % TREATED 0.65	• Data were for chlorobenzene only. • These data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low. • The treatment mechanism for the more volatile compounds may be volatilization as opposed to immobilization. Air pollution control systems may be necessary to minimize cross media impacts from these volatile emissions. • It is not recommended that this technology be selected if this is the only treatability group present.
PCBs, HALOGENATED DIOXINS, FURANS, AND THEIR PRECUSORS (W02)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 0 — 0 % TREATED 0	• Incomplete quantitative data were available to evaluate treatment effectiveness. These quantitative data and additional qualitative information suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low. • It is not recommended that this technology be selected if this is the only treatability group present.
HALOGENATED PHENOLS, CRESOLS, AMINES, THIOLS, AND OTHER POLAR AROMATICS (W03)	4 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 2.5 — 61 % TREATED 1.1	• Data were from pentachlorophenol only. These data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low, the effectiveness of this technology on these contaminants may be different than the data imply, due to limitations in the test conditions. • It is not recommended that this technology be selected if this is the only treatability group present.
HALOGENATED ALIPHATIC COMPOUNDS (W04)	9 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 11 — 88 % TREATED 0.24	• Though these data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low the reductions in mobility may be due to volatilization of the volatile compounds during treatment. • Air pollution control systems may be necessary to minimize cross media impacts from these volatile emissions. • It is not recommended that this technology be selected if this is the only treatability group present.
HALOGENATED CYCLIC ALIPHATICS, ETHERS, ESTERS, AND KETONES (W05)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 0 — 0 % TREATED 0	• Data were not available for this treatability group. Data for compounds with similar physical and chemical characteristics suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low. • It is not recommended that this technology be selected if this is the only treatability group present.
NITRATED COMPOUNDS (W06)	0 PAIRS 0 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 0 — 0 % TREATED 0	• Data were not available for this treatability group. Data for compounds with similar physical and chemical characteristics suggest that this technology is potentially effective in certain situations, particularly where the initial concentrations are low.
HETEROCYCLICS AND SIMPLE NON-HALOGENATED AROMATICS (W07)	12 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 23 — 73 % TREATED 5.8	• Though these data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low, the reductions in mobility may be due to the volatilization of volatile organic compounds during treatment. • Air pollution control systems may be necessary to minimize cross media impacts from these volatile emissions. • It is not recommended that this technology be selected if this is the only treatability group present.
POLYNUCLEAR AROMATICS (W08)	2 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 3.0 — 99 % TREATED 0.03	• These limited data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low.
OTHER POLAR NON-HALOGENATED ORGANIC COMPOUNDS (W09)	7 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 20 — 77 % TREATED 5.6	• These limited data suggest that this technology is potentially effective in certain situations, particularly where the initial concentration is low. • The treatment mechanism for the more volatile compounds may be volatilization as opposed to immobilization. Air pollution control systems may be necessary to minimize cross media impacts from these volatile emissions. • It is not recommended that this technology be selected if this is the only treatability group present.
NON-VOLATILE METALS (W10)	24 PAIRS 67 % BENCH 33 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 28 — 81 % TREATED 0.34	• This technology works well on these contaminants. • High levels of oil and grease may interfere with the process. • Soluble salts of Mg, Sb, Zn, Cu, and Pb may interfere with the pozzolan reaction. • High levels of sulfates may interfere with the process. • Pretreatment may be required to increase pH.
VOLATILE METALS (W11)	33 PAIRS 100 % BENCH 0 % PILOT 0 % FULL	AVERAGE CONCENTRATIONS (ppm) / AVERAGE MOBILITY REDUCTION UNTREATED 610 — 93 % TREATED 1.4	• Based on the pilot scale data this technology works well on these contaminants. Some bench scale data was not representative of optimum conditions. • High levels of oil and grease may interfere with the process. • Soluble salts of Mg, Sb, Zn, Cu, and Pb may interfere with the pozzolan reaction. • High levels of sulfates may interfere with the process. • Pretreatment may be required to increase pH.

Figure 8
Final Conclusions by Treatment Technology - Immobilization

Structural Functional Group	Concentration Range (ppm)**	Threshold Concentration (ppm)**	Percent Reduction Range
Halogenated Non-Polar Aromatics	0.05 - 10	100	90 - 99.9
Dioxins	0.00001 - 0.05	0.5	90 - 99.9
PCBs	.01 - 10	100	90 - 99.9
Herbicides	0.002 - 0.02	0.2	90 - 99.9
Halogenated Phenols	0.5 - 40	400	90 - 99
Halogenated Aliphatics	0.5 - 2	40	95 - 99.9
Halogenated Cyclics	0.5 - 20	200	.90 - 99.9
Nitrated Aromatics	2.5 - 10	10,000	90.9 - 99.99
Heterocyclics & Non-Halogenated Aromatics	0.5 - 20	200	90 - 99.9
Polynuclear Aromatics	0.5 - 20	400	95 - 99.9
Other Polar Organics	0.5 - 10	100	90 - 99.9

* If the constituent concentration of the untreated waste is less than the threshold concentration, use the concentration range; If It is more than the threshold concentration, use the percent reduction range.

** Total Waste Analysis

Figure 9
LDR Guide 6A
Alternate Treatability Variance Levels for CS&D - Organics*

Structural Functional Group	Concentration Range (ppm)**	Threshold Concentration (ppm)**	Percent Reduction Range
Antimony	0.1 - 0.2	2	90 - 99
Arsenic	0.27 -1	10	90 - 99.9
Barium	0.1 40	400	90 - 99
Chromium	0.5 - 6	120	95 - 99.9
Nickel	0.5 - 1	20	95 - 99.9
Selenium	0.005	0.08	90 - 99
Vanadium	0.2 - 22	200	90 - 99
Cadmium	0.2 - 2	40	95 - 99.9
Lead	0.1 - 3	300	99 - 99.9
Mercury	0.0002 - 0.008	0.06	90 -99

* If the constituent concentration of the untreated waste is less than the threshold concentration, use the concentration range; if it is more than the threshold concentration, use the percent reduction range.

** TCLP Analysis

Figure 10
LDR Guide 6A
Alternate Treatability Variance Levels for CS&D - Inorganics

AVAILABLE TECHNOLOGY TRANSFER ASSISTANCE

It is recommended that treatability studies be conducted for each site containing soil and debris which requires treatment. To assist in the process of planning and performing these treatability studies, a number of sources of pertinent current information exist. In terms of guidance documents and technical resources, the following are important sources of information:

- Summary of Treatment Technology Effectiveness for Contaminated Soil, U.S. EPA, EPA/540/2-89/053
- Superfund Treatability Clearinghouse Abstracts, U.S. EPA, EPA/540/2-89/001
- Technology Screening Guide for Treatment of CERCLA Soils and Sludges, U.S. EPA, EPA/540/2-88/004
- Guide for Conducting Treatability Studies Under CERCLA, U.S. EPA, EPA/540/2-89/058
- Inventory of Treatability Study Vendors, U.S. EPA, EPA/540/2-90/003a
- Various Superfund Innovative Technology Evaluation (SITE) Program Reports

In addition to the abovementioned references, there also is a valuable network of U.S. EPA and other Agency, university, vendor and consulting engineering personnel focusing on the challenging technical issues of waste treatment. Some elements of this network include the following:

- Superfund Technology Support Project (TSP)
- Superfund Technical Assistance Response Teams (START)
- OSWER Technology Innovation Office (TIO)
- National Advisory Council for Environmental Policy and Technology (NACEPT)

CONCLUSION

The data and conclusions presented in this paper represent the most current information available in the Superfund program. The U.S. EPA recognizes that with each additional treatment test performed, more valuable information will be generated regardless of whether the test was successful or unsuccessful. Timely and complete technology transfer is the key to establishing the necessary justifications for treatability variances as well as to developing appropriate land disposal restrictions for contaminated soil and debris based upon best demonstrated available technologies. Therefore, the U.S. EPA continues to seek all treatment results for evaluation for regulatory development and for timely technology transfer.

In order to participate in this important technology transfer process, please send all available information on the treatment of contaminated soil and debris to U.S. EPA OERR or to CDM Federal Programs Corporation at the following addresses:

Carolyn K. Offutt/Richard Troast
Hazardous Site Control Division (OS-220)
U.S. Environmental Protection Agency
401 M. Street, S.W.
Washington, D.C. 20460
(703) 308-8330/308-8323

Joan O'Neill Knapp
CDM Federal Programs Corporation
13135 Lee Jackson Memorial Highway
Suite 200
Fairfax, VA 22033
(703) 968-0900

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2. U.S. EPA, Memorandum on "Analysis of Treatability Data for Soil and Debris: Evaluation of Land Ban Impact on Use of Superfund Treatment Technologies" (OSWER Directive 9380.3-04) in response to Superfund Management Review: Recommendation 34A., U.S. EPA, Washington, DC, November 30, 1989.
3. U.S. EPA, Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions," OSWER Directive 9347.3-06FS, U.S. EPA, Washington, DC, July 1989, Revised September 1990.
4. U.S. EPA, Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions," OSWER Directive 9347.3-07FS, U.S. EPA, Washington, DC, December 1989, Revised September 1990.

Weathering Resistance of Stabilized Petroleum Sludge

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ABSTRACT

A multiyear research project has been undertaken to investigate the stabilization/solidification of a petroleum sludge. Recent papers have presented the results of short-term testing (TCLP) of the stabilized material. In order to evaluate long-term environmental effects, durability testing was conducted on samples of the stabilized petroleum sludge. Conclusions and recommendations based on these durability tests are presented in this paper.

Under current laboratory procedures, the stabilized sludge samples cure in a humid environment for 2 weeks before further testing. A study was conducted to determine whether the test results were significantly affected by the curing time. Individual samples were tested at daily and weekly intervals up to 4 weeks and monthly thereafter. Results indicate that the maximum unconfined compressive strength occurs at approximately 28 days. Depending upon the stabilization reagents, the total organic carbon (TOC) concentration in the extract increased or remained unchanged with increased curing time beyond 28 days.

To further study long-term environmental effects, a wet/dry study was conducted. Each sample was placed in a bath of water for 24 hours and oven-dried for 24 hours. This 48-hour cycle was repeated 12 times on each sample. Very limited physical degradation was apparent for each mix during cycles of wetting and drying. The sludge stabilized with cement kiln dust was not as resistant to wet/dry testing as sludge stabilized with a mixture of attapulgite, fly ash quicklime and cement.

Since the project is located in the mid-Atlantic region, the stabilized material may also be subjected to freeze/thaw stresses. The freeze/thaw samples were frozen for 6 hours and thawed for 42 hours. The process was repeated for 12 cycles on each sample.

Consolidation data are used to predict the total settlement and time-rate of deformation due to an applied load of overlying material. Although additives used to solidify the sludge are cementitious, the resulting strength and stiffness is not that of concrete. The compression indices indicate that the stabilized mass has the properties of a stiff clay.

Permeability tests were performed to determine the rate of transport of fluids through the stabilized sludge. The average hydraulic conductivity of the material is 2×10^{-6} cm/sec. The TOC of the effluent was an order of magnitude greater than the influent concentration indicating a release of encapsulated organics due to permeation with tap water.

INTRODUCTION

The refinery processes used in the past to produce lubricating oil from crude oil generated significant quantities of acidic petroleum sludge. The common practice was to dispose of this sludge in open lagoons. In the early 1970s, the manufacturing process was altered to eliminate the production of acidic sludge—but the lagoons remained.

Among the alternative remediation techniques identified for these sludge lagoons is stabilization/solidification, the subject of the research reported in this paper. Remedial technologies are sought which result in more permanent solutions than landfilling. Such solutions include bioremediation, incineration, vitrification and stabilization/solidification. A multiyear research project has been undertaken to evaluate the effectiveness of stabilization/solidification for the acidic petroleum sludge.

Stabilization is a process employing additives to reduce the hazardous nature of a waste by converting the waste and its hazardous constituents into a form that: (1) minimizes the rate of contaminant migration into the environment or (2) results reduced toxicity. Solidification is the process of improving the engineering properties of a material through the addition of stabilization reagents. This paper will use the term stabilization to denote both stabilization and solidification processes.

The first year of the research included a review of existing literature and the development of the laboratory testing procedures. A survey of stabilization vendors also was conducted. The second year included laboratory testing of 250 stabilized test mixes. Laboratory testing included unconfined compression and Toxicity Characteristics Leaching Procedure (TCLP). The final phase of the project will include a field study of sludge stabilization.

The laboratory testing focused upon two aspects of stabilized sludge performance. The first aspect was short-term evaluation of the toxicity reduction and engineering properties of the stabilized samples.[1] The second aspect of laboratory testing, the focus of this paper, studied the durability of the stabilized monolith under weathering conditions including freeze/thaw and wet/dry stresses.

STABILIZATION REAGENTS

Reagents for the stabilization of the acidic petroleum sludge were classified into two groups: binders and sorbents. Binders include those materials which, when added to the contaminated material, improve the strength of the material. Fly ash and lime, cement and kiln dust are binders used for the solidification studies described in this paper.

Sorbents for the stabilization of the organic waste were added in order to reduce the contaminant transport rates from the treated waste. The sorbent materials used in the studies described in this paper include bentonite, attapulgite and organically modified clays.

LABORATORY TESTING PROGRAM

Physical Property Tests

Each stabilized sample was mixed using a 500-gram sample of untreated sludge. Upon sampling, the density, moisture content, loss on ignition and pH were determined for the untreated material. A mechanical rotary mixer was used to mix the reagents with the untreated

material. The samples were then compacted into a 2.8-in. diameter cylindrical mold using standard proctor energy. The compacted samples were allowed to cure in a humid environment for 2 weeks.

After the 2 week cure period, the samples were extruded and tested in unconfined compression. The specimens were tested to their maximum unconfined compressive strengths, or 15% axial strain, whichever occurs first. The pH of the sludge averaged 3.2 with an average loss on ignition of 78.2% and an average water content of 45.6%. Thus, the sludge is both very acidic and very organic.

Chemical Tests

Once the sample was crushed in unconfined compression, it was further disaggregated by passing the material through a 3/8-in. sieve. The disaggregated material was extracted using a modified form of the Toxicity Characteristic Leaching Procedure (TCLP). The test procedure has been modified to use sulfuric acid instead of acetic acid as the extraction acid. This modification allows for the measurement of the total organic carbon concentration (TOC) in the extract. Studies have shown that no significant difference exists between the use of sulfuric acid in place of acetic acid for these sludges.[2]

Samples of the extract were analyzed for TOC and metals. A 1-L aliquot of the remaining extract was used for a methylene chloride acid/base extraction. The extract was then condensed to 1 mL for injection into a Hewlett-Packard gas chromatograph/mass spectrometer. The concentrations of individual organic contaminant present in the sludge was then measured. The TCLP extract was found to have varying concentrations (depending upon the stabilization mix) of several organics including phenol, methyl phenol and naphthalene. The average TOC in the extract from all stabilized mixes was 187 mg/L.

CONCLUSIONS AND RECOMMENDATIONS BASED ON LABORATORY TESTING

Candidate mixes for the stabilization of the acidic petroleum sludge were selected from these studies.[3] For the durability studies reported in this paper, the following two types of mixes were used: (1) cement kiln dust and (2) fly ash, quicklime, cement and attapulgite. For the second type of mix, that with fly ash, quicklime, cement and attapulgite, two mix formulations were used with different sludge to attapulgite ratios. As measured in the extraction fluid from the TCLP, the following parameters were selected to evaluate stabilization effectiveness:

- Total organic carbon concentration
- Phenol
- Methyl phenol
- Naphthalene
- Chromium
- Lead
- Mix cost
- Unconfined compressive strength
- Volume increase

DURABILITY TESTS

The laboratory analyses discussed above effectively evaluated the mixes in the short-term. The test parameters are effective for initial evaluation of the stabilized/solidified mixes. It is recognized that under long-term environmental stresses (i.e., weathering), physical and chemical degradation of the samples may occur. The remainder of this paper discusses the evaluation of the effects of long-term stresses upon the stabilized samples.

Results of the short-term testing have been previously presented.[1,4,5] From these results, three candidate mixes were selected for the long-term durability analysis. The mix proportions are shown in Table 1. The following section of this paper describes the tests conducted on each of the samples and discusses the results of these tests.

DURABILITY TESTING PROGRAM AND RESULTS

Curing Time Study

The short-term laboratory procedure had employed a 2-week cure

time. A study was conducted for each of the selected test mixes to evaluate the characteristics and property changes of the stabilized monolith as a function of time. For each of the three candidate mixes, samples were tested at curing times of 1, 7, 14, 21 and 28 days, and 2 and 3 months. With the exception of the curing time, the laboratory procedures remained unchanged for these replicate samples.

Shown in Figure 1 is the relationship between the curing time and the unconfined compressive strength for the three candidate mixes. For each test series, the unconfined compressive strength increases by approximately 300% from 1 day to 28 days of curing. Series I used cement kiln dust as the solidification agent; it exhibited the lowest strength of the three tested. Series II and III both used attapulgite, fly ash, quicklime and cement in the solidification process. Series II had an attapulgite to sludge ratio of 0.6, whereas Series III had an attapulgite to sludge ratio of 0.4. The higher attapulgite to sludge ratio resulted in higher strengths as expected, although the increase is not dramatic.

Table 1
Mix Ingredients and Proportions (by weight)

Sludge/cement kiln dust (S/CKD)	1/1.5
Sludge/attapulgite/fly ash/quicklime/cement (S/A/FA/QL/C)	1/.6/.75/.25/.5/.3
Sludge/attapulgite/fly ash/quicklime/cement (S/A/FA/QL/C)	1/.4/.75/.25/.5/.3
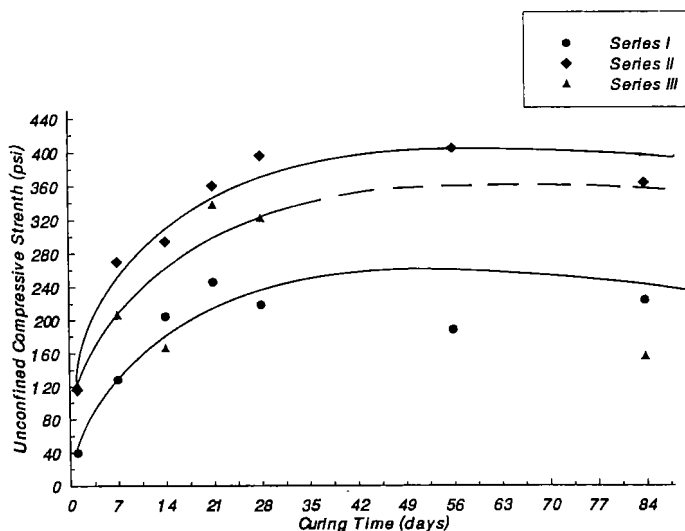
Figure 1
Relationship Between Unconfined Compressive Strength and Curing Time

The reduction in the TOC of the extract was studied as a function of curing time as shown in Figure 2. In the case of the cement kiln dust-stabilized sample, the reduction in TOC (in the extract) decreased as curing time increased. For the candidate mixes using attapulgite, curing time has little effect upon the TOC in the extract. The data also show that cement kiln dust was not as effective as the attapulgite mixes in reducing the TOC of the extract in the TCLP.

Wet/Dry Testing

Wet/dry testing was conducted to quantify the resistance of the stabilized materials to degradation as a result of wet/dry cycles following the procedure outlined in ASTM D-4843. The samples were mixed, compacted using standard proctor energy, allowed to cure for 1 week and extruded for testing. For each candidate mix, three test samples and three control samples were formed. The test samples were sub-

jected to 12 cycles of wetting in deionized water for 24 hours and drying at 60°C for 24 hours. Each 48-hour segment of wetting and drying constituted one cycle.
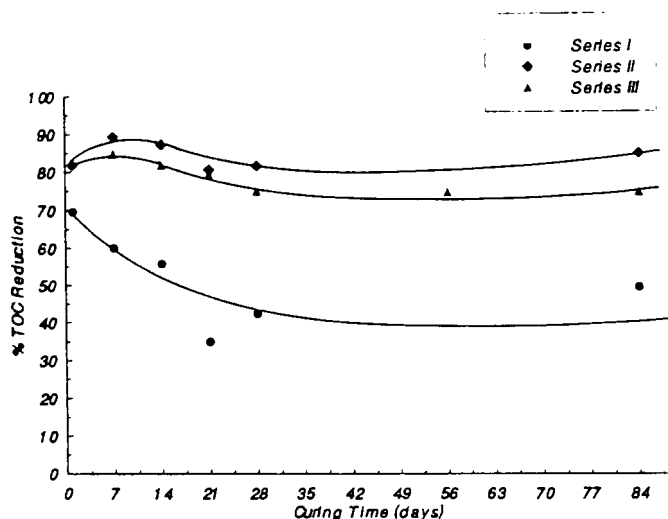
Figure 2
Relationship Between TOC Reduction and Curing Time

The corresponding control samples were not subjected to the stress of drying. Instead, these samples were placed in a humid environment for 24 hours. The total material loss was obtained by drying and weighing the material which spilled off the sample. The relative material loss is the difference between the total material loss for the test samples and the total material loss for the control samples. Samples were tested for metal and organic contamination using the modified TCLP described above.

Results of wet/dry testing are presented in Table 2. As shown in Table 2, the total material loss was greatest for the cement kiln dust-stabilized sample. The total material loss was least for the sample having an attapulgite to sludge ratio of 0.4., although the sample having an attapulgite to sludge ratio of 0.6 was similar in magnitude. Since the relative material loss is quite small when compared with the total material loss, the tests demonstrated that the material degradation was primarily a result of the wetting cycles with little impact from the drying cycles. All mixes were quite resistant to physical degradation due to wetting and drying as indicated by the low values of material loss. Failure usually is defined as a relative material loss of 30%.

Table 2
Wet/Dry Test Results

Stabilization Mix & Proportions	Total Material Loss (%)	Relative Material Loss (%)	TOC Reduction (%)
S/CKD (1/1.5)	1.81	0.15	72.3
S/A/FA/QL/C (1/.6/.75/.25/.5/.3)	1.09	0.26	66.9
S/A/FA/QL/C (1/.4/.75/.25/.5/.3)	0.90	0.28	71.0

Freeze/Thaw Testing

Freeze/thaw testing was conducted to evaluate the resistance of the stabilized materials to cycles of freezing and drying. The literature indicated that freeze/thaw cycles often are more destructive than the wet/dry cycles. Samples for the freeze/thaw testing were mixed and compacted into plexiglass cylinders 1.75 inches in diameter and 3.00 inches in length. As with the wet/dry analyses, test and control samples were prepared for each candidate mix. Samples were cured in a humid

environment for 1 week. After curing, test samples were placed in the freezer for 24 hours at a temperature less than −20°C. This freeze period was followed by 24 hours of thawing in deionized water.

The results of the freeze/thaw testing are shown on Table 3. As with previous data, the cement kiln dust-stabilized samples did not perform as well as the samples stabilized with fly ash, quicklime, cement and attapulgite. The reduction in TOC was greatest for the sample having an attapulgite to sludge ratio of 0.6, which was only slightly better than an attapulgite to sludge ratio of 0.4. The material loss was greatest for the sample stabilized with cement kiln dust and essentially the same for the attapulgite-stabilized samples. Since the relative material loss is quite large when compared with the total material loss, the tests demonstrate that the material loss is primarily due to the freezing cycles.

A comparison of the freeze/thaw test results with the wet/dry test results indicates that the freeze/thaw stresses are more critical than the wet/dry stresses with respect to physical degradation. With respect to TOC, the wet/dry stresses are more critical.

Table 3
Freeze/Thaw Test Results

Stabilization Mix & Proportions	Total Material Loss (%)	Relative Material Loss (%)	TOC Reduction (%)
S/CKD (1/1.5)	6.46	5.22	72.4
S/A/FA/QL/C (1/.6/.75/.25/.5/.3)	2.69	1.62	91.4
S/A/FA/QL/C (1/.4/.75/.25/.5/.3)	2.41	1.43	89.6

One-Dimensional Compression

In order to assess the time rate and magnitude of the settlement of the stabilized mass, consolidation tests were run on the three candidate mixes. For this test, a 1-in. thick by 2.5-in. diameter specimen of the cured stabilized material is subjected to increasing vertical pressure and constrained from lateral deformation (one-dimensional compression). Loads were applied to stress the samples to 0.25, 0.5, 1, 2, 4, 8 and 16 tons per square foot. The samples were then unloaded to stresses of 8, 2, 0.5 and 0.001 tons per square foot. The time rate of deformation was recorded for all loading increments. The compressibility is indicated by the compression index, defined as:

$$Cc = de/d\log\sigma'_v \qquad (1)$$

where
de = change in void ratio
$d\log\sigma'_v$ = change in applied stress

The results of the consolidation testing are summarized in Table 4. Note that the values of the compression index are in the range of those typical for stiff clays. The data also show a significant apparent preconsolidation pressure for the samples stabilized with attapulgite. Thus, stabilized materials loaded in the field at stresses less than these values will not be subject to large deformations.

Table 4
Consolidation Test Results

Stabilization Mix & Proportions	Pre-Consolidation Pressure (tsf)	Compression Index
S/CKD (1/1.5)	0.6	0.218
S/A/FA/QL/C (1/.6/.75/.25/.5/.3)	4.5	0.217
S/A/FA/QL/C (1/.4/.75/.25/.5/.3)	3.5	0.475

PERMEABILITY

Permeability tests were conducted on the stabilized monoliths in order to assess the hydraulic conductivity of the materials and to examine the contaminant transport from the stabilized material as a result of water infiltration. Triaxial permeability tests were conducted at an effective consolidation pressure of 10 psi, a backpressure of 50 psi and a differential seepage pressure of 5 psi. The permeant was potable tap water with a TOC of 10 mg/L. Chemical analyses were conducted on the effluent to determine the extent of transport from the sample.

Presented in Figure 3 are the permeability test results for a sludge sample stabilized with cement kiln dust. The hydraulic conductivity, which was initially 3×10^{-6} cm/sec, decreased to 2×10^{-6} cm/sec after 5 days. The slight decrease in conductivity is typical of cementitious materials which continue to hydrate with time after mixing.
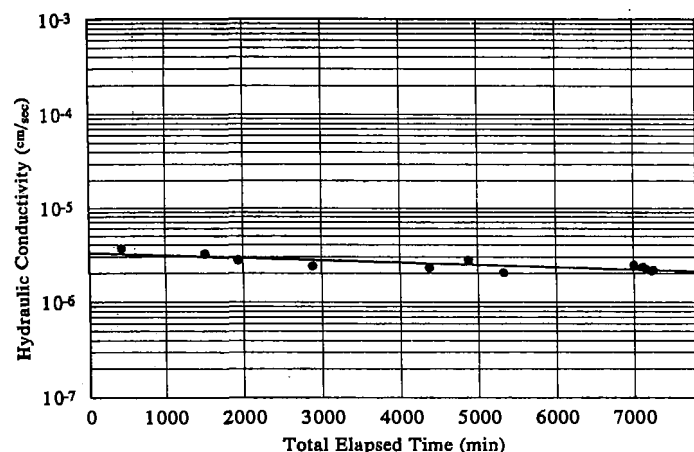
Figure 3
Hydraulic Conductivity Test Results
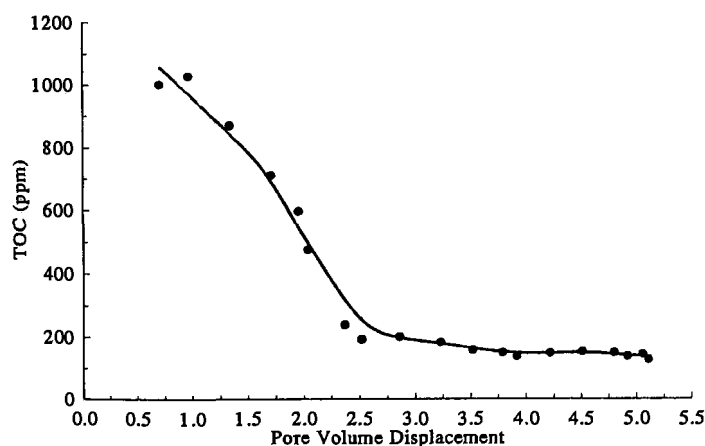
Figure 4
TOC of Hydraulic Conductivity Test Effluent

Chemical analysis of the effluent (Figure 4) show an initially high (>100 mg/L) TOC decreasing with time, i.e., pore volume displacement. It is postulated that the initially high TOC is the result of free organics within the stabilized matrix. The lower TOC reflects a steady-state diffusion from the stabilized matrix to the permeating water.

CONCLUSIONS

As a result of the studies of the stabilization of acidic petroleum sludges described herein, we have concluded that:

• The unconfined compression strength increases with curing time to approximately 28 days with little increase beyond that time.
• The initial TOC reduction decreased with increased curing time.
• No significant physical degradation occurred due to wet/dry testing
• Freeze/thaw testing resulted in greater physical degradation of the samples than wet/dry testing.
• Mixes containing fly ash, quicklime, cement, and attapulgite were more effective in stabilizing the acidic petroleum sludge than cement kiln dust.
• Compression characteristics of the stabilized sludge are similar to those of stiff clays.
• The hydraulic conductivity of the stabilized materials is low (in the range of 2×10^{-6} cm/sec).
• Permeation with tap water caused release of organics from the stabilized monolith.
• The release of organics decreased with the duration of permeation.

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Selecting Innovative Treatment Technologies:
A Practitioner's Guide

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ABSTRACT

The U.S. EPA provides a number of tools for decision-makers who must evaluate technologies to remediate contaminated soils and groundwater. This paper provides a "road map" to guide the reader through the variety of U.S. EPA resources available on innovative treatment technologies.

Some of the available resources include screening guides that assist site managers in matching waste types with appropriate technologies; a bibliography, entitled *Selected Alternative and Innovative Treatment Technologies for Corrective Action and Site Remediation*, listing relevant and current U.S. EPA reports on remedial technologies and how to obtain them; the ROD System (RODS) data base, which contains information on technologies selected for individual sites; Superfund Innovative Technology Evaluation (SITE) reports, which provide performance data on innovative technology demonstrations; and the Alternative Treatment Technology Information Clearinghouse (ATTIC), which is a computerized library of treatability studies.

Additional resources to be available in the near future include information on technologies used at removal and remedial sites and their implementation status; an expert system to help select appropriate biological treatment processes for remedial sites; and an enhancement of ATTIC with treatment technology case histories from the Department of Energy, the Department of Defense and the Department of the Interior.

INTRODUCTION

SARA mandated the use of permanent remedies at Superfund sites. By definition, these remedies reduce the toxicity, mobility and volume of contamination. As noted in the *Management Review of the Superfund Program* (commonly referred to as the 90-Day Study), decision-makers are hesitant to select newly developed or innovative technologies for a variety of informational, institutional and economic reasons. The Technology Innovation Office (TIO) was created in 1990 within the U.S. EPA's Office of Solid Waste and Emergency Response (OSWER) to identify and remove impediments to the broader application of innovative technologies to hazardous waste remediation. One of TIO's primary goals is to assist those who select hazardous waste cleanup technologies to identify and use new or innovative technologies when remediating contaminated soils and groundwater.

A principal impediment to the use of innovative and alternative treatment technologies is the lack of up-to-date, objective data with which to initially evaluate a technology's performance and cost. Such data must be available early in the remedy screening process in order for an innovative technology to be fully considered during the feasibility study. In an effort to overcome this particular roadblock, the U.S. EPA has created a number of reference sources for use by U.S. EPA

employees and others. These resources include computerized data bases, a reference library, numerous publications and the availability of dedicated groups of technical experts. Many of these resources are available to the general public with no user fees.

The purpose of this paper is to publicize these computerized, bibliographic and technical resources, to encourage their use and to present a "road map" or logical approach to their efficient application. The "Practitioner's Guide to Identifying Innovative Technologies"
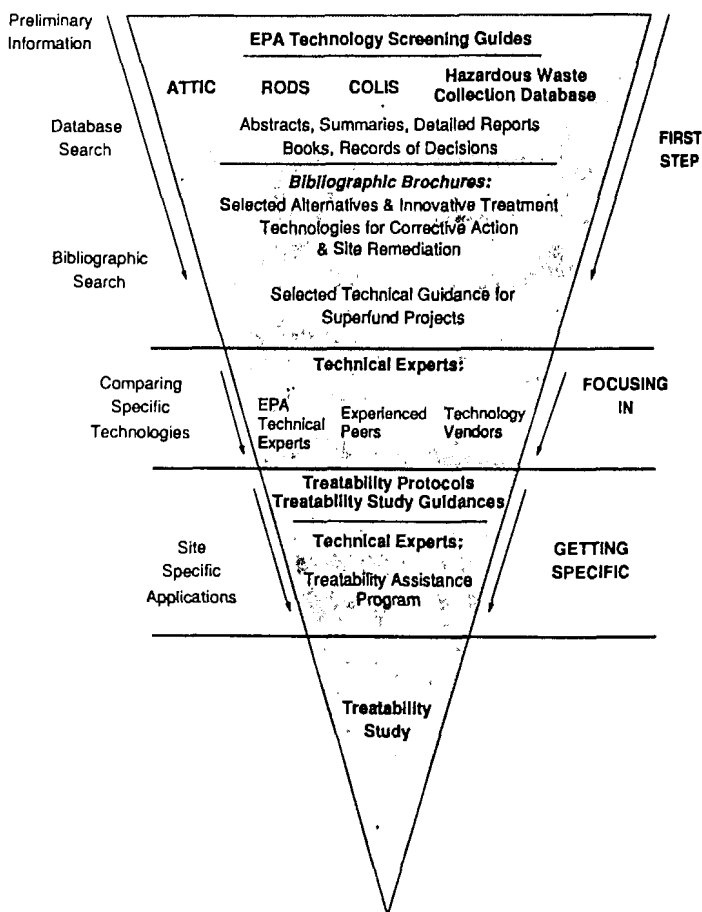
Figure 1
Practitioner's Guide to Identifying Innovative Technologies

Table 1
U.S. EPA Screening Guidelines for Treatment Technologies

- Technology Screening Guide for Treatment of CERCLA Soils and Sludges EPA/540/2-88/004
- Treatability Potential for EPA Listed Hazardous Wastes in Soil NTIS PB89-166581
- Treatability Potential for 56 EPA Listed Hazardous Wastes in Soil NTIS PB89-1744446
- Treatability of Hazardous Chemicals in Soils: Volatile and Semi-Volatile Organics NTIS DE89-016892
- Bioremediation of Contaminated Surface Soil NTIS PB90-164047
- Treatment Technology Fact Sheets:

  Innovative Technology: Soil Washing
  OSWER Directive 9200.5-250-FS (Fact Sheet)

  Innovative Technology: In-Situ Vitrification
  OSWER Directive 9200.5-251-FS (Fact Sheet)

  Innovative Technology: BEST-TM Solvent Extraction Process
  OSWER Directive 9200.5-253-FS (Fact Sheet)

  Innovative Technology: Glycolate Dehalogenation
  OSWER Directive 9200.5-254-FS (Fact Sheet)

(Fig. 1) provides an ordered approach to using the various data bases, publication sources and technical experts currently available from the U.S. EPA. This Guide can be used as a first step in identifying potential technologies that may be applicable to a specific contaminated site, as well as serving as a final check on available cost and performance data concerning various innovative remediation technologies that have already been identified through other means.

THE FIRST STEP

The streamlining of the Superfund remedial program in recent years requires the identification of remedial technologies during the early data gathering phases of the RI. During the early identification of technologies in the RI, the analyst needs to sift quickly through available information and identify what might be worth examining in more detail. A similar analysis may be conducted when time permits an engineering evaluation prior to a removal action.

The U.S. EPA has prepared several screening documents which support an initial assessment of the possible application of technologies at sites. These documents (Table 1) provide an overview of potential technology use based on physical site characteristics and contaminant information. This information will help the analyst begin to identify potentially feasible technologies, to identify interfering waste and/or site characteristics and to identify process limitations. The screening guides should help focus attention on important technical issues and help identify key words or phrases for use during computer searches. Following this initial screening, data bases may be searched to identify useful references.

The U.S. EPA has created four data bases that are useful places to begin bibliographic technology research: ATTIC, the Hazardous Waste Collection Data Base, RODS and COLIS. The most recently developed of these four data bases, and likely the most pertinent to a technology search, is ATTIC—the Alternative Treatment Technology Information Clearinghouse. ATTIC is the primary technology transfer mechanism for disseminating information concerning the Superfund Innovative Technology Evaluation (SITE) program and also contains abstracts and executive summaries from more than 1,500 technical documents and reports from states, industry, NATO, DOD, DOE other countries, Superfund RODs and various Superfund treatability studies. ATTIC can be accessed through modem-equipped personal computers or through a systems operator. The system is designed to search for key words with minimum effort, a site manager can receive short abstracts and summaries of possible applicable technologies. Should these summaries seem relevant, full copies of reports can be obtained through several sources including the U.S. EPA Library. Access to the on-line ATTIC system is available through the ATTIC system operator. Technical information requests also can be made by calling the system operator at (301) 816-9153.

The second data base of potential use during an early technology search is the Hazardous Waste Collection Database (HWCD), housed within the U.S. EPA Headquarters library. The HWCD, established in 1986 to support the information needs of the U.S. EPA's Superfund office, is a bibliographic data base containing abstracts of U.S. EPA and other government agency reports, trade books, policy and guidance directives, legislation and regulations concerning hazardous waste. Although the subject matter of HWCD is far more wide-ranging than the topic of innovative technologies, it is searchable by subject, reference title and key words using a menu. A data base thesaurus is available to aid users in designing efficient searches. One may contact Felice Sacks, the U.S. EPA Headquarters Head Hazardous Waste Superfund Librarian, at (202) 382-5934 for more information concerning the HWCD system.

A third useful data base is the Records Of Decision System (RODS) data base. The RODS data base contains the text of the signed Superfund Records of Decision. It facilitates comparing technologies used at sites with similar physical characteristics and waste conditions. The data base is menu-driven and provides rapid information searches. A search can be conducted on such fields as site name, remedy, key contaminants or the full text of the ROD. RODS is maintained on the U.S. EPA's IBM mainframe computer, which is located in Research Triangle Park, North Carolina. The RODS data base is available to the general public through the CERCLIS Hotline at (202) 252-0056 or the RODS staff at (202) 245-3770.

The fourth data base of interest is COLIS—the Computerized On-Line Information Systems. COLIS is part of the U.S. EPA's Risk Reduction Engineering Laboratory's (RREL) Technical Information Exchange. Three COLIS data bases are currently in operation:

- Case History File: This file contains information on site characteristics, respond methods, costs and cleanup problems related to spills, waste sites and underground storage tank management.
- Library Search System: This subsystem allows free form searching through catalog cards and full length abstracts of documents in the TIX library. Users may conduct their own literature searches using their own key words—they are not limited to a standard set of key words.
- SITE Application Analysis Report File: This subsystem allows free form searching of reports containing cost and performance data gathered from the U.S. EPA's SITE demonstration program. The reports are on-line in their entirety.

COLIS is accessible through the ATTIC system, or the system operator can be contacted at (201) 906-6871.

In addition to data bases services, the U.S. EPA also has prepared two brochures that will help identify U.S. EPA documents concerning the use of innovative and alternative remedial technologies. These brochures are titled *Selected Alternative and Innovative Treatment Technologies for Corrective Action and Site Remediation* (EPA/540/8-90/008, Oct. 1990) and *Selected Technical Guidance for Superfund Projects* (EPA/540/8-89/004, May 1989). Each of these two brochures lists more than 70 U.S. EPA documents relating to Superfund and remedial technologies. Both of these brochures are available free from the U.S. EPA's Center for Environmental Research Information (CERI) at (513) 569-7562.

FOCUSING IN

Each of these four computerized information sources allows users to gather a large number of potentially useful references in a relatively short period of time. The next step, therefore, is to pare down the reference list to those documents truly of interest. The technology screening guides listed in Table 1 should be helpful in this regard by assisting site managers to obtain a sense of the relevancy of individual references. The U.S. EPA and other sources also make available technology-specific publications and technical experts that can be consulted for detailed information regarding potentially useful remediation technologies.

Technology Specific Publications

By using general knowledge of site characteristics and an overview of potentially effective treatment technologies obtained from the screening guides mentioned above, the site manager has at this point identified references to a relatively small number of remediation technologies that are potentially useful. The next step is to locate and review documents concerning these technologies so that these few technologies can be compared with each other.

During the review of screening documents and technical literature, the analyst may become aware of important site characteristics which will determine the feasibility of some treatment processes. These factors may concern the physical or chemical character of the waste and suggest the need to promptly gather additional site data. Thus, an iterative process may develop where additional site data will be necessary to thoroughly assess technologies prior to conducting treatability studies.

Technical Experts

One of the challenges facing site managers is the need to assess the value of an innovative technology for the specific characteristics of a site. When reviewing the literature and considering technologies, the analyst should be aware of the developmental status of different technologies. By definition, innovative technologies are neither fully commercialized nor ready for "off-the-shelf" use. These technologies have limited performance and cost data and lack extensive field experience. The status of these processes may rapidly change, and new information is constantly being generated as demonstration projects and treatability studies are completed. Therefore, especially for new technologies, personal contact with technical experts, experienced peers and technology vendors is very important.

The U.S. EPA's Risk Reduction Engineering Laboratory (RREL) and Robert S. Kerr Environmental Research Laboratory (RSKERL) have experts on numerous treatment technologies that can quickly steer a site manager to pertinent and relevant information. The U.S. EPA sponsors several programs through each laboratory to provide this type of consultation. At the RREL, the U.S. EPA has established:

- The Engineering and Treatment Technical Support Center
- The Treatability Assistance Program
- The Superfund Technical Assistance Response Team

These three programs offer expertise in contaminant source control particularly in: above ground treatment units; materials handling; treatment of soils, sludge and sediments; and treatment of aqueous and organic liquids. They are intended to serve U.S. EPA site managers primarily, but are available to the public on a limited basis. For further information regarding these programs, one can contact Ben Blaney at (513) 569-7406.

Similarly, at the RSKERL, the U.S. EPA has established a Technical Support Center to deal with in situ biorestoration of soils and technologies affecting groundwater. For further information concerning these programs, one can contact Richard Scoff at (405) 332-8800.

The U.S. EPA has published reference guides to help identify ongoing programs and individuals who are working in specific technical areas. These guides are listed in Table 2. In addition, the SITE program has ben actively working with developers of innovative technologies for the last 4 yr. The program has a technology transfer effort intended to provide support to those in the hazardous waste site remediation community. The annual SITE Program brochure lists the U.S. EPA Office of Research and Development project managers and their associated

Table 2
EPA Reference Guides to Technical Experts

- Groundwater Research: Technical Assistance Directory
  EPA/600/9-89/048
- Environmental Protection Agency, Office of Research and Development: Technical Assistance Directory CERI-88-84
- ORD Topical Directory EPA/600/9-86 006
- Technical Support Services for Superfund Site Remediation: EPA 540 8-90 011 October 1990

technologies of interest. For additional information, one can contact John Martin at (513) 569-7758.

The five Hazardous Substance Research Centers are another source of technical expertise funded by the U.S. EPA (Table 3). These university-based centers, each of which has established special relations with a pair of U.S. EPA Regions, focus on problems common within their geographic regions, with emphasis on a specific area of research. These areas of specialization include groundwater remediation, incineration, bioremediation, recovery of metals and other physical and chemical treatment of surface and subsurface contaminants. The centers perform long- and short-term research on all aspects of hazardous substance generation, management, treatment and disposal. The centers are committed to technology transfer, as well. The activities of these centers are described more fully in *Hazardous Substance Research Center: Annual Report FY 1989* (January 1990). For a copy of this report or more information regarding these research centers, one can contact Karen Morehouse at (202) 382-5750.

Table 3
Hazardous Substance Research Centers and Directors

- Dr. Richard Magee, Director
  Hazardous Substance Management Research Center
  New Jersey Institute of Technology
  Newark, New Jersey 07102
  201/596-3233

  Region-Pair 1/2: CT, MA, ME, NH, NJ, NY, PR, RI, VI, VT

- Dr. Walter J. Weber, Jr.
  Dept. of Civil Engineering
  2340 C.G. Brown Building
  University of Michigan
  Ann Arbor, Michigan 48109-2125
  313/763-2274

  Region-Pair 3/5: DC, DE, IL, IN, MD, MI, MN, OH, PA, VA, WI, WV

- Dr. Michael R. Overcash
  Dept. of Chemical Engineering
  North Carolina State University
  Raleigh, North Carolina 27695-7001

  Region-Pair 4/6: AL, AR, FL, GA, KY, LA, MS, NM, NC, OK, SC, TN, TX

- Dr. Larry E. Erickson
  Dept. of Chemical Engineering
  Durland Hall
  Kansas State University
  Manhattan, Kansas 66506
  913/532-5584

  Region-Pair 7/8: CO, IA, KS, MO, MT, ND, NE, SD, UT, WY

- Dr. Perry L. McCarty
  Center Director
  Dept. of Civil Engineering
  Stanford University
  Stanford, California 94308
  415/723-4131

  Region-Pair 9/10: AK, American Samoa, AZ, CA, Guam, HI, ID, Northern Mariana Islands, NV, OR, WA

GETTING SPECIFIC

After identifying innovative treatment technologies with a potential for success at a site, treatability studies will likely be necessary to ascertain the effectiveness of technologies for the given site conditions and waste characteristics. The U.S. EPA provides several services to help make this task easier. The most basic are the publications entitled *Treatability Studies Under CERCLA: An Overview* (OSWER Directive 9380.3-02FS) and *Guide for Conducting Treatability Studies Under CERCLA, Interim Final* (EPA/540/2-89/058). These publications

are available through the Superfund Docket and CERI, respectively (Table 2).

Through the Risk Reduction Engineering Laboratory, the U.S. EPA sponsors the previously mentioned Treatability Assistance Program. This program offers a list of contractors available to perform treatability studies, a comprehensive data base of all aqueous treatability studies and brief bulletins describing the applicability of various technologies. The Treatability Assistance Program is also in the process of developing generic technology specific treatability study protocols.

CONCLUSION

The U.S. EPA is assembling a comprehensive set of materials to make hazardous waste site managers aware of the resources available concerning innovative remedial technologies and to help steer them toward use of innovative remedial technologies. A logical approach to use of these materials is:

- To reference screening guides and assess overall technology potential
- To conduct a series of comprehensive data base searches
- To consult available bibliographies
- To screen the computer-generated reference lists, abstracts and bibliographies and obtain those publications and documents identified as having direct relevance to the project
- To contact recognized experts in the field of hazardous waste site remediation and engineering
- To conduct treatability studies using site-specific conditions and wastes

The Technology Innovation Office continues it's efforts to make more technology-specific information available to the hazardous waste site remediation community. Future plans call for the development of an innovative technology vendor data base, the expansion of the ATTIC system to include other data bases (thereby offering one-stop shopping), the development of a computerized expert system to assist in the selection of appropriate types of biological treatment and an expansion and improvement of SITE program information availability.

A critical factor in the success of the innovative technology information systems is the timeliness of the information it contains. "Innovation" by definition means "new," and all data in the U.S. EPA systems need to be continually updated or the system becomes simply one more impediment to using innovative technologies. Data and information concerning innovative technologies must be made widely available before these technologies can be fully evaluated and their potentials realized.

The U.S. EPA's Technical Innovation Office would also like to integrate information from outside sources, such as remediation contractors, other federal agencies and private industry, into its various technology transfer mechanisms. We have begun an outreach program designed to help collect and collate cost and performance data for innovative remediation technologies wherever it is available.

DISCLAIMER

The opinions expressed in this article are those of the authors, and do not necessarily reflect the policy position of the U.S. EPA.

Considerations in the Design of Pump-and-Treat Remediation Systems

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ABSTRACT

A common means to contain and/or remediate contaminated groundwater is to extract the water and treat it at the surface. This process is referred to as pump-and-treat technology. Practical considerations in the design of pump-and-treat systems are reviewed, with emphasis on the "pump" portion of the technology. Pre-design analysis and post-implementation monitoring also are emphasized. Basic guidance is given on how to use hydrogeological and chemical data to determine when, where and how pump-and-treat technology can be used successfully.

Factors which affect the time required to achieve a specific groundwater cleanup goal also are discussed. These factors include certain combinations of hydrogeological conditions and geochemical properties. The variables also include the presence of nonaqueous phase liquids (NAPLs), chemical desorption from the soil matrix and media that exhibit significant spatial variability. Such conditions and properties result in longer remediation performance periods for all corrective actions, including pump-and-treat technologies.

Case studies illustrate the proper design of pump-and-treat technology. As with any remedial technology, limitations at various sites may require that different remedial technologies be combined to improve remediation performance.

INTRODUCTION

Sources of groundwater contamination can range from leaky tanks, landfills and spills to the less obvious, such as chemicals in the soil dissolving from nonaqueous phase liquids (NAPLs) or chemicals desorbing from the soil matrix. Several options can be used to attempt containment and/or cleanup of groundwater contamination.

First, however, a distinction needs to be made between source removal and groundwater cleanup. Source removal typically refers to excavation and removal of wastes and/or contaminated soil. It also can include vacuum extraction. Source containment includes chemical fixation or physical encapsulation; if effective, its result is similar to source removal in that it eliminates the potential for continued chemical transport from the waste source to groundwater.

Groundwater containment/cleanup options include physical containment (e.g., construction of low-permeability walls and covers), in situ treatment (e.g., bioreclamation) and hydraulic containment/cleanup (e.g., extraction wells and intercept trenches/drains). To ensure complete cleanup, several methods may be combined to form a treatment train. This paper focuses only on hydraulic containment/cleanup, in particular, pump-and-treat technology.

In a pump-and-treat system, contaminated groundwater or mobile NAPLs are captured and pumped to the surface for treatment. This process requires locating the groundwater contaminant plume or NAPLs in three-dimensional space, determining aquifer and chemical proper-ties, designing a capture system and installing extraction (and in some cases injection) wells. Monitor wells/piezometers used to check the effectiveness of the pump-and-treat system are an integral component of the system. Injection wells are used to enhance the extraction system by flushing contaminants (including some in the vadose zone) toward extraction wells or drains. A pump-and-treat system may be combined with other remedial actions, such as low-permeability walls, to limit the amount of clean water flowing to the extraction wells, thus reducing the volume of water to be treated.

Whether the objective of the pump-and-treat system is to reduce concentrations of contaminants to an acceptable level (cleanup) or to protect the subsurface from further contamination (containment), the system components are:

- A set of goals or objectives
- Engineered components such as wells, pumps and a treatment facility
- Operational rules and monitoring
- Termination criteria

Each of these components must be addressed in the design and evaluation of a pump-and-treat technology.

Pump-and-treat technology is appropriate for many groundwater contamination problems.[1,2] However, the physical-chemical subsurface system must allow the contaminants to flow to the extraction wells. Consequently, the subsurface must have sufficient hydraulic conductivity to allow fluid to flow readily and the chemicals must be transportable by the fluid, thus making the use of pump-and-treat systems highly site-specific.

One way to evaluate the effectiveness of a remediation technology is through a study of case histories. Lindorff and Cartwright[3] discuss 116 case histories of groundwater contamination and remediation. The U.S. EPA [4,5] presents 23 case histories of groundwater remediation. More recently, groundwater extraction has been evaluated via case histories.[6] Based on these reviews, conditions which inhibit the easy flow of contaminants to pumping wells include:

- Heterogeneous aquifer conditions where low-permeability zones restrict contaminant flow toward extraction wells
- Chemicals that are sorbed or precipitated on the soil and slowly desorb or dissolve back into the groundwater as chemical equilibrium changes in response to the extraction process
- Immobile nonaqueous phase liquids (NAPLs) that may contribute to a miscible contaminant plume by prolonged dissolution (e.g., a separate phase gasoline at residual saturation)

The main limitation of pump-and-treat technology is the long time that may be required to achieve an acceptable level of cleanup. Limitations are discussed further in Mackay and Cherry[7] and Mercer et al.[2] For these limitations, modifications to pump-and-treat technology, such as

pulsed pumping, may be appropriate. Pump-and-treat technology also may be combined with other remedial alternatives, such as vacuum extraction and/or bioremediation. One should realize that no single technology is a panacea for subsurface remediation under complex conditions.

CONCEPTUAL DESIGN AND LIMITATIONS

When to Select Pump-and-Treat Systems

Figure 1 presents a decision-flow diagram for groundwater contamination. For groundwater contamination, the first decision concerns whether a remedial action (G3) is necessary. If a risk assessment shows the need for a remedial action, then the options shown in Figure 1 are containment (G4), in situ treatment (G5) or pump-and-treat (G6). If G5 is selected, then other decisions are necessary but not discussed here. If G4 is selected, then the containment can be either physical (G7) or hydraulic (G8). Physical containment generally has not worked well[8] and is not discussed further; hydraulic containment is achieved by pump-and-treat technologies (G11). As indicated previously, if the source of the groundwater contamination is not removed, then containment may be necessary as opposed to G5 or G6.

If pump-and-treat (G6) is selected, the next decision is whether to use wells (G9) or drains (G10). If the hydraulic conductivity is sufficiently high to allow flow to wells, then select wells. For low-permeability material, drains may be required. If wells have been selected, a decision must be made whether to use extraction wells (G12), injection wells (G13) or a combination. Injection wells will reduce the cleanup time by flushing contaminants toward the extraction wells. For the extraction wells, decisions need to be made concerning continuous pumping (G16), pulsed pumping (G17) and/or pumping combined with containment. Continuous pumping maintains an inward hydraulic gradient; pulsed pumping allows maximum concentrations to be extracted efficiently; containment can be used to limit the inflow of clean water that needs to be treated. The injected water can be treated water (G19); for biodegradable contaminants, it can contain nutrients and/or electron acceptors (G20) to enhance in situ biodegradation; or, for NAPLs, it can consist of enhanced oil recovery (EOR) materials (G21). For problems involving groundwater contamination, some form of pump-and-treat technology almost always will be used.
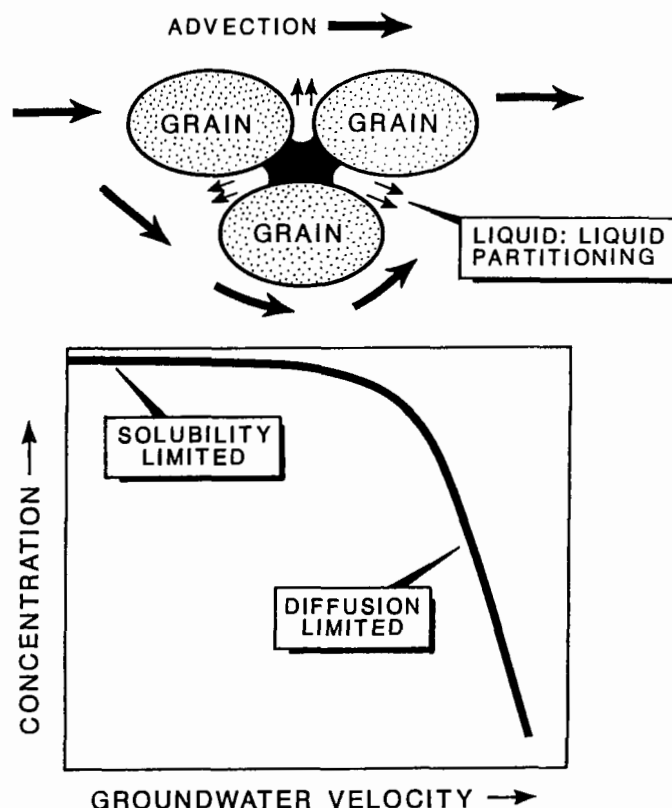
Figure 2
Liquid Partitioning Limitations of
Pump-and-Treat Effectiveness (from Keely[20])

Limitations of Pump-and-Treat Systems

For pump-and-treat technology to remediate an aquifer in a timely fashion, the contaminant source must be eliminated. Otherwise, unremoved contaminants will continue to be added to the groundwater
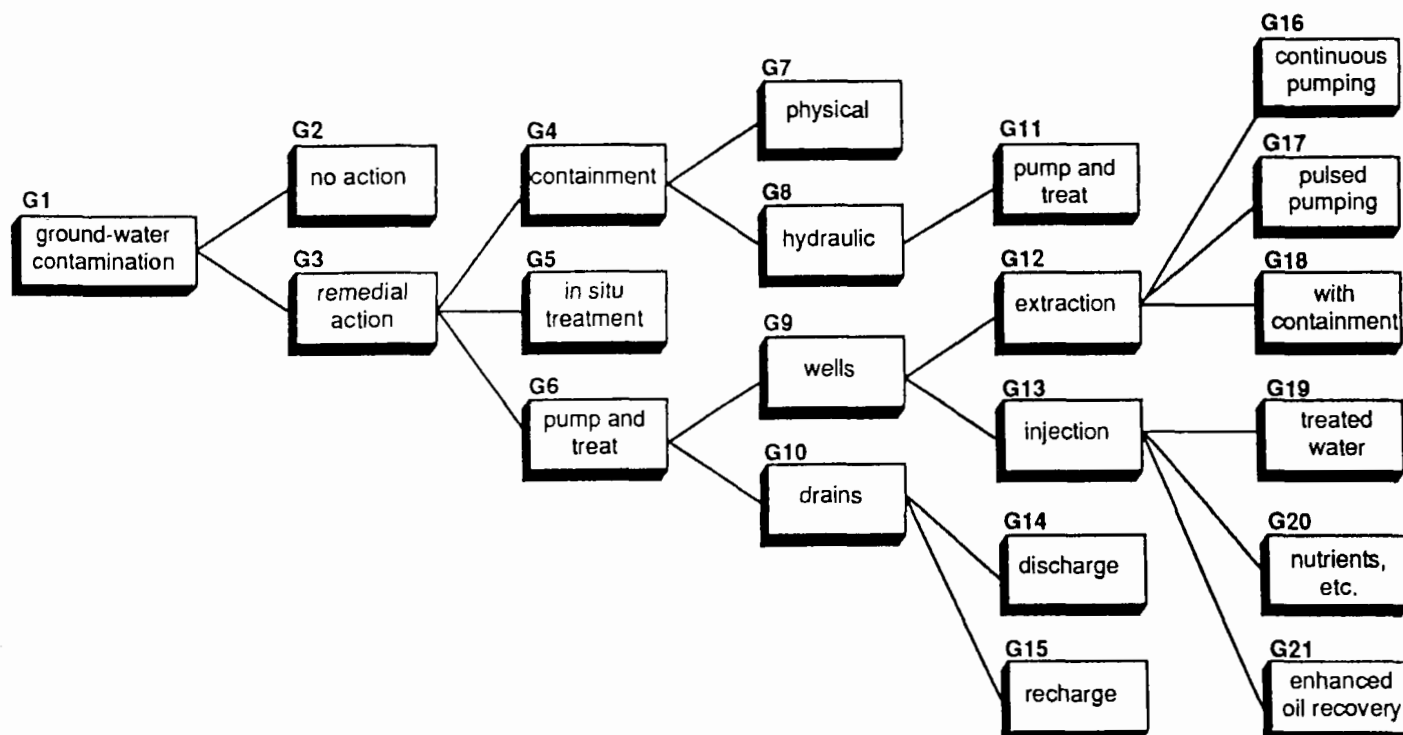
Figure 1
Decision-flow Diagram for Groundwater Contamination

system, prolonging cleanup. Excavation is one of several options available for source removal. NAPLs at residual saturation are one of the most difficult sources of groundwater contamination with which to deal. Particular difficulty is posed by substances such as halogenated aliphatic hydrocarbons, halogenated benzenes, phthalate esters and polychlorinated biphenyls (PCBs) which, in their pure form, are DNAPLs. When NAPLs are trapped in pores by interfacial tension, diffusive liquid-liquid partitioning controls dissolution. Flow rates during remediation may be too rapid to allow aqueous saturation levels of partitioned contaminants to be reached locally (Figure 2). If insufficient contact time is allowed, the affected water may be advected away from the residual NAPLs before approaching chemical equilibrium and replaced by water from upgradient. Because groundwater extraction generally does not efficiently clean up this type of source, some other remedial action may be required.

Mobile chemicals may be treated using pump-and-treat technology. For sorbing compounds, however, the number of pore volumes that will need to be removed depends on the sorptive tendencies of the contaminant, the geologic materials through which it flows and the groundwater flow velocities during remediation. If the velocities are too rapid to allow contaminant levels to build up to equilibrium concentrations locally (Figure 3), then the affected water may be advected away before approaching equilibrium. Efficiency in contaminant removal may be low and will tend to decrease with each pore volume removed.

The hydrogeological conditions favorable to pump-and-treat technology are high permeability (greater than about 10^{-5} cm/sec) and homogeneity. If the hydraulic conductivity is too low (less than about 10^{-7} cm/sec) to allow a sustained yield to a well, groundwater extraction via pumping wells is not feasible. Determining pump-and-treat feasibility is site-specific; a hydraulic conductivity range that works at one site may not work at another site. For example, if the plume is small and the natural hydraulic gradient low, a pump-and-treat system pumping at a very low rate in a low-permeability unit may be feasible.
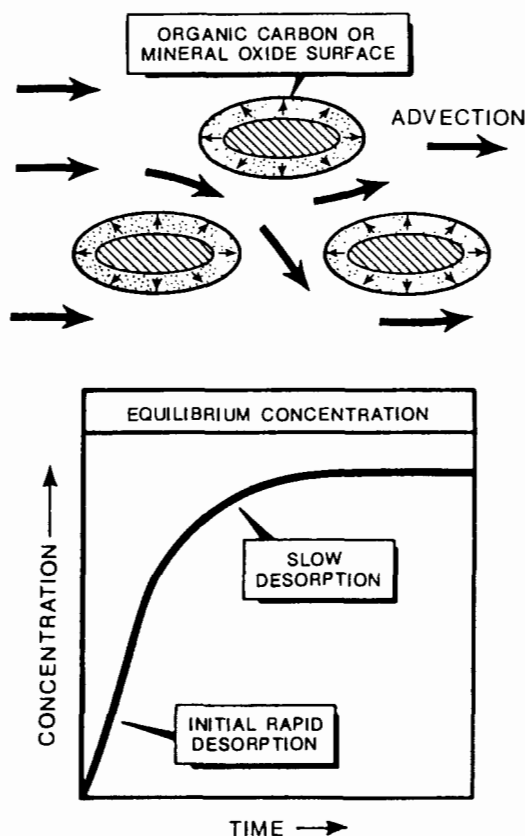
Figure 3
Sorption Limitations to Pump-and-Treat
Effectiveness (from Keely[20])

However, this same permeability may result in containment failure at another site.

For heterogeneous conditions (Figure 4), advected water will sweep through zones of higher hydraulic conductivity, removing contamination from those zones. Although heterogeneous conditions only are illustrated in the vertical in Figure 4, they are generally a three-dimensional phenomenon. Movement of contaminants out of the low hydraulic conductivity zones is a slower process than advective transport in the higher hydraulic conductivity zones. The contaminants either are slowly exchanged by diffusion with the flowing water present in larger pores or move at relatively slower velocities in the smaller pores. A rule of thumb is that the longer the site has been contaminated and the more lenticular (layered) the geologic material, the longer will be the tailing effect. The water and contaminants residing in the more permeable zones are those first mobilized during pumping. Thus, pump-and-treat technologies work in heterogeneous media, but cleanup times will be longer and more difficult to estimate than for similar systems in more homogeneous media.
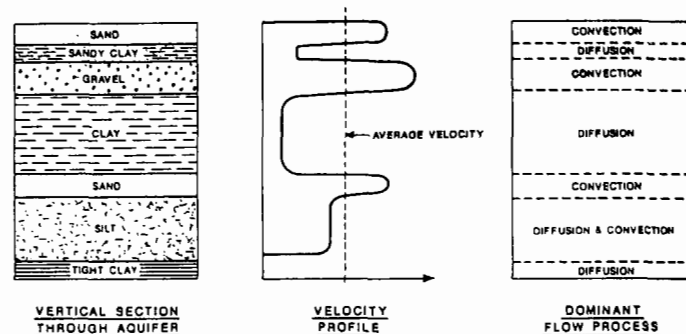
Figure 4
Effect of Geologic Stratification on Tailing
(from Keely[20])

Using Models for Pump-and-Treat Design

At many sites it is advantageous to have multiple extraction wells pumping at low rates rather than one well pumping at a high rate. Analytical or numerical modeling techniques are used to evaluate alternative designs and help determine optimal well spacings, pumping rates and cleanup times.[9] For example, a generic modeling study examining the effectiveness of various restoration schemes is presented in Satkin and Bedient.[10] There also are approaches combining groundwater models with linear and nonlinear optimization.[11] Fluid pathlines and travel times in groundwater systems also can be estimated from particle tracking codes.[12] In addition, there are numerous analytical solutions that may be used to estimate pumping rates and well spacings once aquifer properties are known. These solutions are included in Ferris et al.,[13] Bentall,[14] Walton[15] and Jacob.[16] In the following examples, both numerical and analytical models were used to estimate well spacings, pumping rates and cleanup times.

Numerical Model Example

A proposed pump-and-treat system for a hazardous waste site was evaluated using a numerical model and described by Ward et al.[17] The goal of the pump-and-treat system was to contain and clean up contamination. The results of the transport simulations are summarized in Figure 5. This figure shows the distribution inventory of the mass of volatile organic compounds (VOCs) at the site over time. At any given time, the initial VOC mass can be distributed in three categories: (1) mass remaining in groundwater, (2) mass removed by the extraction system and (3) mass leaving the domain unremediated. The mass in groundwater diminishes with time. However, some mass leaves the system uncaptured by the proposed corrective action. Thus, this pump-and-treat system will fail to contain the contamination.
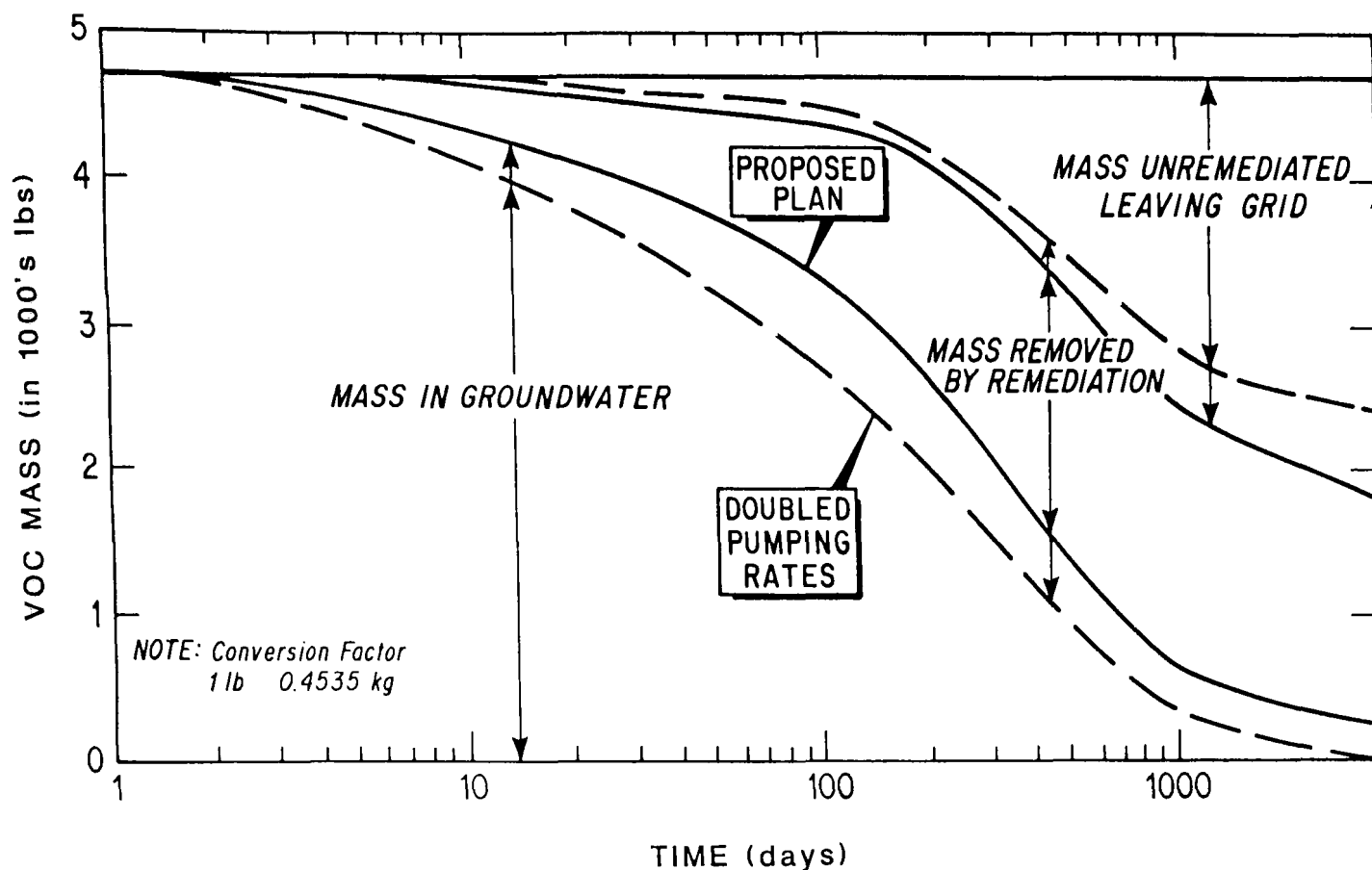
Figure 5
Calculated VOC Inventory versus Time
(from Ward et al.[17])

To assess the effect of increasing discharge and injection rates on plume capture, simulations were performed in which the total extraction and injection rates were doubled. The increased pumping rates reduced the VOC mass left in groundwater, but still failed to contain a portion of the plume (indicated by the dashed line in Figure 5). Thus, final pumping rates will need to be even greater. These results show the importance of plume capture analysis and emphasize the need for performance monitoring and the use of a model in monitoring program design.

The analysis of the above pump-and-treat system indicated declining contaminant concentration at the seven proposed extraction wells with time (Figure 6). Most wells exhibit a decreasing trend after a few weeks of operation. For each tenfold increase in the time of system operation, the concentration of VOCs decreases by a factor of ten. Some wells exhibit a temporary increase in concentration as zones of contamination are flushed toward the extraction wells. The effect of sorption also was examined with the model. A nearly linear relationship exists between retardation and time of remediation for a specific level of contaminant.

Analytical Model Example

Scoping calculations to estimate the pumpage required to capture a plume in a confined aquifer may be performed using the semi-analytical model RESSQ.[18,19] RESSQ is applicable to two-dimensional contaminant transport subject to advection and sorption (no dispersion, diffusion or degradation can be considered) in a homogeneous, isotropic, confined aquifer of uniform thickness when regional flow, sources and sinks create a steady-state flow field. RESSQ calculates groundwater flow paths in the aquifer, the location of contaminant fronts around sources at various times and the variation in contaminant concentration with time at sinks.
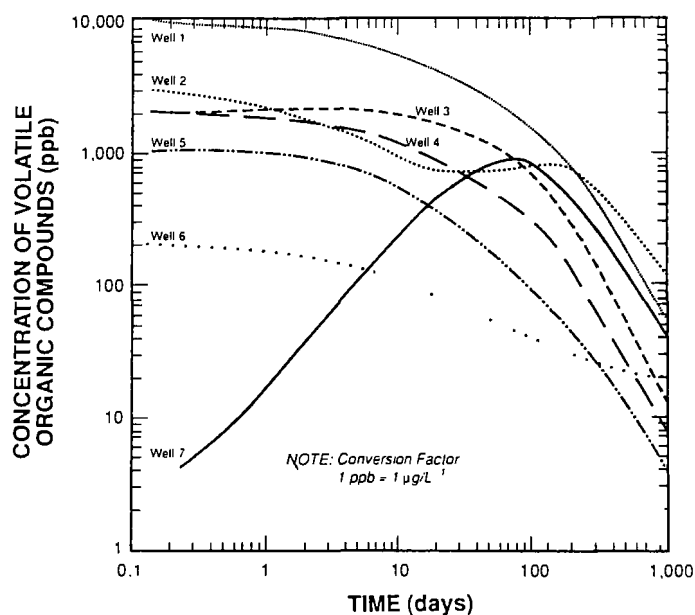
Figure 6
Calculated Extraction Well Concentrations versus Time
(from Ward et al.[17])

For example, the site is located in glacial deposits and consists of a leaking landfill with an associated plume (Figure 7). The goal is to design a capture well network for the plume. The site is more complex than the conditions simulated with RESSQ. A sand lens (not shown)

causes the plume to narrow with distance from the landfill. For these scoping calculations, the flow system considered is at the front of the plume where the wells are placed. For this location, a groundwater velocity of 0.205 ft/day (75 ft/yr) was estimated using Darcy's equation. The aquifer is 30 feet thick and the plume width is approximately 600 feet. The regional flow rate is 600 ft x 30 ft x 0.205 ft/day = 3690 ft³/day or 19.2 gpm. The total pumping rate of the wells will need to be approximately 20 gpm to capture the plume.
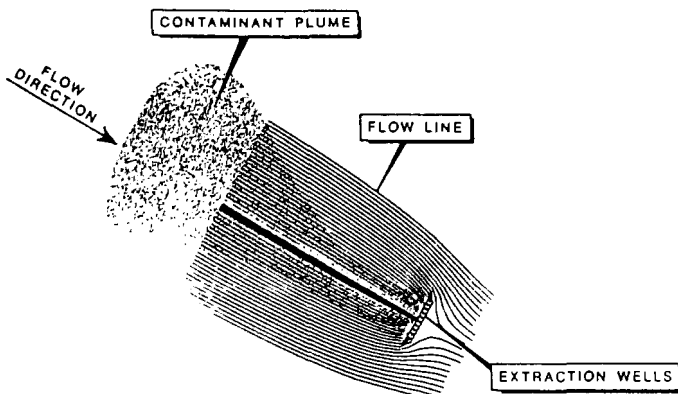
Figure 7
Simulation to Capture Front of the Plume:
10 Wells, 25 Feet Apart, Pumping at 2 gpm Each

Next, the maximum pumping rate that is sustainable without the wells going dry must be determined. The computation of drawdown at a single well in a multiple-well installation is not precise when a single water table aquifer of infinite extent is assumed. For 10 wells pumping at 2 gpm each, the maximum drawdown is calculated using the Theis solution and superposition[15] as 32 ft. This is an overestimate, as the leakage from the layers below and other sources (e.g., delayed yield) in the vicinity are not considered. Therefore, 10 wells at 2 gpm is considered acceptable from the considerations of drawdown. An optimum well spacing of 25 ft was determined based on guidelines provided by Javandel and Tsang.[19]

Streamtubes representing uniform regional flow were generated using RESSQ (Figure 7). The streamtubes trace the movement of the contaminants in the plume by advective transport. To ensure that contaminants do not escape between wells, the two streamtubes at the middle of the plume were divided into 5-foot wide spacings. The resulting calculations using RESSQ confirmed that the proposed pumping system would effectively capture the plume.

OPERATION AND MONITORING

Whatever remediation system is selected for a particular site, the following need to be described clearly:

- Performance standards (remedial objectives)
- Monitoring program
- Contingencies (modification to the existing remediation)

Remedial action objectives are the goals of the overall remediation. To ensure that these are met, appropriate monitoring must be conducted. If the monitoring indicates that the goals are not being met, then contingencies must be specified concerning changes to the remediation system that will ensure that the goals are reached or will specify alternate goals where original goals cannot be practically achieved.

According to Keely,[20] numerous compliance criteria and compliance point locations are used as performance standards. Compliance criteria can be divided into three categories: chemical, hydrodynamic and administrative control. Chemical compliance criteria are risk-based[21] and include Maximum Contaminant Limits (MCLs), Alternate Concentration Limits (ACLs), detection limits and natural water quality. Hydrodynamic compliance criteria may include demonstrated prevention or minimization of infiltration through the vadose zone, maintenance of an inward hydraulic gradient at the boundary of the contaminant

plume, or providing minimum flow to a surface water body. Administrative control compliance criteria range from reporting requirements, such as frequency and character of operational and post-operational monitoring, to land-use restrictions, such as drilling bans and other access-limiting restrictions.

Once the remedial action objectives are established and a remedial system is designed to meet these standards, the next step is to design a monitoring program that will evaluate the success of the remedial system. The monitoring criteria will be important in establishing the required monitoring program. Water quality monitoring is important; water-level monitoring also is important and is less expensive and subject to less uncertainty.

The location of monitor wells is critical to a successful monitoring program. For pump-and-treat technology, extraction and injection wells produce complex flow patterns locally, where previously there were different flow patterns.[20] Another possibility is that previously clean portions of the aquifer may become contaminated. Thus, monitor well locations should be based on an understanding of the flow system as it is modified by the pump-and-treat system. Modeling techniques discussed previously can be used to help in site-specific monitoring network design.

To determine the flow system generated by a pump-and-treat system, field evaluations must be made during the operational phase. Consequently, in addition to data collection for site characterization, data need to be collected during and after pump-and-treat system operation. Post-operational monitoring is needed to ensure that desorption or dissolution of residuals do not cause an increase in the level of contamination after system operation has ceased. This monitoring may be required for approximately 2 to 5 years after system termination and will depend on site conditions.

Because of the uncertainties involved in subsurface characterization, a pump-and-treat system may require modification during the initial operational stages. Modifications may result from improved estimates of hydraulic conductivity or more complete information on chemistry and loading to the treatment facility. Other modifications may be due to mechanical failures of pumps, wells or surface plumbing.

Switching from continuous pumping to pulsed pumping is one modification that may improve the efficiency of contaminant recovery. Pulsed pumping is the intermittent operation of a pump-and-treat system. The time when the pumps are off can allow the contaminants to diffuse out of less permeable zones and into adjacent higher hydraulic conductivity zones until maximum concentrations are achieved in the latter. For sorbed contaminants and residual NAPLs, this nonpumping period can allow sufficient time for equilibrium concentrations to be reached in local groundwater. During the subsequent pumping cycle, the minimum volume of contaminated groundwater can be removed at the maximum possible concentration for the most efficient treatment. The durations of pumping and nonpumping periods (approximately 1 to 30 days) are site-specific and only can be optimized through trial-and-error operation. By occasionally cycling only select wells, possible stagnation (zero or low flow) zones may be brought into active flowpaths and remediated.[20]

If plume capture must be maintained, it will be necessary to maintain pumping on the plume boundaries and perhaps only use pulsed pumping on the interior of the plume. Termination of the pump-and-treat system occurs when the cleanup goals are met. In addition to meeting concentration goals, termination also may occur when optimum mass removal is achieved and it is not practical to reduce contaminant levels further.

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Application of Innovative Treatment Technologies At NPL Sites

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INTRODUCTION

SARA fundamental changes in the U.S. EPA's approach to hazardous waste site remediation by providing a clear preference for the use of permanent remedies. The NCP[1] codifies the U.S. EPA's policy preference for treatment as well. Consistent with this direction, the Agency has made significant progress in this area. For the last 2 fiscal years (FY 88 and FY 89), more than 70% of our RODs for source control remedies included provisions for treatment of some portion of the waste at sites. These treatment technologies include several well-known technologies which are available for "off the shelf" use on contaminated soils and sludges such as rotary kiln incineration and solidification/stabilization. However, concerns regarding the costs or effectiveness of these methods under a variety of site conditions have caused the Agency to actively seek the development of new and innovative technologies to remediate hazardous waste sites.

Our ability to develop and use new technologies leading to more cost-effective site cleanups may well determine the eventual success of the nation's efforts to implement the Superfund and RCRA corrective action programs. The Agency's recent Superfund Management Review (90-Day Study)[2] recognized the importance of this issue and called for the creation of a separate U.S. EPA office charged with the responsibility of stimulating the use of new technologies at Superfund sites. The Technology Innovation Office was created by the U.S. EPA this year to work with both the public and private sectors to accomplish this goal.

The goals of this Office support a strategy to overcome impediments that restrict the broader use of new technologies. These impediments are regulatory, institutional and informational in nature.

Regulatory impediments relate primarily to regulatory and permitting requirements under RCRA. The evaluation of new hazardous waste treatment technologies is an unusual area of new product engineering which requires a permit to develop such technologies in addition to a permit for operation. The recently completed RCRA Implementation Study[3] highlights areas for attention which will make it easier for technology developers to perform testing with hazardous wastes not on Superfund sites.

Institutional impediments have their roots in human nature: people are reluctant to take unnecessary risks. U.S. EPA project managers may not see sufficient advantage in trying something new, or private consulting engineering firms may not be willing to risk their reputations and company assets on untried technologies. PRPs and owners/operators do not want to pay twice for solutions. The Technology Innovation Office will be sponsoring a number of outreach initiatives to provide more training and create incentives to overcome these barriers.

Informational impediments concern both technical and market issues. The Agency's Office of Research and Development has an ongoing program to assist vendors in developing innovative and emerging technologies. The Superfund Innovative Technology Evaluation (SITE) program provides an opportunity for developers to demonstrate their capabilities to the U.S. EPA. The program produces performance and cost data which are necessary for the engineering evaluation of new technologies. The Technology Innovation Office is also undertaking initiatives to develop a computerized vendor information system and to better define the hazardous waste remediation market. These efforts will help foster greater communication between firms that are developing new technologies, the financial community and potential users.

MARKET FOR CONTAMINATED SITE REMEDIATION

The potential market for new and innovative technologies is very broad and rapidly evolving. In addition to problems at Superfund sites, which are discussed later in the paper, a recent Congressional Budget Office report[4] estimates a future obligation of nearly $150 billion over the next 30 years to remediate hazardous waste problems at federal facilities. These facilities primarily include Department of Defense and Department of Energy sites. Federal facilities may present unique opportunities for innovative technology because of the unusual nature of the sites. Often these sites are contaminated with pollutants related to the production of munitions or nuclear devices not commonly found on sites owned and operated by individuals. These sites may contain very large quantities of contaminated material if they were operated for long periods of time.

In addition, all facilities issued a RCRA permit after November 8, 1984, must take corrective action for contamination at or from the facility, including releases that result from past disposal. The primary responsibility for corrective action belongs to the owner/operator of the individual facilities. In the recent RCRA Implementation Study, the U.S. EPA estimates that approximately 80% of 4,700 treatment storage or disposal facilities may require some form of corrective action.

Leaking underground storage tanks represent another potential market for innovative technologies. Estimates of the number of leaking underground tanks vary, but current data suggest at least 10% of more than 2 million tanks may be leaking. Based on information supplied from states, approximately 50% of these sites are petroleum product retailers and 5% involve hazardous waste.

Moreover, some individual states have site inventories which rival the number on the Federal NPL. Non-NPL sites include those that the U.S. EPA or states have assessed and found to be ineligible for the NPL, unassessed or unscored sites that may or may not be eligible for the NPL, sites that states have not reported to the U.S. EPA and undiscovered sites. Accurate data are not available on the number of non-NPL sites, since many still have not been identified. A December 1987 GAO report[5] stated that neither states nor the U.S. EPA has identified all potential sites. The report estimates that between 130,000 and 425,000

sites may eventually have to be evaluated for possible cleanup action. Some states have active site discovery programs underway, while other states rely solely on citizen reports of potential sites.

The contamination problems at this broad array of sites vary widely with various combinations of volatiles, semivolatiles, metals and radioactive mixed waste. In addition, assumptions regarding cleanup levels vary depending on whether Federal or state agencies are responsible for remediation. As a result, no single technology is expected to dominate the cleanup market. Combinations of technologies with several unit processes in series will often be required, but narrow market niches will also develop. This suggests an overall market capable of supporting a variety of technologies.

MAKING INNOVATING TECHNOLOGY MORE AVAILABLE

Interest in the hazardous waste site remediation market on the part of technology developers is evident from the response to SITE program requests for proposals. Approximately 115 proposals were received from five solicitations for the SITE innovative demonstration program, while 210 proposals were received from four solicitations for emerging technologies program.

The Technology Innovation Office is interested in achieving an increase in the supply of new technologies to help satisfy the diverse and growing demand for remediation services. In the Superfund program, innovative technologies are being chosen with increasing frequency. In FY 1987, almost 80% of the treatment technologies chosen for source control were conventional. By contrast, in FY 89 less than 50% of the chosen technologies were conventional. At present, however, relatively few innovative technologies have been employed in actual cleanup efforts. It is obviously important to have firms with commercial equipment available to bid competitively for work when it is advertised. Improving the balance between supply and demand for new technologies can be enhanced through better communication between technology developers, investors and site managers.

The Technology Innovation Office is initiating an effort to provide an opportunity for innovative technology developers to display information about the performance and status of their units. A series of questions are being compiled to profile new technologies for source control and in situ groundwater remediation. Vendors will provide information to the U.S. EPA which will be entered into an on-line data base and made available through ATTIC, the Office of Solid Waste and Emergency Response Electronic Bulletin Board and other sources. The system will help PRPs, government representatives and their consultants keep informed about the latest information on new technologies.

A second initiative to increase communication involves a compilation of information on the market or potential demand for new technologies. This market assessment is intended to help developers and investors make long-term strategic decisions and to help alert the remediation community to upcoming opportunities to bid on specific projects. The analyses will be published periodically in monographs devoted to this subject. The analysis which follows was prepared as part of the initial effort in this area.

SUPERFUND TECHNOLOGY SELECTION

Table 1 provides an overview of Superfund source control remedies by fiscal year since the 1986 Amendments. The table shows an increase in the selection of treatment remedies and in the number of RODs specifying innovative treatment technologies.

Figure 1 provides a more detailed look at the chosen technologies. The data are derived from RODs and anticipated design and construction activity. A comparison of similar compilations prepared separately for FY 87, FY 88 and FY 89 shows a trend away from the selection of solidification/stabilization and incineration (both on-site and off-site). Correspondingly, the largest increases are in the selection of vapor extraction and bioremediation technologies.

SITE CHARACTERIZATION

Table 2 groups NPL sites into 14 categories. Since sites may fall into multiple categories, the total number of sites given exceeds the NPL inventory of 1218 which was used for this analysis. The table also gives

Table 1
Overview of Source Control Remedies
FY 1987-1988

FY	RODs Signed	Source Control RODs (Final & Interim)	RODs Selecting One or More Treatment Technologies for Source Control	RODs Selecting Innovative Treatment Technologies for Source Control
87	77	50	25	8
88	151	99	70	31
89	143	104	70	43

ROD=Record of Decision

Treatment Technologies Specified - 210
Number of RODs - 165

* Sources include solids, soils, sludges and liquid wastes; waste sources do not include ground water or surface water
** Also includes sites where location of incineration is to be determined
( ) Number of times this technology was selected
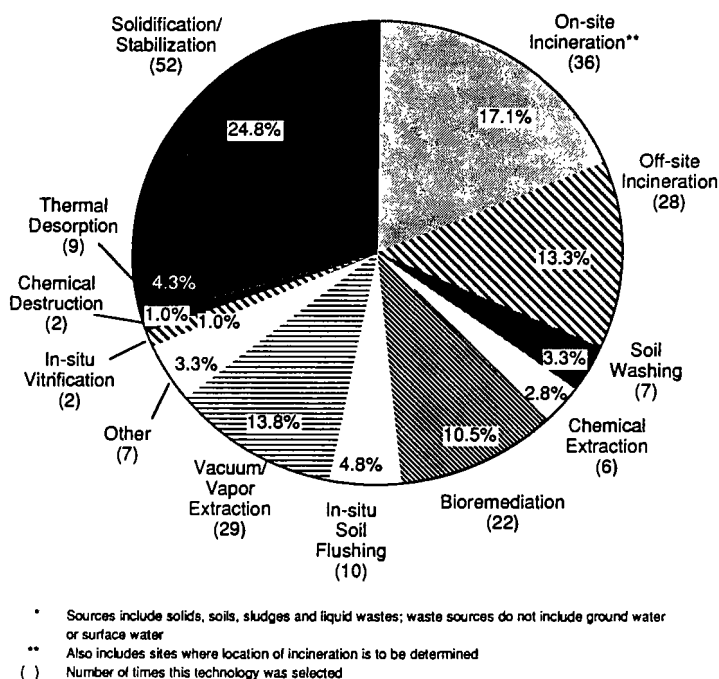
Figure 1
Source Control Treatment*
Fiscal Year 1987-1989

the categories for sites with signed RODs through FY 89. These figures include RODs for groundwater and source control.

Table 3 provides background on the criteria used to develop this classification system. Waste source, site description and constituent information primarily come from site summaries which are prepared when sites are proposed for inclusion on the NPL. Data for the five primary contaminants come from ROD Summaries. All this information has been placed into a new data base which provides technical characteristics for NPL sites.

Table 4 shows the distribution of selected innovative technologies for the site categories. However, when sites are categorized by the presence of a specific compound, that compound may not necessarily be targeted by the selected technology. Table 5 provides a summary of the occurrence of contaminated media for the different site categories.

Table 2
Number of NPL Sites in Each Site Category
(Total Number of Sites with RODs = 465)
(Total Number of NPL Sites = 1218)

Category	Number of sites with RODs	Total number of sites
WOOD PRESERVING	25	60
BATTERY/LEAD	8	25
PLATING	10	48
PCB	63	156
PETROLEUM	16	43
MINING WASTE	18	37
MUNICIPAL LANDFILL	42	145
INDUSTRIAL LANDFILL	124	361
DIOXIN	20	30
VOLATILE ORGANICS	237	702
MIXED WASTE	7	39
ASBESTOS	8	16
PESTICIDES	39	114
OTHERS	92	178

Note: Analysis based on information from RODs and NPL site summaries. Each site may fall under more than one category.

Table 3
Site Categories, Criteria Used for NPL Site
Analysis, and Five Primary Contaminants for Sites
with RODs in Each Category

Category	Waste Source	Site Description	Constituent	Five Primary Contaminants
Wood Processing	Lumber and Wood Products			Arsenic, Chromium, Polynuclear Aromatic Hydrocarbons, Benzene, Pentachlorophenol
Battery/Lead	Batteries			Nickel, Cadmium, Arsenic, Chromium Polynuclear Aromatic Hydrocarbons
Plating	Electroplating			Chromium, Cadmium Trichloroethene Lead, Zinc
PCB			PCB	PCB, Lead, Toluene Trichloroethene Polynuclear Aromatic Hydrocarbons
Petroleum	Petroleum Refining and Related Industries			Volatile Organics, PCB, Arsenic Trichloroethene Benzene
Mining Waste	Metals, Coal, Oil and Gas, Nonmetallic Metals			Lead, Cadmium, Arsenic, Zinc, Benzene
Municipal Landfill		Municipal Landfill		Lead, Vinyl Chloride Benzene, Chromium Trichloroethene
Industrial Landfill		Industrial Landfill		Lead, Chromium, Benzene 1,1,2,2 Tetrachloroethylene, Trichloroethene
Dioxin			Dioxin	Dioxins, Benzene, Arsenic, Polynuclear Aromatic Hydrocarbons, Pentachlorophenol
Volatile Organics			All VOCs	1,1,2,2 Tetrachloroethylene, Volatile Organics, Chromium, Lead, Trichloroethene
Mixed Waste			Radioactives Plutonium, Radium, Strontium, Thallium, Thorium, Uranium	Radium, Radioactives, Trichloroethene*, Toluene*, , Total Xylenes*, Chlorobenzene*
Asbestos			Asbestos	Asbestos, Nickel, 1,1,2,2 Tetrachloroethylene, Trichloroethene, Benzene*, Toluene*, Ethyl Benzene*
Pesticides			All Pesticides	Pesticides, Chromium, Lead, Benzene, Delta-BHC, Trichloroethene
Others				Chromium, Lead, Zinc, Nickel, Cadmium

*Contaminants of equal frequency

Table 4
Frequency of Innovative Technologies at NPL Sites with RODs

CATEGORY	Vacuum/vapor extraction	Bioreme-diation	Soil washing	Solvent/chemical extraction	Chemical dechlori-nation	Thermal desorption	In-situ vitrifi-cation
WOOD PRESERVING		9	4				
BATTERY/LEAD			1				
PLATING							
PCB	3	2		3	3	3	
PETROLEUM	1	3					
MINING WASTE							
MUNICIPAL LANDFILL	1	1					1
INDUSTRIAL LANDFILL	1	2	2	2		1	1
DIOXIN		5		1			
VOLATILE ORGANICS	22	14	6	4	2	9	1
MIXED WASTE							
ASBESTOS							
PESTICIDES	4	1					
OTHERS	3	4				1	

Note: Some sites are categorized by the presence of a specific compound which is not necessarily targeted by the selected technology.

Table 5
Occurrence of Contaminated Media at NPL Sites with RODs (Number of Sites)

Category	Soil	Sludge	Sediments
WOOD PRESERVING	18	5	4
BATTERY/LEAD	7	1	4
PLATING	6	0	0
PCB	55	5	21
PETROLEUM	6	1	1
MINING WASTE	4	0	1
MUNICIPAL LANDFILL	13	1	3
INDUSTRIAL LANDFILL	49	5	11
DIOXIN	17	2	3
VOLATILE ORGANICS	133	14	30
MIXED WASTE	5	0	1
ASBESTOS	6	0	1
PESTICIDES	31	3	6
OTHERS	10	1	2

At the time of writing this paper, additional analyses were being conducted to be presented verbally at the Superfund '90 Conference. Some of the additional work will include: total volumes of waste to be remediated will be determined by media. These data will include waste volumes for all technologies specified in RODs including land disposal, incineration, solidification/stabilization and innovative technologies. Average volumes will then be calculated for each site category leading to an estimate of total volumes by category and media. The CERCLIS data base will then be used to determine the status of remedial design and remedial action activities. This information should help vendors better understand the market and plan for commercializing their technologies.

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DISCLAIMER

The opinions expressed in this article are those of the authors and do not necessarily reflect the policy or position of the U.S. EPA.

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Treatability Studies on Soil Contaminated With Heavy Metals, Thiocyanates, Carbon Disulfate, Other Volatile and Semivolatile Organic Compounds

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ABSTRACT

On behalf of U.S. EPA, PEI Associates, Inc. performed laboratory screening level treatability studies to support the ongoing RI/FS for the Halby Chemical site in Wilmington, Delaware. These studies were designed to address the applicability of solidification/stabilization and xanthate flotation for treatment of metals in soils. In addition to these technologies, low-temperature thermal desorption was evaluated as a pretreatment step to remove compounds in soils that may impede the solidification/stabilization process and biological treatment was evaluated for treatment of carbon disulfide and those thiocyanate compounds that were present at high levels in soils and groundwater.

The results from these studies indicate that: (1) aerobic and anaerobic carbon disulfide- and aerobic-thiocyanate degrading organisms are present in soils and biodegradation of carbon disulfide and thiocyanate compounds (as indicated by microbial growth and oxygen consumption) can occur in the laboratory with the indigenous microbial population under aerobic conditions and sufficient amounts of nutrients; (2) while low-temperature thermal desorption may not be needed as a pretreatment step prior to solidification/stabilization, it can successfully remove most volatile and semivolatile organic compounds in soils at temperatures between 300° and 500°F and between 15 and 30 minutes residence time; and (3) the soils, themselves, do not leach appreciable amounts of metals under TCLP test conditions and of the two binders studied (asphalt and cement), asphalt appears to be the better binder for reducing leachate concentrations of arsenic and copper. Significant flotation/separation of metals from soils using xanthates was not achieved in our limited laboratory studies; however, further studies may be needed to more fully evaluate the applicability of this technology for removing heavy metals from soils. Additional feasibility and treatability studies are recommended prior to remedy selection.

INTRODUCTION

Since the enactment of SARA, RI/FS have included detailed evaluation of treatment alternatives for soils and groundwater. Recently, the U.S. EPA developed general procedures and guidelines for conducting treatability studies during the RI/FS as part of the remedy selection process reported in the U.S. EPA's ROD documents.[1] This guidance document, entitled *Guide for Conducting Treatability Studies Under CERCLA* (Interim Final), established three general levels of treatability testing that can be used to provide the necessary technological information to support the FS and remedy selection process.

This paper presents results from laboratory screening level treatability studies performed on soils contaminated with volatile and semivolatile organic compounds, as well as heavy metals and inorganic compounds.[2] This work was conducted by PEI Associates, Inc. on behalf of U.S. EPA, Office of Research and Development under the U.S. EPA

Contract No. 68-03-3413, Work Assignment No. 2-60. The overall approach for these studies was modeled after the policies and guidelines given in U.S. EPA's guidance document.[1]

Four treatment technologies were evaluated for treatment or removal of organic and inorganic compounds found in soils collected from the Halby Chemical Site in Wilmington, Delaware. They are low-temperature thermal desorption, solidification/stabilization, xanthate flotation and biological treatment. Each technology was evaluated as a primary treatment step, except low-temperature thermal desorption, which was evaluated as a pretreatment step prior to solidification/stabilization. The biological treatment study was conducted as a critical first step to evaluate the feasibility of biological treatment for selected compounds. Xanthate was evaluated as a flotation/separation agent to remove heavy metal particles from other soil material. All four technologies were evaluated at the laboratory screening tier, as defined in the U.S. EPA treatability study guide.[1]

SITE DESCRIPTION

The Halby Chemical site covers approximately 14 acres in a highly industrialized area in Wilmington, New Castle County, Delaware. As Figure 1 illustrates, the site is situated in a tidal marshland that is bordered on the north and west by Interstate 495, on the east by Conrail Railroad and on the south by Terminal Avenue. The Christina River and adjacent marsh area are located east of the site.

The Halby Chemical Company and the Witco Chemical Company produced sulfur compounds from 1948 to 1977. Specific raw materials used in the manufacturing process are shown in Table 1 and the products and associated byproducts known to have been produced at the plant are shown in Table 2. The principal chemicals that were manufactured or used at the chemical facility include carbon disulfide, ammonium thioglycolate (ATG), isooctyl thioglycolate (IOTG) and ammonium thiocyanate. In addition to these compounds, pyrite ore (iron sulfide) with trace amounts of heavy metals and coke piles have been stored on and adjacent to the site.

From 1948 to 1964, the wastewater, cooling water and surface run-off were discharged into an unlined lagoon. The lagoon waters discharged to the Christina River through a drainage ditch connected to Lobdell Canal southeast of the site. The lagoon presently receives run-off from the railroad tracks on the east side of the site and from the highway northwest of the site. Currently, a drainage ditch along I-495 drains the lagoon waters during tidal fluctuations into the Christina River. Although chemical production activities stopped in 1977, the site is still used for storage of carbon disulfide in above ground tanks. Areas adjacent to the site also are used for storage of coke piles (north of the site) and for truck washing (west of the site).
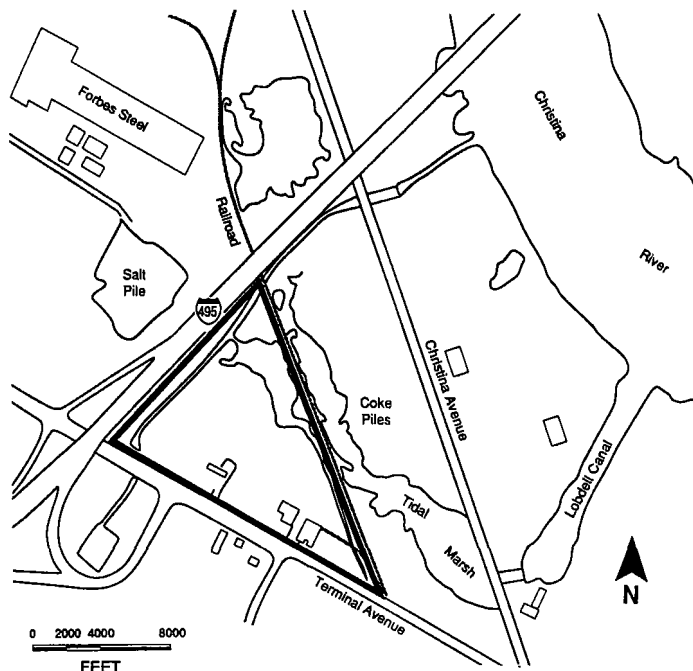
Figure 1
Map of Halby Chemical Site in Wilmington, Delaware

**Table 1
Raw Materials Used at the Halby Site**

Ammonium hydroxide
Anhydrous ammonium
Carbon disulfide
Potassium Hydroxide
Sodium hydroxide
Monochloroacetic acid
Isooctyl alcohol
Isopropyl ether
Monoethanolamine
p-Toluene sulfonic acid
Solvay dense soda ash
Sulfuric acid

**Table 2
Products and Byproducts Produced at the Halby Site**

Ammonium thioglycolate (ATG)
Isooctyl thioglycolate (IOTG)
Ammonium thiocyanate
Sodium sulfide
Sodium thiocyanate
Sodium hydrosulfide
Potassium thiocyanate
Monoethanolamine thioglycolate

SOIL CONTAMINATION

The site soils and sediments are contaminated by a complex chemical mixture of VOCs (including carbon disulfide, chlorinated ethylenes and benzene compounds), semivolatiles (including pyrene, benzo[a]pyrene, phenanthrene, fluorene, chrysene, fluoranthene and acenaphthene) and inorganic compounds (ammonium thiocyanate, arsenic, copper, cobalt, lead, manganese, mercury, vanadium and zinc) at widely varying concentrations ranging from approximately 100 ppb to 1%. In the sediments and surface soils, the highest concentrations of these compounds appear to be located at the southern end of the site near the tanks and chemical plant building, with lower levels in the northern and eastern portions. Subsurface soils are also contaminated with similar VOCs, semivolatiles and inorganic compounds to a depth of approximately 10 feet.

The lateral and vertical extent of contamination at the Halby Chemical site is complex and variable. The coexistence of various classes of com-

pounds means that several treatment technologies, either as operable units or combined in treatment trains, may need to be evaluated in the feasibility study. In addition, because the area is primarily industrial, the use of in situ treatment methods for remediating soils and ground-water may be evaluated in the RI/FS.

TECHNOLOGY DESCRIPTIONS

Several soil treatment technologies were identified by PEI and the U.S. EPA for further study during the technology screening stage of the RI/FS. Of these, solidification/stabilization and xanthate flotation were evaluated for applicability as primary treatment processes for treatment of the metals in the soils. Low-temperature thermal desorption was tested as a pretreatment step prior to solidification/stabilization. Microbial activity on site was assessed as an indicator of the site's potential for supporting bioremediation of organic contaminants, especially carbon disulfide and thiocyanate compounds that are present at high levels in soils and water.

Figure 2 presents the overall treatability scheme for this project and Table 3 presents the experimental plan. Table 4 summarizes the analytical testing program for the soil, groundwater and treatment residual fractions. Soil collected from the Halby Chemical site was subjected to physical, chemical and biological characterization tests to delineate the soil characteristics that may influence treatment effectiveness. Each separate soil sample (surface soil and sediment) was homogenized prior to chemical analysis and testing to ensure that representative samples are tested for each technology and that the results from those technologies with similar starting matrices can be compared. The soil was analyzed for a select list of indicator compounds (Table 4) to provide initial concentration data for determining the effectiveness of the technologies.
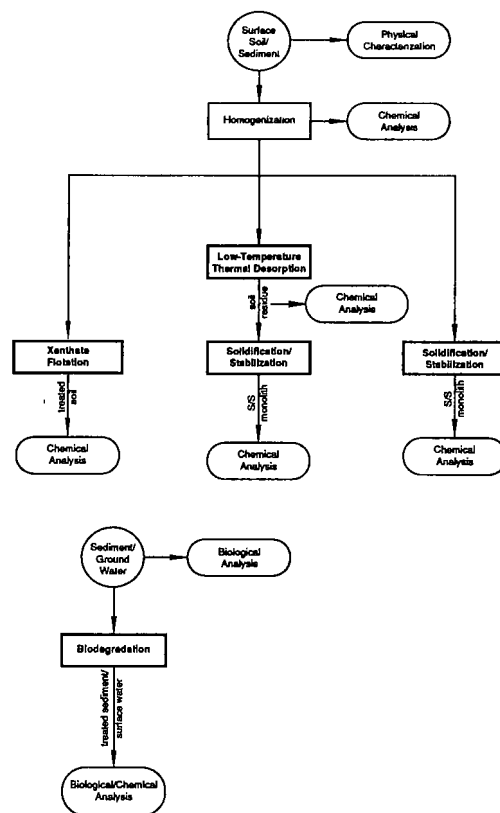
Figure 2
Overview of Treatability Scheme

The low-temperature thermal desorption studies were performed at two temperatures (300° and 500°F) and two residence times (15 and 30 minutes). The VOC, semivolatile and inorganic/metal indicator compounds were measured in the soil residues from all tests. The tests were

conducted using soil that contained high levels of VOCs and semivolatile contaminants.

Table 3
Experimental Plan

	Matrix	Test conditions	No. of repli-cates	Total No. of test runs
Low-temperature thermal desorption	Surface soil/sediment	3 temperatures x 2 residences	2	6
Solidification/stabiliza-tion	Thermal residues	2 binders x 2 mix + ratios + 4 blanks	2	12
Solidification/stabiliza-tion	Surface soil/sediment	1 binder x 2 mix ratios	2	4
Xanthate flotation	Surface soil/sediment	1 reagent + 1 reagent/frother	2	4
Biodegradation	Sediment/ground water composite	2 treatments + 2 controls	2	8

The solidification/stabilization studies were performed on thermally-pretreated soils from the low-temperature thermal desorption (500°F and 30 minutes) test run and on soil samples that were not thermally treated. For the thermally-pretreated soils, two binders (asphalt and portland cement Type II) were evaluated each at two binder/waste mix ratios (0.25 and 0.4 for cement and 0.5 and 1.0 for asphalt). Asphalt was considered as a binder agent, because an asphalt plant is located near the site. For the previously untreated soils, only cement was evaluated at the same two mix ratios used for the thermally-pretreated soils (i.e., 0.25 and 0.4). The starting materials and the stabilized products were subjected to leach testing using the U.S. EPA's TCLP test

and the extracts were analyzed for the metal indicator compounds. In addition, unconfined compressive strength tests were run on the stabilized products.

Xanthates are the reaction products of carbon disulfide and alcohol and an alkali-metal hydroxide. The initial alcohol/hydroxide reaction forms an alkoxide, which then reacts with carbon disulfide to give the alkali-metal xanthate. Alkali metal xanthate salts are soluble in water and readily decompose in acidic environments to liberate carbon disulfide and the corresponding alcohol. Xanthates are used extensively. in the minerals processing industry as collectors in the selective separation of nonferrous metal sulfide ores from gangue (mixtures of undesirable ores, silicates and non-ore material).

This process exploits a surface chemistry phenomenon, where the xanthate compound selectively coats the metal sulfide particle increasing its hydrophobicity and affinity to gas bubbles. The bubbles lift the metal sulfide particles to the surface where they can be skimmed off and collected in a separate vessel. The degree of flotation accomplished is dependent upon the particular xanthate chosen and the presence of activators, such as cupric sulfate, or depressants, such as cyanide salts. Frothing agents can be added to enhance the life of the bubbles and allow for a more efficient separation.[3] Although this process has been previously used in the mining industry, it has not been previously demonstrated on contaminated soils. Nevertheless, the presence of high concentrations of carbon disulfide in the surface soils and in above ground tanks on-site caused us to consider testing this mining process at the laboratory screening level using a pre-formulated xanthate reagent (potassium amyl xanthate) with a frothing agent (2-ethylhexanol). The soil and the recovered froth would be analyzed for the metal indicator compounds.

Table 4
Summary of Analytical Testing

Parameter	Low-temperature thermal desorption		Solidification/ stabilization		Xanthate flotation		Biological studies	
	Untreated soil	Treated soil	Untreated soil	Treated soil	Untreated soil	Treated soil	Water	Composite
VOCS	2	8						
Semivolatiles	2	8						
Metals	2	8	4[a]	16[a]	2[b]	4[b]		
Other inorganics	2	8						
Biological parameters							2	8
Other parameters	2		4	8			2	8

VOCs	Semivolatiles	Metals	Inorganics	Biological Parameters
Carbon disulfide	Chrysene	Arsenic	Ammonia	TOC (total organic carbon)
Tetrachloroethene	Pyrene	Chromium	Cyanide (total)	Oxygen consumption
Methylene chloride	Fluoranthene	Cobalt		Microbial density
Toluene	Benzo(b)fluoranthene	Copper		Nitrogen (as ammonia)
2-butanone	Benzo(k)fluoranthene			Orthophosphate
	Benzo(a)pyrene	Mercury		pH
		Zinc		

Other parameters

UCS (s/s)
Moisture content (LTTD)
Particle size analysis (LTTD)

[a] TCLP extracts analysis.

[b] Because no visible separation occurred, these analyses were not performed.

The biological studies involved an initial assessment of the biological and chemical characteristics of site soil and groundwater, followed by a series of treatments evaluating the degradative activity of the indigenous microbial population. Microbial growth and oxygen consumption were measured to evaluate the potential for biological treatment of carbon disulfide and ammonium thiocyanate in soils and groundwater.

PROJECT OBJECTIVES

The objective of these treatability studies was to determine the applicability of the four treatment technologies to treat or remove the organic and inorganic indicator compounds in soil. For low-temperature thermal desorption, the specific test objectives were to remove semivolatile organic compounds and those compounds, such as carbon disulfide, ammonia and cyanide/thiocyanate compounds, that may impede the solidification/stabilization process. For biological treatment, the test objectives were to identify and evaluate conditions under which indigenous microorganisms will degrade carbon disulfide and thiocyanate compounds. The test objective for xanthate flotation was to reduce inorganic indicator compounds from soils and the objective for solidification/stabilization was to reduce the leachate concentration of inorganic indicator compounds. Table 5 includes specific target levels for the semivolatile organic indicator compounds for the low-temperature thermal desorption and metal indicator compounds in soils for xanthate flotation. These target levels are based on site-specific human health and environmental risks. Under the solidification/stabilization studies, the preliminary target levels for metals indicator compounds in TCLP leachate is 1 mg/L.

Table 5
Treatment Objectives for Treatability Studies

Indicator compound	Soil[a]	TCLP extract[b], mg/L
Semivolatiles (low-temperature thermal desorption studies)		
Benzo[a]pyrene	8 mg/kg[e]	NA[d]
Chrysene	8 mg/kg[e]	NA
Fluoranthene	8 mg/kg	NA
Benzo(b)fluoranthene	8 mg/kg	NA
Benzo(k)fluoranthene	8 mg/kg	NA
Metals (solidification/stabilization and xanthate flotation)		
Arsenic	50 mg/kg	1
Cobalt	1,000 mg/kg[f]	1
Copper	300 mg/kg	1
Chromium	NS[c]	1
Zinc	260 mg/kg	1
Mercury	1 mg/kg	1
Physical parameters (solidification/stabilization)		
UCS	50 psi[b]	NA

a Based on NOAA-recommended levels for sediments in the marsh area next to the Halby site, except as noted.
b Arbitrarily values set for study.
c NS = Not specified.
d NA = Not applicable.
e Based on 10⁻⁶ human health risk levels.
f Based on preliminary target cleanup levels for human health

EXPERIMENTAL DESIGN AND PROCEDURES

The following discussion summarizes the experimental design and testing procedures, including sample collection and preparation, biological treatment, xanthate flotation, low-temperature thermal desorption treatment and solidification/stabilization studies. A discussion of the analytical results and interpretation follows this section.

Sample Collection and Preparation

Samples of surface soil and sediment were collected at two locations in the process plant area of the Halby Chemical site. These surface soil and sediment samples were combined in a 30-gallon steel drum and used for the low-temperature thermal desorption, solidification/stabilization and xanthate flotation studies. A separate, sterilized container was used to collect the sediment sample for the biological

studies. Groundwater from well SMW-01 was collected in three sterilized, 1-gallon, amber glass jars for the biological treatment study. Prior to groundwater sampling, four well volumes were bailed from the well. In addition to these samples, subsurface soils were collected at two locations in the lagoon area (Fig. 1) in anticipation of performing additional treatability studies.

The sediment and groundwater samples for biological studies were packed in ice and sent to the bioremediation testing laboratory (IT Corporation, Knoxville, Tennessee) for analysis and treatability testing. The 30-gallon drum containing surface soils and sediments was manifested as hazardous waste and shipped to the U.S. EPA T & E facility in Cincinnati, Ohio, for treatability testing. Upon receipt at the T & E facility, the 30-gallon drum was placed in an insulated drum overpack with dry ice for proper storage in the hazardous waste storage area prior to testing.

Soil/sediment samples were withdrawn from the drum using an aluminum scoop and homogenized by hand for 10 minutes in a stainless steel pan under a laboratory hood. Large fragments and debris were removed by hand from the pan during mixing and placed back in the steel drum. The soil was mixed until uniform in color and texture. Homogenized soil used in all the treatability studies was stored in a 5-gallon stainless steel container at 4 °C. Stainless steel spoons were used to transfer the soils from the container to the testing apparatus and appropriate sample containers for analysis.

Biological Studies

Prior to testing, the sediment and groundwater samples were stored at 4 °C. Water samples were taken by pipette. Sediment samples were homogenized and pulverized with a mortar and pestle, with large-sized particles removed by sieve.

The biological studies involved an initial biological characterization step followed by a series of treatment test runs. Under the biological characterization step, the sediment and groundwater were tested for the following parameters:

- Microbial enumeration of heterotrophic bacteria, as well as specific thiocyanate- and carbon disulfide-degrading bacteria
- Nutrient analysis for nitrogen (as ammonia) and orthophosphate compounds in groundwater and lagoon sediment
- Ph of soil and groundwater
- Total organic carbon (TOC) in groundwater

Under the treatment test runs, a composite sample consisting of 1 part sediment and 10 parts groundwater (by volume) was subjected to one of four treatments:

- Treatment 1 (nutrients and oxygen) -- Restore™ 375 brand microbialnutrients (1000 mg/L) were added to the treatment vessel. The head space, which constituted 50% of the total volume, was filled with air.
- Treatment 2 (oxygen only) -- No nutrients were added; the head space was filled with air.
- Treatment 3 (nutrients only) -- 1000 mg/L of Restore™ 375 brand nutrients were added; the head space ambient air was purged and replaced with helium.
- Treatment 4 (biologically inhibited) -- 100 mg/L mercuric chloride was added to inhibit all biological activity.

The treatment vessels were sealed with Teflon® -lined silicon septa. Sulfide and thiocyanate compounds were added to the composite treatment runs. Oxygen levels were measured at frequent intervals for a period of 14 days by taking 50 μl of head space gas with a gas-tight syringe and injecting the gas sample into a quantitative oxygen sensor. Injections of air were also made at each sampling point. Microbial growth was also monitored at the start and finish of the two-week period.

Xanthate Flotation

Soil was homogenized and a portion was sampled for analysis of the metal indicator compounds. The homogenized soil was then mixed with deionized water and potassium amyl xanthate in a 4-liter glass beaker. A frothing agent, 2-ethylhexanol, was added to the beaker. The mix-

ture was stirred and air was bubbled through to facilitate flotation of the insoluble metal sulfides present. Figure 3 illustrates the xanthate flotation process evaluated in the study. The froth was then skimmed from the surface and collected in sample containers for analysis of metal indicator compounds. The liquid was decanted and the remaining soils were collected for analysis of metal indicator compounds.
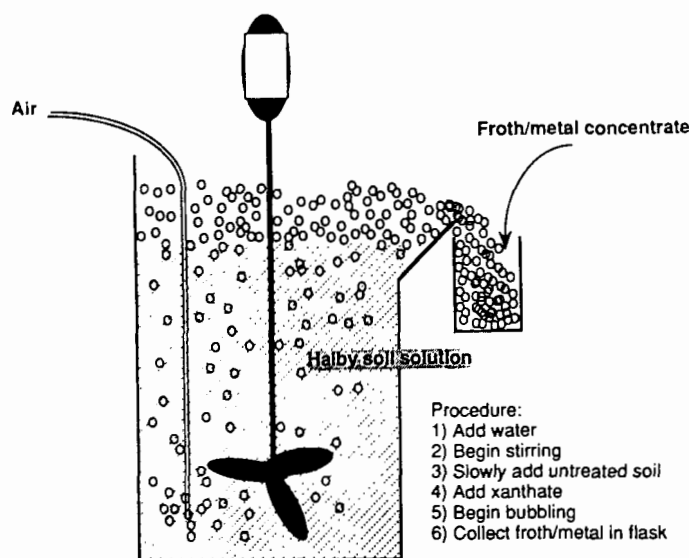
Figure 3
Xanthate Flotation

Low-Temperature Thermal Desorption

Thermal treatment of homogenized soils was performed by placing approximately 800 g of soil in a 4-liter reaction flask with a stirring paddle and heating indirectly and gradually until the soils reached the target temperature (300 °F or 500 °F). Figure 4 illustrates the testing apparatus used in the study. The soil was then heated at that temperature (± 7%) for 15 or 30 minutes. The reactor vessel was continuously purged with nitrogen gas to reduce the possibility of fire or explosion. After completion of the test run, the heating mantle was turned off and the sample allowed to cool to ambient temperatures, prior to transferring the solid residue to sample containers for analysis. Eight samples (two temperatures x two reaction times x two replicate runs) were generated at the end of the experiments. To prepare samples of thermally-treated soil for solidification/stabilization, additional 800-g soil samples were heated at 500 °F for 30 minutes. The evolved gases from the 500 °F and 30 minute test runs were condensed in a cold-finger condenser, collected in a 1-liter volumetric flask and composited for analysis of the indicator compounds.

Solidification/Stabilization

Portland cement Type II was added to the thermally-pretreated and untreated soil samples at binder/waste mix ratios of 0.25 and 0.4 (by weight). Sufficient water (approximately 25% by weight of total solids) was added to the mixtures to pass the slump test. In the case of the thermally-pretreated soils, petroleum-based asphalt was pre-heated to approximately 140 °C and soils were heated to 60 °C and then added at binder/soil mix ratios of 0.5 and 1.0 (by weight). In addition, blank samples were prepared by mixing clean sand and the binder (cement or asphalt) at the above mix ratios. The mixtures were poured into rigid plastic molds and allowed to cure in zip-lock storage bags for a minimum of 14 days. A total of 12 stabilized products (two binders x two mix ratios x two replicates + four blanks) for the thermally treated soils and 4 stabilized products (one binder x two mix ratios x two replicates) for the untreated soils were generated and subjected to unconfined compressive strength and TCLP tests for metal indicator compounds.
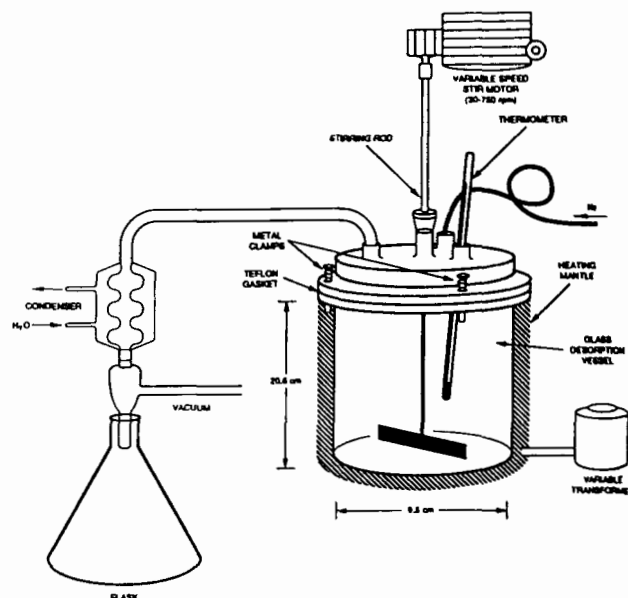
Figure 4
Diagram of Desorption Vessel

RESULTS AND DISCUSSION

The following paragraphs summarize the analytical results and discussions for each of the four treatment technologies. Overall conclusions concerning the applicability of these technologies for remediation of the soils are presented in the following section.

Biological Studies

The initial biological characterization produced the following results (Tables 6 to 9):

- Ph of the groundwater is within acceptable range for bioremediation and the soils are only slightly acidic
- Groundwater is deficient in orthophosphate
- Aerobic carbon disulfide and thiocyanate degraders were present in sediment samples; however, the microbial population in groundwater is low. Aerobic thiocyanate) and carbon disulfide-degrading microbes comprised approximately 10% of the total aerobic microbial population found in the sediment and water
- Anaerobic carbon disulfide degraders were detected in sediment and groundwater. A relatively high concentration of anaerobic carbon disulfide degraders was found in the sediment sample. No anaerobic thiocyanate degraders were observed in sediment or groundwater
- Metabolic activity and microbial growth were observed on the organic carbon contained in the site water samples.

Based on these results, we conclude that site soils contain adequate amount of aerobic and anaerobic carbon disulfide degraders and aerobic thiocyanate degraders. Site groundwater contains lower levels of both aerobic and anaerobic carbon disulfide degraders, but little or no thiocyanate degraders.

The results from the four treatment runs are shown in Table 10 and Figure 5. The results of these experiments indicate that addition stimulates the growth and metabolism of carbon disulfide- and thiocyanate-degrading microbes (Treatments 1 and 2). A deficiency of s appears to inhibit the growth of thiocyanate degraders, only (Treatment 2). The results for microbial population density in Treatment 3 are not valid because of a leak in the treatment vessel that introduced oxygen to the system. The presence of oxygen in Treatment 3 probably inhibited the growth of anaerobic microbes. The increased population density of heterotrophs and carbon disulfide degraders observed in the killed control treatment (Treatment 4) may be indicative of the presence of mercury-resistant organisms. Based on these results, thiocyanate degraders appear to be able to grow only in the presence of oxygen and nutrients; carbon disulfide degraders are able to grow under aerobic conditions with or without nutrients.

Table 6
Inorganic Nutrient Concentration and pH of Site Samples

Sample	Orthophosphate, ppm	Ammonia, ppm	pH
Sediment	190	49	5.9
Water-1	<DL	201	6.5
Water-2	<DL	196	6.3
Water-3	<DL	191	6.3
Water-4	<DL	211	6.3

Table 7
Total Dissolved Carbon Content of Site Groundwater Samples

Sample	Total carbon, μg/mL	Total inorganic carbon, μg/mL	Total organic carbon, μg/mL
Water-1	436	184	252
Water-2	465	210	255
Water-3	471	213	257
Water-4	468	210	260

Table 8
Aerobic Microbial Enumeration[a]

Sample	Heterotrophs	Thiocyanate degraders	CS_2 degraders
Sediment	290,000	28,000	26,000
Water-1	180	Not detected	40
Water-2	1,000	Not detected	60
Water-3	70	Not detected	80
Water-4	130	Not detected	170

[a] Data recorded as colony-forming units per milliliter of water or gram dry weight sediment.

Table 9
Anaerobic Microbial Enumerations[a]

Sample	Heterotrophs	Thiocyanate degraders	CS_2 degraders
Sediment	40,000	Not detected	75,000
Water-1	140	Not detected	Not detected
Water-2	1,300	Not detected	120
Water-3	430	Not detected	220
Water-4	290	Not detected	120

[a] Data recorded as colony-forming units per milliliter groundwater or gram dry weight sediment.

Table 10
Microbial Enumerations for the Investigation of Biological Activity in Sediment and Groundwater Slurries

Sample	Heterotrophs	Thiocyanate degraders	CS_2 degraders
Initial (feasibility)	4.4×10^5	4.2×10^4	4×10^4
Nutrients + O_2 (Treatment 1)	1.8×10^8	1.6×10^8	2.5×10^7
O_2 (Treatment 2)	1.7×10^8	3.1×10^5	7.5×10^8
Anaerobic (Treatment 3)	5.5×10^7	1×10^5	5.2×10^8
Biological-inhibited (Treatment 4)	9.5×10^7	2×10^4	8.5×10^8

[a] Data are presented as colony-forming units per milliliter of slurry; treatments are described in the text.

Xanthate Flotation

Although several attempts were made to encourage long-lasting frothing action, no significant froth was observed and, therefore, no apparent separation of metal particles from the soil. Consequently, no chemical analysis was performed on the treated and untreated soils.

The negative results from the study may have occurred as a result of one or several of the following factors:

- Inadequate equipment for mixing and bubbling action
- Too great a liquid to solids mix ratio
- Presence of too little (or no) metal sulfide particles in the soil for flotation
- Too small particle size or too little xanthate reagent to effect reaction between xanthate and metal particle
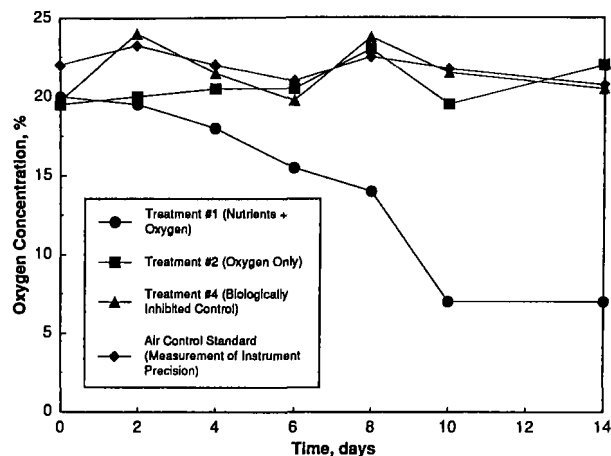
Figure 5
Oxygen Consumption Data by Water-Sediment Slurries. Air Control is a Standard Obtained by Quantifying the Oxygen Content in Air at Each Sampling Point

Further jar studies may be necessary in order to determine whether the flotation process did not work as a result of the equipment and experimental design or because of a lack of chemical reaction between the xanthates and metals in soils. While we assumed that metals in the soil were present in a sulfide form on the basis of site operating history, they may actually be in other forms.

Low-Temperature Thermal Desorption

Table 11 and Figures 6 through 8 give a comparison of contaminant concentrations in untreated and thermally-pretreated soils. Together, these table and figures illustrate several findings:

- The concentrations of volatile and semivolatile organic compounds and total cyanide decreased significantly after thermal treatment at 500 °F for 30 minutes
- The concentration of metals and inorganic compounds remained fairly constant (concentrations varied within normal range of variability expected for analyses) in the soils throughout the thermal studies

The apparent increase of certain VOCs (i.e., toluene, methylene chloride and 2-butanone) after thermal treatment at 300°F may be the result of high moisture content of the raw soils, which reduced the analytical recovery and quantitation of these soluble compounds. The low percent recoveries (30 to 40%) of these VOC compounds in the matrix spike samples of the raw soils give some support for this theory. Other possible explanations for the apparent increase in VOC concentrations may be degradation of other organic compounds during thermal treatment.

In addition to analyses of soils, condensate collected in the flask from the 500°F and 30 minute test runs was composited and analyzed for the organic and inorganic indicator compounds. The analytical data indicated that semivolatile and metals are present at or below their solubility limits and that most VOCs are not present above detectable levels. The absence of VOCs in the collected condensate may have been due to the fact that noncondensable vapors and some of the condensate were drawn through a vacuum line that was located below the condenser. Therefore, it is expected that the VOC concentrations in the off-gases from low-temperature thermal desorption will actually be much higher than indicated in these analyses.

Solidification/Stabilization

Table 12 and Figure 9 give the results of TCLP leachate analysis for metals from cement-based solidification/stabilization of thermally-pretreated soils (500°F and 30 minutes runs) and untreated soils. Table 13 and Figures 9 and 10 present the TCLP leachate data for metals from cement- and asphalt-based solidification/stabilization of the thermally-pretreated soils. From these tables and figures, the following conclusions can be made:

- TCLP leachate concentrations of arsenic, chromium and mercury from the thermally-pretreated soils and untreated soils are well below the TCLP regulatory levels that are used to classify wastes as characteristically hazardous (40 CFR Part 261.24). In addition, for these unsolidified soil samples, leachate concentrations of all metal indicator compounds are at or below the treatment target level of 1 mg/L.
- Although leachate concentrations are low, those for arsenic and copper are significantly reduced by asphalt binder at both mix ratios; the cement binder did not perform as well as the asphalt and in the case of arsenic and copper, it resulted in increased concentrations.
- Both the asphalt and cement binders significantly reduced concentrations of zinc in the leachate.
- Increased chromium concentrations observed in leachate from cement-based products may have resulted from chromium in either the portland cement material or the tap water used during the mixing process, since the levels are comparable to those found for the two blank samples. Chromium is generally known to leach more readily under basic conditions such as those created by the cement process. Chromium is present at levels near or below detection limits in the leachate from the asphalt-based products.
- Leachate levels of the metal indicator compounds are similar for the cement-based products of thermally-pretreated soil and untreated soils.

As shown in Table 11, the moderate to high concentrations of metals (between 200 and 150 mg/kg) present in the thermally-pretreated and untreated soils apparently do not readily leach in appreciable amounts under TCLP test conditions. Leachate concentrations of these metals may be much greater, however, in multiple extraction tests or other leach tests that are designed to address long-term leaching rate over time. The need for solidification/stabilization of soils should be investigated by conducting additional leach testing of the soils.

While the asphalt appears to be the better binder of the two studied for arsenic and copper, the lower leachate levels reported for the asphalt-based products may be partially due to higher dilution by asphalt than by cement (i.e., higher binder to soil mix ratios). In addition, several issues should be evaluated further prior to selecting asphalt as the solidifying/stabilizing agent for previously untreated soils: (1) need for dewatering of the soils prior to mixing, (2) potential VOC emissions during mixing and (3) potential leaching of volatile and semivolatile organic compounds. Therefore, additional feasibility analyses and bench-scale studies may be warranted to evaluate these issues, if solidification/stabilization is deemed necessary for reduction of metals leaching from soils to surface and ground waters.

CONCLUSIONS AND RECOMMENDATIONS

Based on these preliminary studies, the following overall conclusions are drawn:

- Bacteria capable of degrading carbon disulfide and thiocyanate are present in the soils under aerobic conditions with sufficient nutrient supply. The presence, growth and metabolism of aerobic carbon disulfide and thiocyanate degraders suggests the possibility of using an above ground bioreactor treatment system.
- Xanthate flotation/separation of heavy metals from soils was not successful under the limited experimental conditions tested.
- While low-temperature thermal desorption at temperatures between 300° and 500°F and between 15 and 30 minutes residence time can successfully remove VOCs and semivolatile organic compounds from soils, it may not be needed as a pretreatment step prior to solidification/stabilization.
- The soils, themselves, do not leach metals at appreciable levels under TCLP test conditions. However, among the two binders tested, asphalt binder appears to be the much better binder material for reducing

Table 11
Analytical Results for Untreated (Raw) and LTTD Treated Soil Samples

Sample	NH3	As	Cr	Co	Cu	CN	Zn	2-But	CS2	MeCl	TCE	Tol	Chry	Pyr	Fluor	B(b)F	B(k)F	B(a)P	Percent moisture
Untreated (raw) soil samples	116	217	NA	11.0	285	41.0	1380	ND(10)	ND(5)	21	180	370	4800	7100	7800	4500	1600	1900	20.1
A	115	248	NA	11.7	328	32.6	1230	ND	ND	24	150	150	3500	8300	7900	3800	1900	1700	20.8
B	115	232	NA	11.3	306	36.8	1305	ND	ND	22	165	260	4150	7700	7850	4150	1750	1800	20.4
Average																			
LTTD treated soil samples (300°F, 15 min)	196	288	317	19	377	16.0	1410	190	17	180	5	160	2200	1400	3700	2500	1300	ND(660)	0.05
A	195	283	310	19	406	22.8	1580	220	22	190	7	140	2400	2400	4600	3000	1500	ND	0.21
B	195	285	313	19	391	19.4	1495	205	19	185	6	150	2300	1900	4150	2750	1400	ND	0.13
Average																			
LTTD treated soil samples (300°F, 30 min)	196	344	297	17.1	351	37.4	1130	300	23	110	8	130	3200	5000	6400	4000	1800	910	0.24
A	185	322	308	17.5	398	43.5	1490	220	7	46	6	60	4900	ND(660)	ND(660)	ND(660)	ND(660)	2700	0.45
B	190	333	302	17.3	374	40.4	1310	260	15	78	7	95	4050	<2830	<3530	<2330	<1230	1805	0.34
Average																			
LTTD treated soil samples (500°F, 15 min)	275	349	272	17.9	390	6.26	1480	29	10	310	6	170	ND(660)	ND(660)	ND(660)	ND(660)	ND(660)	ND(660)	0.09
A	287	300	234	16.0	379	6.19	1600	89	6	200	5	140	ND	ND	ND	ND	ND	ND	0.05
B	281	324	253	16.9	384	6.22	1540	59	8	255	5	155	ND	ND	ND	ND	ND	ND	0.07
Average																			
LTTD treated soil samples (500°F, 30 min)	224	316	255	17.8	363	6.71	1180	15	ND(5)	79[f]	5	5	ND(660)	ND(660)	ND(660)	ND(660)	ND(660)	ND(660)	0.25
A	286	313	274	17.7	370	9.30	1330	43	10	680	5	62	ND	ND	ND	ND	ND	ND	0.10
B	255	314	264	17.7	366	8.00	1255	29	<7	379	5	33	ND	ND	ND	ND	ND	ND	0.17
Average																			

[a] 2-But = 2-Butanone; CS2 = Carbon disulfide; MeCl = Methylene chloride; TCE = Tetrachloroethene; Tol = Toluene

[b] Chry = Chrysene; Pyr = Pyrene; Fluor = Fluoranthene; B(b)P = Benzo(b)fluoranthene; B(k)P = Benzo(k)fluoranthene; B(a)P = Benzo(a)fluoranthene

[c] NA = not analyzed.

[d] ND = not detected.

[e] numbers in parentheses are the method detection limits.

[f] number is considered as an outlier

leachate concentrations of the metal indicator compounds, although dilution of soils by the binder was not taken into account. Additional feasibility and treatability studies are needed if solidification/stabilization is deemed necessary to reduce metal leaching from soils to surface and groundwater.
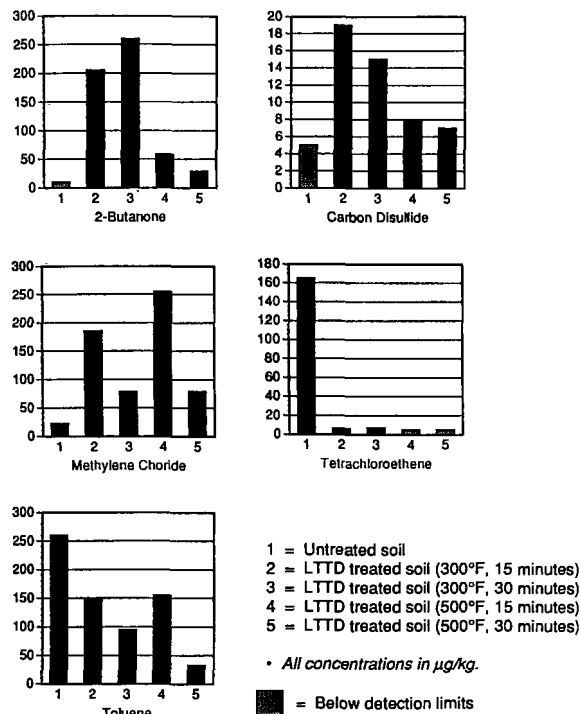
Figure 6
Effectiveness of LTTD Process in Removal
of Volatiles from Soil Samples

1 = Untreated soil
2 = LTTD treated soil (300°F, 15 minutes)
3 = LTTD treated soil (300°F, 30 minutes)
4 = LTTD treated soil (500°F, 15 minutes)
5 = LTTD treated soil (500°F, 30 minutes)

• All concentrations in µg/kg.

▓ = Below detection limits
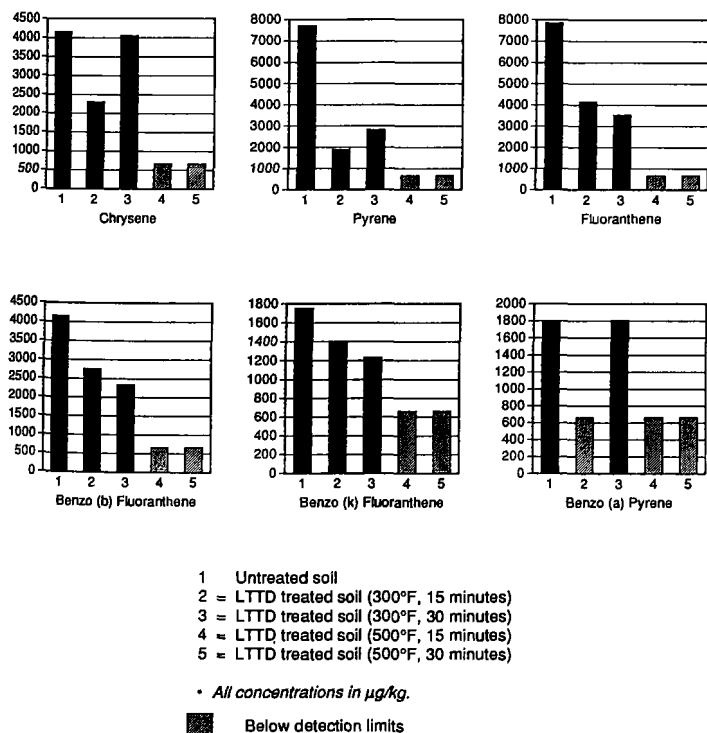
Figure 7
Effectiveness of LTTD Process in Removal
of Semivolatiles from Soil Samples

1 = Untreated soil
2 = LTTD treated soil (300°F, 15 minutes)
3 = LTTD treated soil (300°F, 30 minutes)
4 = LTTD treated soil (500°F, 15 minutes)
5 = LTTD treated soil (500°F, 30 minutes)

• All concentrations in µg/kg.

▓ Below detection limits

1 = Untreated soil
2 = LTTD treated soil (300°F, 15 minutes)
3 = LTTD treated soil (300°F, 30 minutes)
4 = LTTD treated soil (500°F, 15 minutes)
5 = LTTD treated soil (500°F, 30 minutes)

• All concentrations in µg/g.

Figure 8
Effectiveness of LTTD Process in Removal
of Various Inorganics from Soil Samples

Table 12
Results of TCLP Leachate Analysis for Untreated (Raw), Treated and Cement-based Solidified Soil Samples
(mg/L)

Type of sample	Arsenic	Chromium	Cobalt	Copper	Mercury	Zinc
Untreated (raw) soil						
A	0.0131	ND[a] (0.003)[b]	ND (0.03)	0.201	ND (0.0001)	1.62
B	0.0141	ND	ND	0.187	ND	1.51
Average	0.0136	ND	ND	0.194	ND	1.56
LTTD treated soil (500°F, 30 min)						
A	0.0281	ND (0.003)	0.044	0.400	ND (0.0001)	6.10
B	0.0331	ND	0.060	0.419	ND	8.05
Average	0.0306	ND	0.052	0.409	ND	7.07
Solidified raw soil (B/S = 0.25)						
A	0.0515	0.213	ND (0.03)	0.846	ND (0.0001)	ND (0.02)
B	0.0455	0.204	ND	0.814	ND	ND
Average	0.0485	0.208	ND	0.830	ND	ND
Solidified raw soil (B/S = 0.40)						
A	0.0295	0.115	ND (0.03)	0.071	ND (0.0001)	ND (0.02)
B	0.0285	0.123	ND	0.077	ND	ND
Average	0.0290	0.119	ND	0.074	ND	ND
Solidified LTTD treated soil (B/S = 0.29)						
A	0.0741	0.132	ND (0.03)	0.037	ND (0.0001)	ND (0.02)
B	0.0701	0.121	ND	0.025	ND	ND
Average	0.0721	0.126	ND	0.031	ND	ND
Solidified LTTD treated soil (B/S = 0.40)						
A	0.0131	0.17	ND (0.03)	0.440	ND (0.0001)	ND (0.02)
B	0.0121	0.14	ND	0.371	ND	ND
Average	0.0126	0.15	ND	0.405	ND	ND
Solidified blank soil (B/S = 0.25)						
A	0.0071	0.142	ND (0.03)	ND (0.005)	ND (0.0001)	ND (0.02)
Average	0.0071	0.142	ND	ND	ND	ND
Solidified blank soil (B/S = 0.40)						
A	0.0081	0.141	ND (0.03)	ND (0.005)	ND (0.0001)	ND (0.02)
Average	0.0081	0.141	ND	ND	ND	ND

[a] ND = Not detected.
[b] Numbers in parentheses are the method detection limits.

The following additional studies are recommended prior to selecting a final remedy for soils at the Halby Chemical site:

• Conduct a full-scale microbial treatability study to confirm initial findings from this study and to select the treatment scenario best suited to the site conditions and cleanup goals.
• Further xanthate floating laboratory studies examining the effects of: (1) mixing speeds, (2) particle size, (3) water to solids mix ratio,

(4) xanthate flotation agent and concentration and (5) frother concentration/bubbler flow speeds.

- Additional TCLP or other leach testing (preferably a multiple waste extraction test or long-term leach study) of soils to adequately determine the need for solidification/stabilization to reduce the leaching of metals from the soils to the surface and groundwaters.
- Upon determining the need for solidification/stabilization of soils, perform feasibility analysis comparing costs for cement-based and asphalt-based solidification/stabilization processes taking into account the need for dewatering prior to using asphalt. Upon determining the more feasible solidification/stabilization process perform additional banch-scale studies evaluating leachate levels of semivolatile and metal indicator compounds and VOC emissions during mixing, at binder to soil mix ratios between 0.5 and 0.25 (for asphalt) or between 0.25 and 0.40 (for cement).

These additional studies could not be performed under the existing scope and budget, but they are needed to build upon data presented in this paper and to help further refine the design, cost and performance for soil treatment alternatives.

Table 13
Results of TCLP Leachate Analysis for
LTTD-Treated and Asphalt-based Solidified Soil Samples
(mg/L)

Type of sample	Arsenic	Chromium	Cobalt	Copper	Mercury	Zinc
LTTD treated soil (500°F, 30 min)						
A	0.0281	ND (0.003)	0.044	0.400	ND (0.0001)	6.10
B	0.0331	ND	0.060	0.419	ND	8.05
Average	0.0306	ND	0.052	0.409	ND	7.07
Solidified LTTD treated soil (B/S = 0.50)						
A	ND (0.005)	0.006	ND (0 03)	0.165	ND (0.0001)	0.553
B	ND	0.008	ND	0.017	ND	0.329
Average	ND	0.007	ND	0.091	ND	0.441
Solidified LTTD treated soil (B/S = 1.00)						
A	ND (0.005)	ND (0.003)	ND (0.03)	0.013	ND (0.0001)	0.546
B	ND	ND	ND	0.015	ND	0.276
Average	ND	ND	ND	0.014	ND	0.411
Solidified blank soil (B/S = 0.50)						
A	ND (0.005)	ND (0.003)	ND (0.025)	ND (0.005)	ND (0.0001)	0.292
Average	ND	ND	ND	ND	ND	0.292
Solidified blank soil (B/S = 1.00)						
A	ND (0.005)	ND (0.003)	ND (0.025)	ND (0.005)	ND (0.0001)	0.335
Average	ND	ND	ND	ND	ND	0.335

ND = Not detected.
Numbers in parentheses are the method detection limits.

ACKNOWLEDGEMENTS

REFERENCES

1. U.S. EPA, Guide for Conducting Treatability Studies Under CERCLA, Interim Final, U.S. EPA, Washington, DC, 1989.
2. PEI Associates, Inc., "Treatability Study Report for Contaminated Soils and Sediments from the Halby Chemical Site, Wilmington, Delaware." Prepared for U.S. EPA, Office of Research and Development under U.S. EPA Contract No. 68-03-3413, Work Assignment No. 2-60, PEI Associates, Inc., Cincinnati, OH, 1990
3. Rao, S.R., Xanthates and Related Compounds. Marcel Dekker, Inc., New York, NY. 1971

1 = Untreated soil
2 = LTTD treated soil (500°F, 30 minutes)
3 = Solidified raw soil (B/S = 0.25)
4 = Solidified raw soil (B/S = 0.40)
5 = Solidified LTTD treated soil (B/S = 0.25)
6 = Solidified LTTD treated soil (B/S = 0.40)
7 = Solidified blank soil (B/S = 0.25)
8 = Solidified blank soil (B/S = 0.40)

• All concentrations in mg/L.

■ = Below detection limits
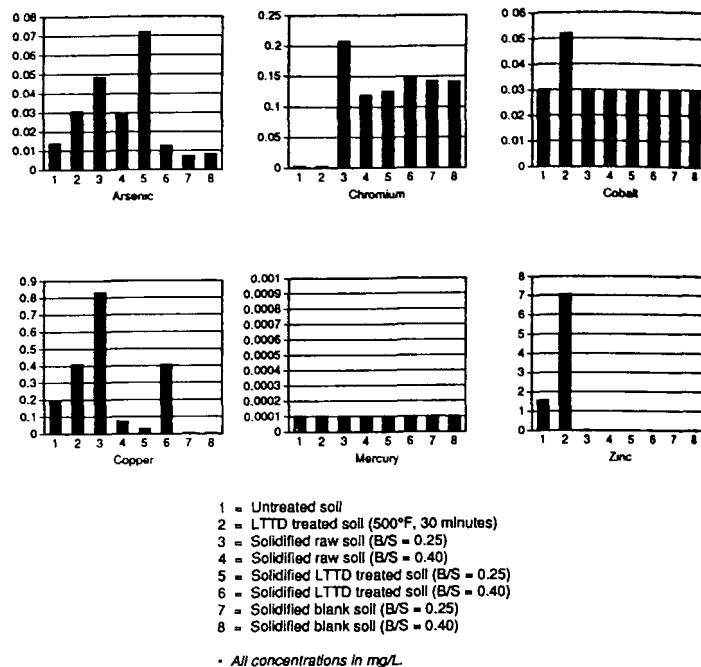
Figure 9
Results of TCLP Leachate Analysis for
Cement-based Solidified Samples

1 = Untreated soil
2 = LTTD treated soil
3 = Solidified LTTD treated soil (B/S = 0.50)
4 = Solidified LTTD treated soil (B/S = 1.00)
5 = Solidified blank soil (B/S = 1.00)
6 = Solidified blank soil (B/S = 0.50)

• All concentrations in mg/L.

■ = Below detection limits
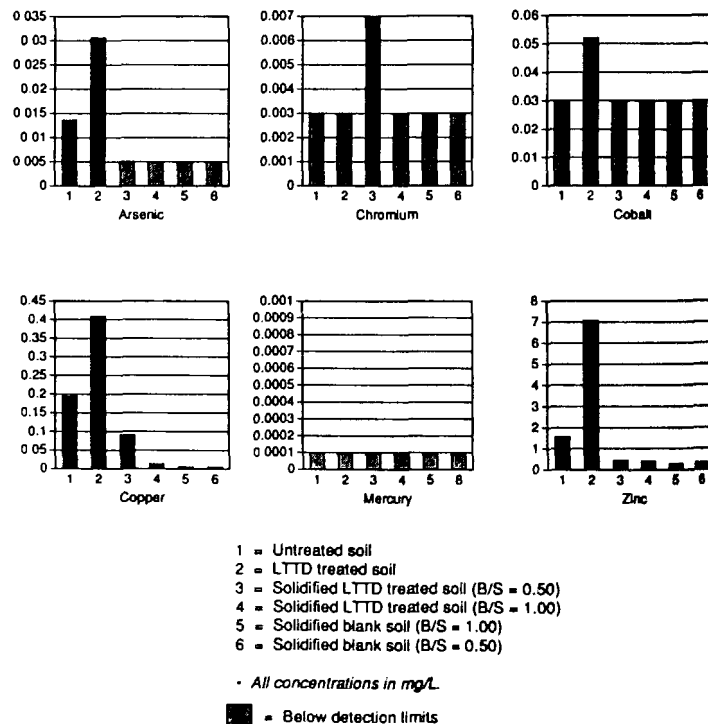
Figure 10
Results of TCLP Leachate Analysis for Asphalt-base Solidified Samples

Acid Extraction and Chemical Fixation of Metal—Contaminated Soil

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ABSTRACT

A detailed bench-scale treatability study of acid extraction and chemical fixation was conducted on the metal-contaminated (cadmium, nickel and cobalt) soil at the former battery plant grounds of Marathon Battery Company Superfund Site situated in the Village of Cold Spring, New York. For acid extraction, five variables, including leaching solvent, pH, soil concentration, contact time and number of extraction stages, were studied. In addition, other related treatment processes, including base recovery, settling and dewatering, also were studied. For chemical fixation, a proprietary reagent consisting of Portland cement, silicate and other additives was used. The most optimum reagent ratio was determined through a screening procedure. TCLP and MEP were performed on the chemically-fixated soils to determine the leachability and persistence. The objective of this paper is to present the treatability study results so that the findings and conclusions can be used to support the remediation of other Superfund or hazardous waste sites with similar contamination.

INTRODUCTION

As part of the RI/FS performed on the former battery plant grounds portion of the Marathon Battery Company Superfund Site, acid extraction and chemical fixation were evaluated for the remediation of the metal-contaminated soils.[1,2] Extensive bench-scale tests were designed and conducted to confirm the applicability and treatability of these two remedial technologies. This paper presents the treatability test methods and results. It is hoped that the findings and conclusions presented in this paper can be used to support the remediation of other Superfund or hazardous waste sites with similar contamination.

BACKGROUND

The Marathon Battery Company site, situated in the Village of Cold Spring, Putnam County, New York, is located across the Hudson River and slightly north from the United States Military Academy at West Point. The site is approximately 40 miles north of New York City. The Marathon Battery Company site is comprised of three study areas: Area I, which consists of East Foundry Cover March and Constitution Marsh; Area II, which encompasses a former batter manufacturing facility, its grounds and the adjacent residential yards; and Area III, which includes East and West Foundry Coves and the Hudson River in the vicinity of the Cold Spring pier (Fig. 1).

EXTENT OF CONTAMINATION

Cadmium, nickel, and cobalt, contamination have been detected in the sediments (Areas I and III) and soils (Area II) in all three areas.[1-8] The source of the contamination is the former Ni-Cd battery manufacturing plant (located in Area II) which operated from 1952-1979.

The measured concentrations of Cd, Ni and Co in the Area II soils are 10 to 5,580 mg/kg, 26 to 2,046 mg/kg and 7 to 161 mg/kg, respectively. Only the surface soils, i.e., upper 2 to 3 ft, are contaminated with these heavy metals. Generally, the soil which is closest to the surface has the highest metal concentrations. The concentration distribution patterns of these metals are very similar. Based on the results of a risk assessment[1] and the recommendation of the Agency for Toxic Substances and Disease Registry, a Cd cleanup level of 20 mg/kg was selected for the site (while Ni and Co contamination are also present, Cd was used in the analysis since it is the most toxic of the three metals). Employing the 20 mg/kg cadmium remediation level, the total volume of metal-contaminated soil requiring remediation was estimated to be 5,250 yd³.
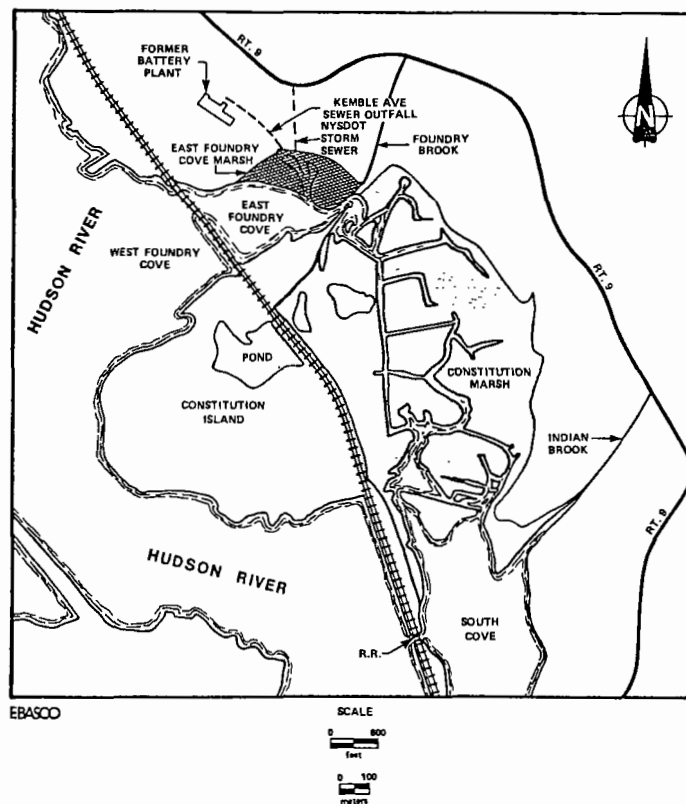
Figure 1
Marathon Battery Site
East Foundry Cove Marsh and Constitution Marsh

TCLP tests were conducted on the soil samples with cadmium concentrations ranging from 114 to 5,580 mg/kg.[1] The results indicate that cadmium concentrations ranging from 3.9 to 97.6 mg/L in the extracts exceed the regulatory limit of 1.0 mg/L. Therefore, the cadmium-contaminated soil at the former battery plant grounds may be considered hazardous under the RCRA. There are no TCLP limits for nickel and cobalt.

TREATABILITY TEST METHODS

Both acid extraction and chemical fixation bench-scale tests were conducted in a U.S. EPA mobile laboratory located on the former battery plant grounds. Acid extraction tests were performed by Ebasco Services Incorporated (Ebasco) and the liquid and solid samples generated during the tests were analyzed by Hittman-Ebasco Associates Incorporated (HEAI). Chemical fixation tests were performed in the on-site laboratory by Chemfix Technologies, Inc. (Chemfix) and the fixated soil samples were shipped to an off-site Chemfix laboratory for further testing and analysis. For conducting these bench-scale tests, a total of approximately 4.0 kg of soil were collected from the area showing the highest levels of Cd, Ni and Co contamination. In order to determine the metal concentrations in the collected soil, 20 samples were taken and analyzed for Cd, Ni and Co. The results indicate that the concentration ranges for Cd, Ni and Co are 856 to 2,873 mg/kg, 585 to 1,829 mg/kg and 40.3 to 84.2 mg/kg, respectively and their corresponding average concentrations are 1,420 mg/kg, 1,060 mg/kg and 52.4 mg/kg, respectively. These results also show that the metal concentrations are quite variable in the soil and therefore, for the acid extraction tests, metal concentrations must be determined for both liquid and solid phases in order to make an accurate evaluation of the effectiveness of this treatment process.

Acid Extraction Test

Acids have often very successfully extracted and recovered metals. The primary purpose of this bench-scale treatability test was to identify an acid which could effectively extract the metals from the contaminated soil so that the metal residual concentrations in the soil would meet the remediation level.

Several variables can affect the amount of metals extracted from a given contaminated soil. For this test, the following five major variables were selected to determine their effects on acid extraction:

- Leaching Solvent: Six leaching solvents were evaluated (i.e., hydrochloric acid, sulfuric acid, nitric acid (HNO_3) and three mixed solutions of sulfuric acid and ferric sulfate designated as M1, M2 and M3 and defined in Table 1).

- pH: Three pH levels were evaluated (i.e., pH of 1, 2 and 3).
- Soil Concentration: Three soil concentrations were evaluated (i.e., 5%, 10% and 15% by weight).
- Contact Time: Six contact times were evaluated (i.e., 1, 2, 4, 12, 24 and 48 hours).
- Number of Extraction Stages: Six extraction stages were evaluated.

Table 1 summarizes the testing conditions used to evaluate the effects of the aforementioned variables on the effectiveness of acid extraction. As indicated in the table, when one variable was evaluated, the other variables were held at preset constant conditions.

Each acid extraction test was carried out by simply mixing a leaching solvent with the metal-contaminated soil at the preset testing conditions of pH, soil concentration, contact time and number of extraction stages (Table 1). The mixing continued until the specified contact time was reached and the mixture was then separated into liquid and solid phases by vacuum filtration. Samples were taken from both the filtrate and filtered solids for analyses to determine the mass distributions of Cd, Ni and Co in the liquid and solid phases. The percentage of a metal extracted from the soil was be calculated by the following equation:

$$\text{Percent Metal Extracted } (\%) = \frac{MML}{(MML + MMS)} \times 100\% \quad (1)$$

where: MML = Metal Mass in the Liquid Phase (or leaching solvent)
MMS = Metal Mass in the Solid Phase (or soil)

For the cases of multiple stages of extraction, no samples were taken from the solid phases during intermediate stages. In addition, fresh leaching solvent was used at each stage of the multiple stages of extraction.

As a part of the acid extraction treatability test, a base recovery test was conducted to examine the possibility of recovering the metals from the spent leaching solvents through precipitation at higher pH levels. Sodium hydroxide was used to raise the pH and three pH levels, i.e., 7, 9 and 11, were evaluated by running a jar test. In addition, zone settling rate tests and Buchner Funnel vacuum filtration tests were performed on the metal sludge generated during the base recovery tests to determine the settleability and dewaterability of the metal sludge. The testing procedures for conducting these tests can be easily found elsewhere[9,10] and are not discussed in this paper.

Chemical Fixation Test

The purpose of this bench-scale test was to confirm whether the metals present in the soil could be chemically stabilized and/or physically encapsulated in the soil so that the metal-contaminated soil could be transformed into a material which:

- Would not exceed maximum allowable concentration in sample leachate when subjected to the RCRA TCLP
- Would satisfy the Multiple Extraction Procedure (MEP) which has been used to estimate the long-term stability of chemically fixated soil under conditions simulating 1,000 years of acid rain

If successful, the metal-contaminated soil would be considered nonhazardous and suitable for disposal in a nonhazardous waste landfill.

The reagent used by Chemfix to chemically fixate the metal-contaminated soil consisted of Portland cement, silicate and other proprietary additives. The optimum reagent ratio was determined by first running a screening test on ten 100-gram soil samples, each mixed with a different reagent ratio. Unconfined compressive strength (UCS) readings were performed at various time intervals during the curing process of these ten mixtures. Once UCS trends were established, three of the best reagent ratios were selected. New samples of these three selected reagent ratios were made and shipped to an off-site Chemfix laboratory for UCS and TCLP tests. The mixture which passed the TCLP test and yielded the best UCS readings was selected for the MEP test. If the mixture passed the MEP test, the associated reagent ratio would be considered as the optimum one to chemically fixate the metal-contaminated soil. A duplicate soil sample was thus made with the

Table 1
Acid Extraction Bench-Scale Treatability Test
Testing Conditions

Variable Evaluated	Leaching Solvent	pH	Soil Concentration (% by wt.)	Contact Time (Hrs.)	Number of Extraction Stages
Leaching Solvent	HCl, H₂SO₄, HNO₃, M1*, M2* & M3*	1.0	5	1	1
pH	HCl H₂SO₄	1,2 & 3	5	1	1
Soil Concentration	HCl H₂SO₄	1.0	5, 10 & 15	1	1
Contact Time	HCl H₂SO₄	1.0	5	1,2,4, 12, 24 & 48	1
Number of Extraction Stages	HCl H₂SO₄	1.0	5	1**	1,2,3, 4,5&6

Notes:

*
	Leaching Solution	Chemical Composition (in 1.0 liter deionized Water)
	M1	10 gr H₂SO₄ + 50 gr Fe₂(SO₄)₃
	M2	20 gr H₂SO₄ + 10 gr Fe₂(SO₄)₃
	M3	50 gr H₂SO₄ + 2 gr Fe₂(SO₄)₃

** One hour contact time per extraction stage

optimum reagent ratio and it was tested again for UCS, TCLP and MEP to confirm the reproducibility of the results.

TREATABILITY TEST RESULTS

The results of the bench-scale treatability tests of acid extraction and chemical fixation on the metal-contaminated soil are discussed below.

Acid Extraction Test Results

All of the leaching solvents tested achieved greater than 90% extraction of cadmium from the contaminated soil (Table 2). For nickel and cobalt, H_2SO_4, M1, M2 and M3 appear to be more effective than HCl and HNO_3 to leach out these two metals from the contaminated soil. Since cadmium was the most hazardous contaminant among the three metals of concern and since the cleanup requirement for cadmium was the most stringent, the effectiveness in extracting cadmium from the contaminated soil became one of the important factors in selecting a leaching solvent. The other factors considered were chemical cost and number and amount of chemicals used. After evaluation of these factors, HCl and H_2SO_4 were selected and the remaining variables were studied using only HCl and H_2SO_4.

Table 2
Effect of Various Leaching Solvents On
Acid Extraction of Metal-Contaminated Soil

Leaching Solvent	Percentage of Metal Extracted, %**		
	Cadmium	Nickel	Cobalt
HCl	92.8	63.8	59.9
H_2SO_4	91.0	81.0	74.3
HNO_3	91.5	68.4	56.1
M1*	90.9	82.9	76.0
M2*	92.5	88.5	83.0
M3*	91.1	82.2	75.8

* See Table 1 for definition.
** Average values of two tests.

The pH levels can significantly affect the effectiveness of a leaching solvent (Fig. 2). A high percentage of metal extraction was achieved when the pH levels were maintained at 1.0 or lower. For HCl, 96.4% Cd, 81.2% Ni and 95.9% Co were extracted from the contaminated soil and for H_2SO_4, 90.3% Cd, 85.6% Ni and 96.3% Co were extracted. It should be mentioned that Figure 2 was plotted based on the final pH levels measured during the tests. For those tests with an initial pH of 3.0, it seemed that the pH levels could not be held at 3.0 throughout the tests.

Under the mixing condition used during testing (i.e., 100 rpm; Phipps and Bird multiple mixer Model No. 7790—300), the effectiveness of the leaching solvents was not affected when soil concentration was up to 10% by weight (Fig. 3). At 15% by weight soil concentration, the percentage of metal extracted was generally decreased. This result could be due to inadequate mixing. Localized soil settlement was observed during the testing of the 15% by weight soil concentration.

Increasing the contact time between soil and the leaching solvents generally increased the amount of metals leached from the contaminated soil (Fig. 4). After 12 hours of contact, no significant increase in metals leached from the soil was observed. After 12 hours of contact, approximately 96% Cd, 93% Ni and 87% Co were extracted from the soil.

Increasing the number of successive extraction stages increased the amount of metals being leached from the contaminated soil (Fig. 5). After three successive extraction stages, no significant increase in metals leached from soil was observed. Approximately 95% Cd, 83% Ni and 78% Co were leached from the soil after three successive extraction stages.

By combining the optimum conditions of the tested variables, it is estimated that at least 94% Cd, 84% Ni and 75% Co can be removed
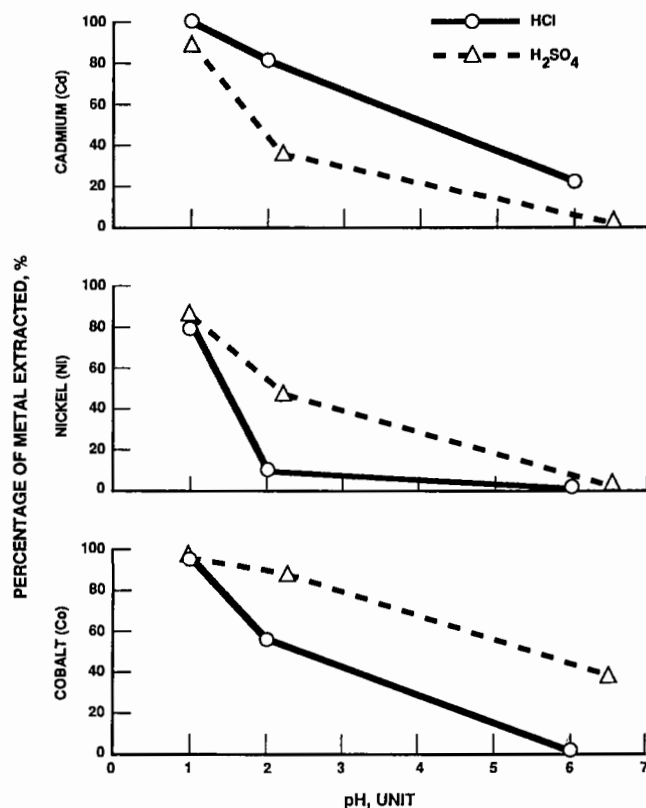
Figure 2
Effect of pH on Acid Extraction of
Metal-Contaminated Soil
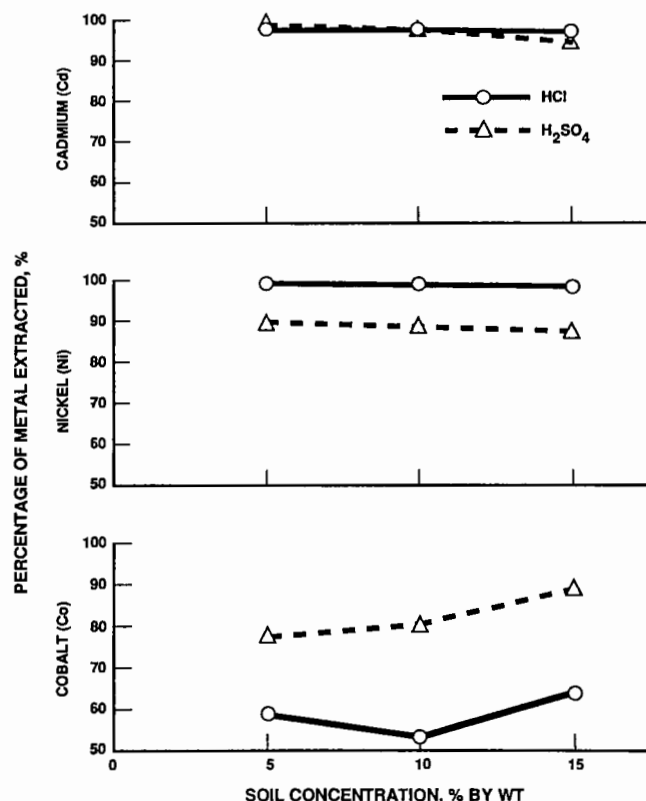
Figure 3
Effect of Soil Concentration on Acid Extraction
of Metal-Contaminated Soil
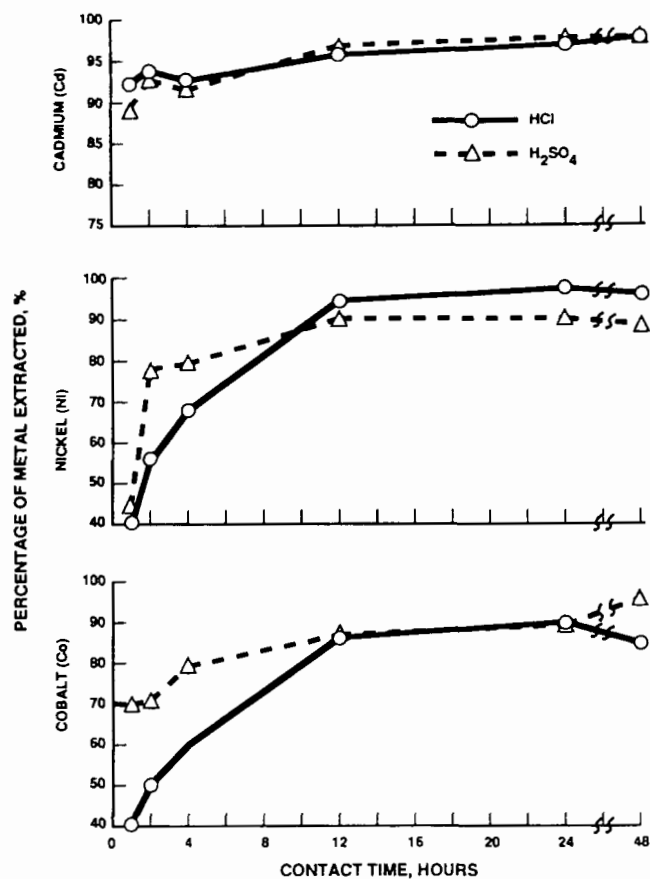
Figure 4
Effect of Contact Time on Acid Extraction
of Metal-Contaminated Soil
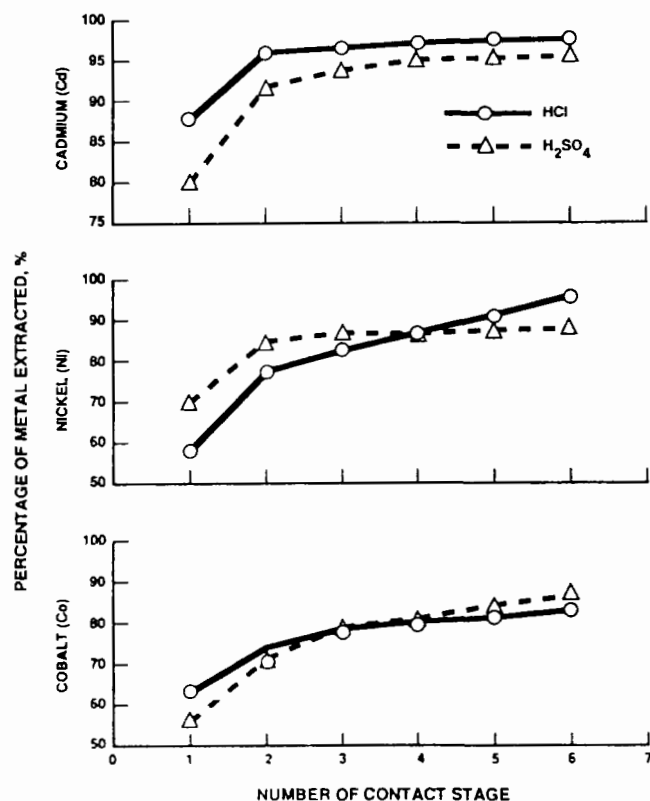
Figure 5
Effect of Number of Contact Stages on Acid Extraction
of Metal-Contaminated Soil
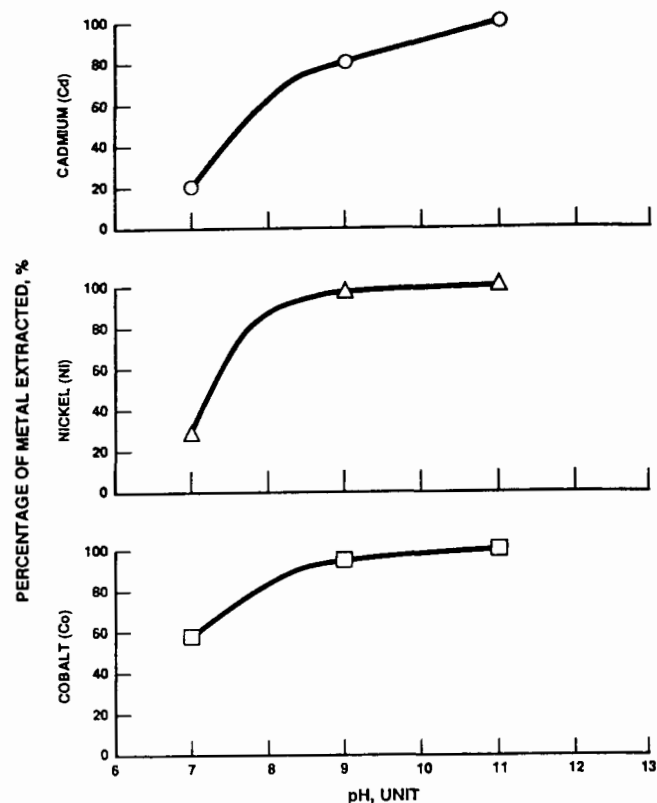
Figure 6
Effect of pH on Metal Removal from
Spent Acid Extraction Solution

from the contaminated soil by using either HCl or H_2SO_4.

Figure 6 indicates that more than 99% of the Cd, Ni and Co in the spent leaching solvents can be removed (or recovered) at pH 11. As the pH level decreased from 11 to 7, the percentage of metal removal decreased. The settling test results indicate that the sludge generated during the base recovery tests was completely settled within 30 minutes. The solids concentration of the settled sludge ranged from 3.4 to 6.3% by weight. The filterability test results indicate that the sludge can be further dewatered by vacuum filtration or the like and the solids concentration can be increased to 15% by weight in the dewatered sludge. The calculated specific resistance is in the range of 10^9 to 10^{10} sec/gr; therefore, chemical additives may be required for assistance during sludge dewatering.

Since the cleanup level for cadmium was 20 mg/kg, the contaminated soil with Cd concentration greater than 330 mg/kg would not be cleaned up to the desired level at the leaching efficiency of 94%. It was estimated that approximately 40% of the metal-contaminated soil had a cadmium concentration greater than 330 mg/kg. Thus, additional treatment may be needed for that volume of the metal-contaminated soil. Therefore, based on the above treatability test results, acid extraction was determined not to be a viable remedial technology for cleanup of the contaminated soil at the site.

Chemical Fixation Test Results

Tables 3 through 5 and Figure 7 summarize the chemical fixation test results. These results are discussed below.

The results of the TCLP test on the three selected reagent ratios (i.e., A, B and C) indicate that a very low quantity of metals leaches from the fixated soils (Table 3). For the three metals of concern, the concentrations of Cd, Ni and Co in the leachates from the TCLP tests were <0.005 to 0.29 mg/L, 0.33 to 0.41 mg/L and <0.05 to 0.06 mg/L, respectively. The Cd concentrations were all less than the TCLP Cd limit of 1.0 mg/L. The fixated soils using reagent ratio B were selected for the MEP test and the results indicate that a very small amount of

metals leaches from the fixated soils during each of the ten leaching steps (Tables 4 and 5). The concentrations of Cd, Ni and Co in the leachates from the MEP tests were <0.005 mg/L to 0.29 mg/L, <0.04 to 0.53 mg/L and <0.05 mg/L, respectively. Again, all the Cd concentrations were less than the TCLP Cd limit of 1.0 mg/L.

Figure 7 shows that the unconfined compressive strength (USC) increased rapidly as the curing time increased. With a curing time of 10 hours, the USC can reach 1500 lb/ft^2 and at the end of two-day curing time, the USC can reach approximately 5 tons/ft^2.

During the application of the Chemfix fixation process to treat the metal-contaminated soil at the former battery plant grounds, 70% by weight of water had to be added into the soil-reagent mixture. After curing, the final volume of the fixated soil was approximately double the original volume of the contaminated soil.

The above treatability test results indicate that the Chemfix fixation process is capable of treating the metal-contaminated soils at the former battery plant grounds. The extraction procedures performed (TCLP and MEP) on the fixated soil samples resulted in leachate contaminant con-

Table 3
TCLP Results on Chemfix Products
(Heavy Metals)

	2/12/88			2/29/88	
	RATIO A	RATIO B	RATIO C	RATIO B	TCLP LIMITS
PARAMETERS	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Arsenic	0.015	0.011	0.004	0.015	5.0
Barium	0.9	0.3	0.2	<0.1	100.0
Cadmium	0.194	<0.005	<0.005	0.290	1.0
Chromium	0.11	0.13	0.16	0.21	5.0
Cobalt	0.05	<0.05	0.06	<0.05	
Lead	<0.05	<0.05	<0.05	<0.05	5.0
Mercury	0.0011	0.0013	0.0015	0.0022	0.2
Nickel	0.33	0.41	0.41	0.33	
Selenium	<0.002	<0.002	0.003	0.003	1.0
Silver	<0.01	<0.01	<0.01	<0.01	5.0

NOTE: TCLP limits for cobalt and nickel are not available.
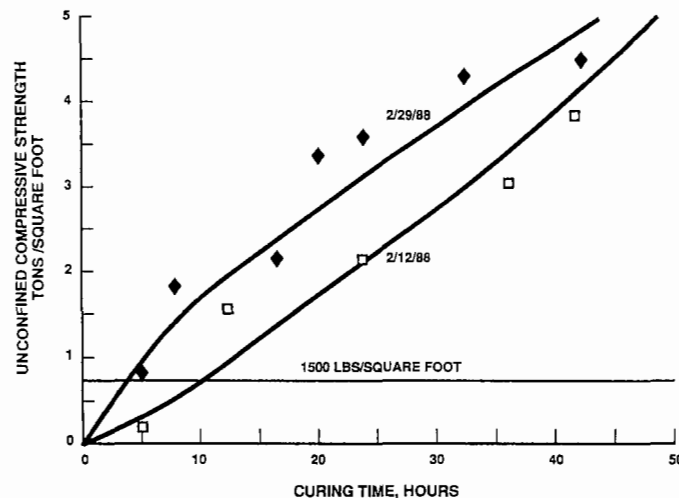
Figure 7
Unconfirmed Compressive Strength vs Curing Time

Table 4
MEP Results of Ratio B Chemfix Product
(Heavy Metals)

PARAMETERS	MEP 1 (mg/l)	MEP 2 (mg/l)	MEP 3 (mg/l)	MEP 4 (mg/l)	MEP 5 (mg/l)	MEP 6 (mg/l)	MEP 7 (mg/l)	MEP 8 (mg/l)	MEP 9 (mg/l)	MEP 10 (mg/l)
Arsenic	0.014	0.012	0.010	<0.002	<0.002	<0.002	<0.002	0.004	<0.002	0.004
Barium	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium	0.021	<0.005	<0.005	<0.005	0.019	0.007	0.021	0.033	0.029	0.010
Chromium	0.20	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cobalt	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mercury	0.0020	0.0015	0.0010	0.0013	0.0016	0.0012	0.0018	0.0019	0.0015	0.0018
Nickel	0.53	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Selenium	0.020	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 5
MEP Results of Ratio B Chemfix Product
(Heavy Metals)

PARAMETERS	MEP 1 (mg/l)	MEP 2 (mg/l)	MEP 3 (mg/l)	MEP 4 (mg/l)	MEP 5 (mg/l)	MEP 6 (mg/l)	MEP 7 (mg/l)	MEP 8 (mg/l)	MEP 9 (mg/l)	MEP 10 (mg/l)
Arsenic	0.015	0.012	0.005	<0.006	<0.002	0.002	0.005	0.002	<0.002	<0.002
Barium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium	0.290	<0.046	0.050	0.099	0.120	0.092	0.103	0.146	0.154	0.130
Chromium	0.21	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cobalt	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mercury	0.0022	0.0011	0.0015	0.0021	0.0015	0.0020	0.0017	0.0022	0.0020	0.0024
Nickel	0.33	0.04	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Selenium	0.023	<0.002	<0.002	<0.004	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

centrations well within the regulatory limits. This chemical fixation treatment can change the hazardous characteristics of the metal-contaminated soil to become nonhazardous.

CONCLUSIONS

Based on the results of the above-described bench-scale treatability tests, the following conclusions are made:

- Since the selected soil cleanup level for the Area II portion of the Marathon Battery Company site is 20 mg/kg Cd, acid extraction is not a viable stand-alone remediation approach for this site.
- Chemical fixation (e.g., the Chemfix fixation process) is capable of eliminating the hazardous characteristics of the metal-contaminated (Cd, Ni and Co) soil at the former battery plant grounds.

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Extraction and Washing Contaminated Soils Using High Pressure Jet Grouting Techniques

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ABSTRACT

Contamination in the ground, particularly under a structure on a congested urban site, poses a unique problem requiring a unique solution. A small site in Hamburg, Germany, presently occupied by three old factory buildings, was contaminated with phenol, a chemical substance which was used in the manufacture of disinfectants. The old factory buildings had subsequently been renovated and are now occupied by a community center and various commercial enterprises.

An extensive site investigation revealed contamination concentrated between and under the buildings. Since off-site disposal of contaminated soils in Germany is difficult and cost-prohibitive, it was necessary to develop reliable methods of removal and on-site treatment of the contaminated soils. Remedial measures on this site required decontamination of soils adjacent to and under the structure while providing adequate ground support of the foundations.

An on-site pilot program was devised using jet grouting techniques to extract and wash contaminated soils. This process utilizes a high pressure air/water jet which erodes and washes away the contaminated substance from the granular soils. Contaminated soil was displaced to the surface where it was collected and cleaned of phenolic contamination by oxidation in a completely self-contained unit. After decontamination, the cleaned material was separated according to composition and then filtered. Cleaned soils were mixed with cement and replaced. The City of Hamburg's Environmental Commission performed tests that indicated levels of phenol in the soil were well below the maximum acceptable limits.

This process, using the combination of jet grouting technique, on-site soil washing and recycling of clean materials has proven successful on this project.

INTRODUCTION

Thousands of hazardous waste sites are known to exist in North America and Europe. Evaluations of many of these sites and their potential for damage (or further damage) to the environment have produced a vast array of remedial techniques. Traditionally, excavation and transport of the contaminated soil to an off-site landfill has been the most commonly used method of site remediation. However, due to land ban legislation and the extremely high cost of off-site disposal, there has been an industry shift to containment and/or on-site/in situ treatment of contaminated soils.

Congested urban areas with contamination in the ground pose particularly difficult challenges for the remediation contractor. Remediation of contaminated soils must make sure that all contaminated soils, even in difficult to access areas (i.e., under developed sites), can be decontaminated while the planned use of the area and integrity of the existing structures is retained. This paper explains how one proven geotechnical technique, jet grouting, was adapted and combined with a new technology, soil-washing, to address a unique environmental problem.

CONTAMINATED SITE

An urban site in Hamburg, West Germany, was occupied by a small manufacturing facility that produced disinfectant until the beginning of the 1960s. The site, with an area of approximately 5,000 square meters, is bordered by a canal on the south side. Three old, but renovated, factory buildings exist on the site, one of which is used as a community center. The other two buildings are occupied by various commercial enterprises. Because of the production and improper handling methods used, the soil and groundwater became contaminated with various concentrations of phenol. West Germany currently has no national approach to establishing cleanup goals for contaminated land. Cleanup control is by provincial governments with use of the "Dutch List" for general guidance and screening.[1]

An extensive site investigation program was undertaken to determine the type and extent of contamination. The soil structure was basically horizontal with layers of peat and sand over a layer of mud at approximately 7 meters below the surface. The center of the contaminated area was located in front of, and underneath, the former disinfectant plant, as shown in Figure 1. Phenol concentrations were determined in both the groundwater and the soil. The highest concentration of contamination was determined to be approximately 2 to 3.5 meters beneath the surface.[2] When the highly concentrated chemicals came into contact with air, they produced an intense odor which made excavation of the soils in this urban area impractical.

The spread of contamination underneath the structures posed a major problem because the integrity of the buildings and the soils they were resting on had to be maintained. It was necessary to find a suitable method of treating the contaminated soils under the structures.

TREATMENT REQUIREMENTS

This complex site required the development of treatment methods that met the following criteria:

- Little or no contact with the contaminated material
- No air emissions during the decontamination process other than properly filtered air
- No open pit excavations
- The program should be able to extract and decontaminate soils underneath the buildings without compromising the support of the structure
- No groundwater lowering could be allowed because you would potentially have to treat large volumes of contaminated water and the dewatered peat layers would likely cause settlement of the structure
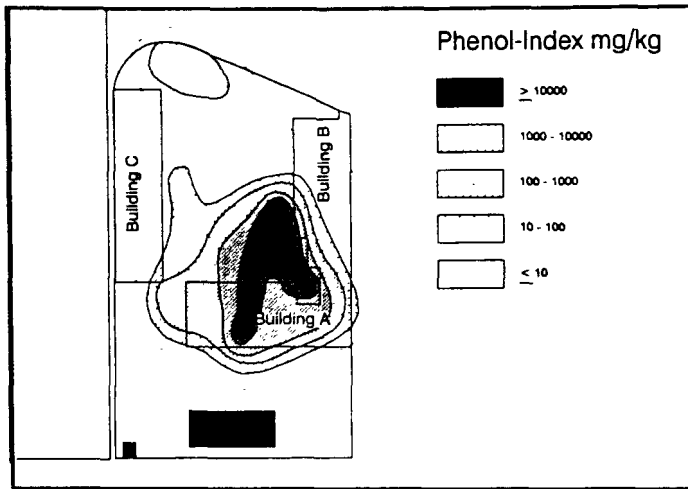
Figure 1
Extent of Contamination
with Respect to Structures

Figure 2
Triple System Jet Grouting

- Little or no off-site transportation and disposal of contaminated materials would be required

Several remedial methods were considered. Because of the high concentration of phenols and their considerable odor, on-site techniques using open-pit excavation methods were neither practical nor did they address contamination underneath the structure. Biological treatment, which was attempted in a prior project, was unsuccessful because of the differing soil conditions (sand and peat with different organic contents and thickness) and rapid changes in contamination concentrations.

TREATMENT SYSTEM

A geotechnical process known as jet grouting by the triple system method was combined with an on-site soil-washing process. Jet grouting is a Ground Modification system used to create in situ cemented geometries of soil (soilcrete). This system was developed primarily for underpinning and/or excavation support but also has been adapted for stabilization of soft soils and more recently has been used for pollution control projects. The triple system (or a triple rod system as it is also known) of jet grouting uses the combination of high pressure water (5,000 to 6,000 psi) shielded in a cone of air to cut and lift the soil to the surface (Fig. 2). In underpinning applications, the void created is simultaneously tremie filled with a pre-engineered backfill (usually a cement slurry).[3]

The water jet is surrounded by a concentric collar of compressed air which concentrates the jet, particularly below the water table. This high pressure water and air stream was designed to erode the surrounding soil but also washes certain contaminants from the coarser grained soils. This medium also becomes the source for the air lift system for displacement of spoil to the surface where it could be collected at the top of the drill hole. This controlled soil removal and washing capability was selected for a full-scale pilot program on the Hamburg site.

Five test columns were installed to monitor and analyze the success of the procedure. The subsoil to be cleaned is made air-tight with a surface sealing work pad over the planned boring area. After advancing the drill through the work pad to the desired depth of treatment, high pressure water and air are forced through the drill rods. The drill rods are rotated and retracted at a predetermined rate. The high energy cutting stream leads to a displacement of the treated soil within a certain distance from the opening in the drill rod. In this case, the treated volume of the soil columns had an effective diameter of approximately 1.5 meters. The soil is eroded and intensely cleansed and mixed with the outflowing water.

The radius of the eroded column can be regulated by altering stream velocity, rotary velocity and suction velocity. This process allows variance in the system to account for differing soil conditions. This cleansing process continues to the surface or upper limit of contamination.
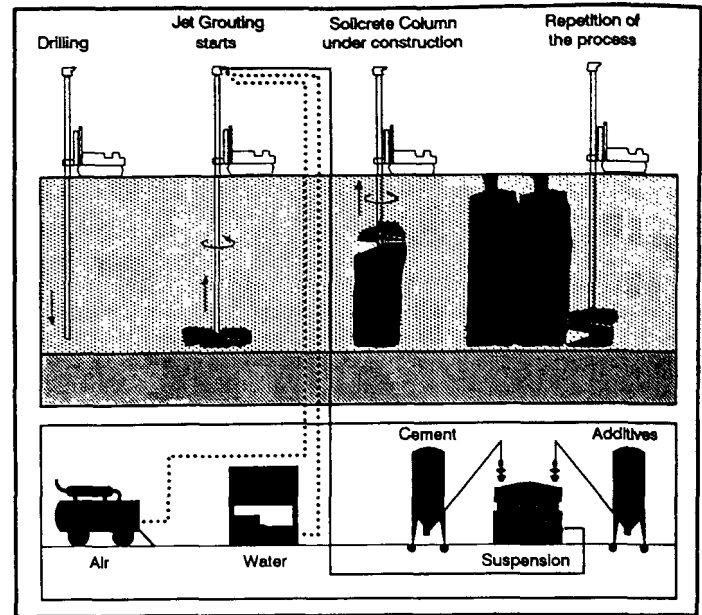
During and after the production process, the stability of the column walls is maintained by the pressure of the suspended material in the column. The use of additives in the cutting water (i.e., bentonite slurry) can be used, if required.

The diameter of the column (i.e., the treated volume of soil) can be mechanically measured at the end of the operation by means of a folding screen which is inserted in the column filled with suspended material. This usually is done in the first test column(s) in order to set parameters for the production work.

The contaminated material consisting of water and soil coming out of the drill hole through the work pad is fed directly into an enclosed soil washing decontamination system (Fig. 3). An oxidation process was used to degrade the phenols.[4] After decontamination, the cleaned material was removed, leaving the fine soil which was separated into dry material and filtrate.

This soil washing process can be repeated as often as desired. The process results in very little contaminated material that has to be disposed of in a secure landfill.

The suspended material remaining in the test column now has to be exchanged for an uncontaminated mixture in the next step of the process.

The clean materials were mixed with purified filtrate water and a bonding agent (in this case cement) to form a competent filling material. This material was then reinjected into the open column displacing the suspended medium which is collected at the surface and treated and reused in the next column.

Soil extraction and treatment was continued in alternating columns refilling one column before jetting the adjacent column. This procedure is standard practice in conventional underpinning and prevents undermining of the structure. The columns are over[lapped to ensure decontamination of the entire volume of soil targeted.

CONCLUSION

This method of contaminated soil extraction and on-site treatment in a closed system proved quite successful in this pilot project. The final product showed a 98% reduction in the level of phenol. Confirming tests by the regulating authority showed that the levels of phenol found in the soil were well below required levels. The combination of the jet stream procedure for eroding and washing the contaminated soil
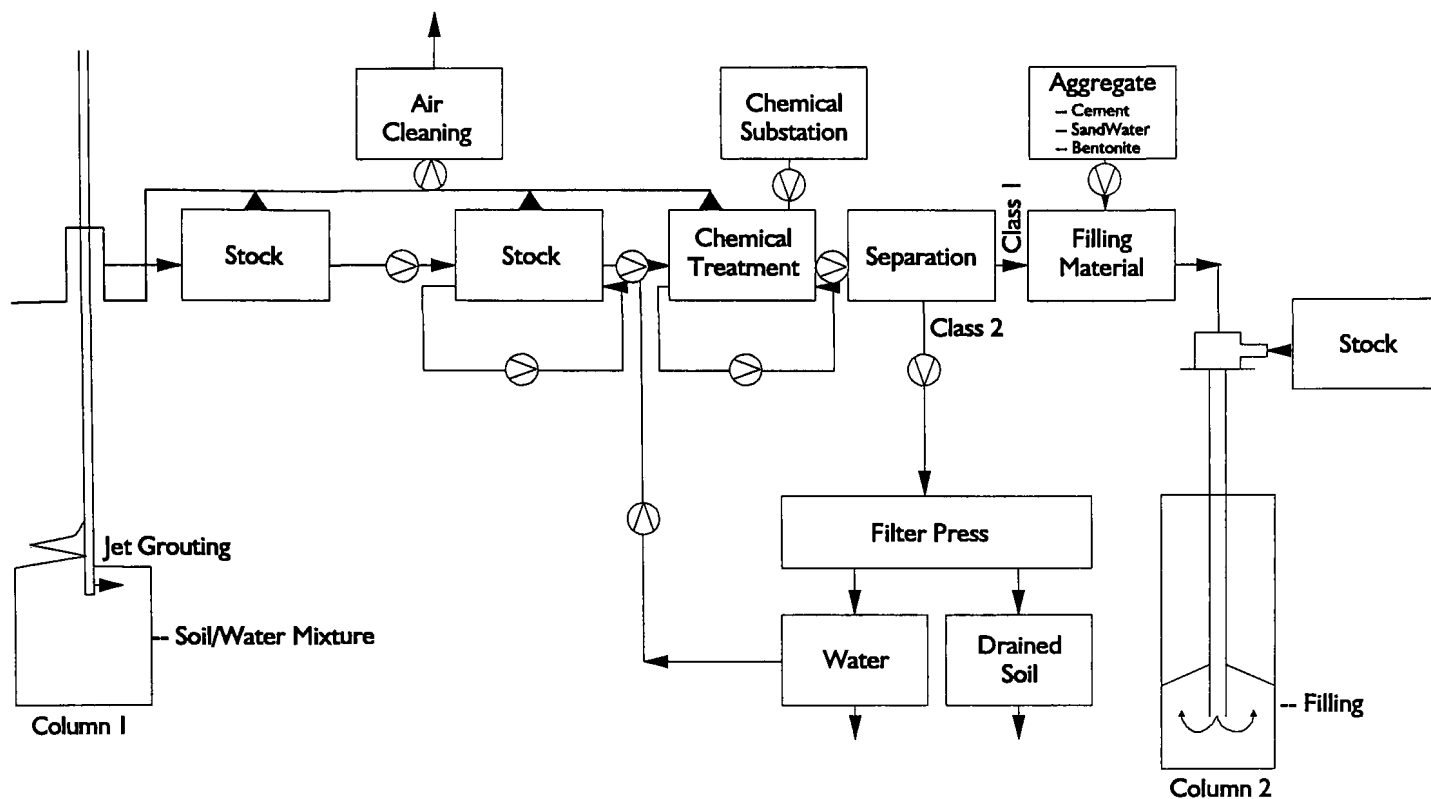
Figure 3
Technology of High Pressure Washing and Treatment

followed by a direct decontamination and recycling of the resulting displaced mixture has several advantages:

- Site access is not as significant an issue as it would be in an excavation and replacement procedure; the triple rod system method of jetting can be done with small jet grouting rigs, if necessary, to access very restrictive locations
- The procedure also has the potential of targeting pockets of contamination in deep or otherwise in accessible locations such as under existing structures
- Due to the closed system of treatment, there is very little contact of the contaminated materials with the surrounding environment
- No lowering of the groundwater is necessary
- The process results in very little off-site disposal of contaminated soil
- The process can potentially be adjusted to treat specific contaminants

Care must be taken during the extraction process not to increase the amount of contaminated water in the treatment zone. Properly staging and planning the remedial program will minimize this problem. Potential chemical reactions of the treatment reagents with the soils and contaminants must be carefully considered. Since most hazardous waste sites contain a mix of contaminants. A treatment approach that may neutralize one contaminant may render another more toxic or mobile.[5]

Jet grouting techniques can be used to support structures while contaminants are removed beneath them and to wash the coarser soil particles in-place and bring the fines with the contaminants to the surface for additional treatment.

Further development of this technique includes using hot water and/or adding steam to the flushing and cutting jet to greatly increase the degree of decontamination of particular pollutants. Addition of a biologically active substance to the jet stream is also a viable option under consideration.

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Cost of Controlling Air Stripper Emissions

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ABSTRACT

Air stripping is a proven technology that frequently is used at Superfund sites to treat groundwater contaminated with certain volatile organic compounds (VOCs). It may be desirable or required by regulations to control the air emissions from air strippers when emission rates of VOCs exceed certain levels. The cost of controlling these air emissions is of interest to the U.S. EPA and others involved in evaluating costs of remedial technologies. This study evaluated cost trends for air stripping with vapor-phase carbon adsorption controls and graphically presents the control costs in terms of dollars per ton of pollutant removed versus groundwater concentration for various treatment rates.

Cost data on existing air stripping operations at Superfund sites are generally very limited in terms of uniformity of data reported and lack of cost category. To produce consistent results, preliminary air stripper and carbon adsorber designs were developed and estimated costs were calculated based on some simplifying assumptions. Three compounds, 1,1-dichloroethylene (DCE), trichloroethylene (TCE) and 1,2-dichloroethane (EDC), were used at various concentrations in groundwater for the purposes of this study. These compounds are commonly found at Superfund sites and have small maximum contaminant levels (MCLs) used as cleanup standards. They represent a range of Henry's Law constants and each may be adsorbed in vapor phase by activated carbon at different holding capacities. VOC inlet flow rates investigated varied from 0.05 to 10 lb/hr and liquid flow rates varied from 500 to 3500 gal/min at a fixed air-to-water ratio. Air strippers were designed using the Sherwood-Holloway Model and vendors supplied design and cost data for the carbon adsorption units. Both regenerative and nonregenerative carbon systems were evaluated.

Estimated capital costs, operation and maintenance costs and annualized costs are presented for the air strippers, carbon adsorption units and the combined systems. Control costs are presented and trends are discussed in terms of cost per ton of VOC adsorbed and cost/1000 gallons of groundwater treated.

INTRODUCTION

PEI Associates, Inc. (PEI) was asked by the U.S. EPA to evaluate the cost of controlling air emissions from air strippers used in groundwater remediation at Superfund sites. This study was initiated to provide additional data for the Office of Emergency and Remedial Response's (OERR) Air Stripper Control Policy in terms of evaluating control costs per ton of pollutant removed. The study also was useful as a tool in evaluating cost trends for air stripping and vapor-phase carbon adsorption controls.

Cost data on existing air stripping operations at Superfund sites have been found to be very limited in terms of uniformity of data reported and lack of cost breakdowns. To produce consistent uniform results for

this study, it was necessary to develop preliminary air stripper and carbon adsorber designs and to calculate estimated costs based on some simplifying assumptions.

The results of the control cost analysis are summarized in Figure 1. Figure 1 is a plot of the cost per ton of volatile organic compound (VOC) adsorbed on the activated carbon versus the groundwater concentration for three different treatment rates. For regenerative carbon adsorption systems at air concentrations greater than 4 ppm, the costs per ton are very similar for the three chemicals investigated because equipment costs predominate. Therefore, one set of lines represents the 500, 1500 and 3500 gal/min flow rates. The inlet pollutant rates (0.5 lb/hr to 10 lb/hr) for the regenerative systems also are shown in Figure 1. Below 4 ppm the nonregenerative carbon adsorption systems show different costs per ton for each chemical because the different carbon use rates control these costs. Best fit lines have been plotted for the nonregenerative carbon adsorption systems used to control each pollutant at low air concentrations.
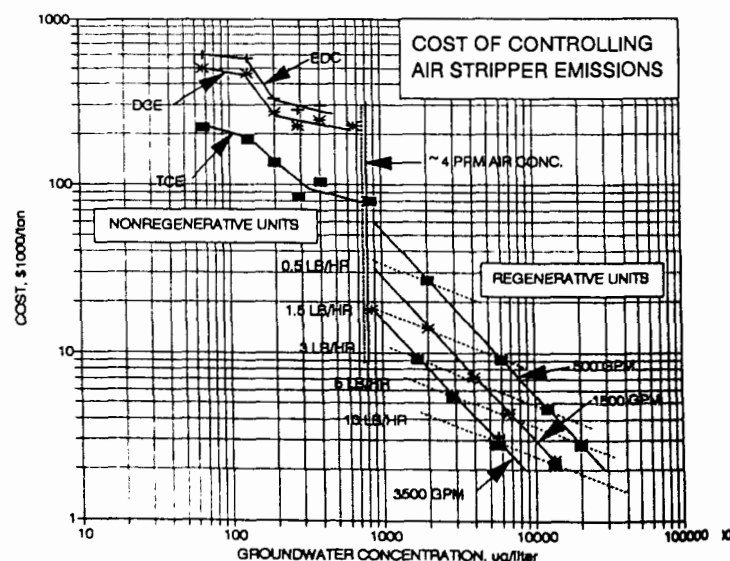
Figure 1
Cost per ton of VOC Adsorbed vs. Groundwater Concentration

CHEMICAL SELECTION

Three chemical compounds were selected for the study based on logical criteria. These chemicals are VOCs commonly found in con-

taminated groundwater at Superfund sites and the groundwater cleanup levels required are significantly small for each chemical. Both air stripping and vapor-phase activated carbon adsorption are technically feasible treatment methods for each chemical. The three chemicals represent a high, medium and low range of Henry's Law constants (a measure of a compound's ability to be stripped). Trichloroethylene (TCE) was selected first because it is a VOC frequently found at Superfund sites, it is a common target for air stripping and it has a midrange Henry's Law constant. Selection of the other two chemicals was aided by consulting the chemical data table in the *Superfund Public Health Evaluation Manual* (SPHEM)[1] and reviewing the Superfund Records of Decision System (RODS) data base.[2] 1,1-Dichloroethylene (DCE) was selected as the VOC with a higher range Henry's Law constant and 1,2-Dichloroethane (EDC) was selected as the VOC with a low-range Henry's Law constant that could be removed from groundwater by air stripping. Tables 1 and 2 present selected data for each chemical. In this study, VOC concentrations in groundwater up to 40,000 μg/liter were investigated.

Table 1
Data on Three Compounds Selected for
Study of Air Stripper Control Costs

Compound	Molecular weight	Henry's Law constant	Vapor pressure, mm hg
1,1-Dichloroethylene (DCE)	97	3.4×10^{-2}	600
Trichloroethylene (TCE)	131	9.1×10^{-3}	57.9
1,2-Dichloroethane (EDC)	99	9.8×10^{-4}	64

Table 2
Typical Concentrations at Superfund Sites

Compound	Frequency[a]	Range of concentrations, μg/liter		Approximate mean concentration, μg/liter	MCL[b], μg/liter	WQC[c] μg/liter
DCE	6	1.7	52,000	400	7	0.033
TCE	18	8	70,000	1,600	5	2.8
EDC (DCA)	4	5	7,000	200	5	0.94

[a]Number of times compound was identified as a contaminant in RODs data base at 28 sites with air stripping.
[b]MCL = Proposed maximum contaminant level for drinking water.
[c]WQC = Water quality criteria (for 1 x 10-6 cancer risk).

ASSUMPTIONS USED FOR PRELIMINARY DESIGN AND COST ESTIMATES

This section presents the assumptions and data items used in the design and cost analysis. The following assumptions were used to design the air stripper and the outlet results were used to size the carbon adsorber:

- The carbon adsorber and air stripper designs were produced for treatment of three chemicals independently: TCE, DCE and EDC.
- The VOC flow rates investigated ranged from 0.05 to 10 pounds/hour in the liquid influent. The inlet rates were assumed to be constant. No "safety factor" for variation in concentration or nonideal effects was included.
- Liquid flow rates of 500, 1500 and 3,500 gal/minin were investigated.
- The air-to-water ratio used in each case was 35 to 1. This ratio was found to provide an adequate air stripper design for the cost estimates on a comparative basis.
- The outlet water concentration was set at 5 micrograms/liter. This parameter also controls the air stripper design efficiency.
- Air and water temperatures were assumed to be 60° F.

With these parameters, the air stripper was designed for optimum height and diameter using the Sherwood-Holloway Model.[3] An assumption used in designing the air stripper was that column dimen-

sions would allow operation at 50 percent of the flooding loadings of water and air. In some cases, there was no feasible single air stripper design and multiple parallel air strippers were used. Once the optimum designs were identified, vendors were contacted to obtain prices for the accompanying carbon adsorbers. The capital costs for the air stripper were calculated from the PDQ$ costing program.[4] The cost for the 1.5 inch Berl saddles packing was obtained from Peters and Timmerhaus.[5] The operation and maintenance costs for the air strippers were assumed to be 62 percent of the capital costs. The operation and maintenance costs for the carbon adsorbers were individually calculated based on carbon use and other factors.

Carbon adsorber costs were obtained from vendors for both regenerative and nonregenerative carbon systems. The regenerative unit is fully automated and has low operating costs (mostly utilities). On the other hand, the nonregenerative unit has a low initial capital cost, but a large cost for off-site regeneration of the spent carbon. The total annualized costs for each type of system were compared to determine whether a regenerative or nonregenerative system should be used.

The annualized costs for both the stripper and the carbon adsorber were obtained by assuming a 10-year project life (operating life and capital recovery period) and a 10 percent interest rate. Costs presented are in 1989 dollars. A number of assumptions were made in determining the adsorber and stripper costs including: the site is accessible and utilities are available, minimum site work is necessary for installation, the system is in continuous operation, operating labor requirements are minimal, the salvage value or disposal cost for the recovered VOC is negligible and there is no salvage value for the used equipment at project end.

The vendors supplied details and costs of exchangeable carbon adsorption units (carbon tanks) and steam-regenerative systems based on air flow volume. General adsorption capacities of carbon for the three chemicals at 4 ppm were used to calculate carbon use for the nonregenerative units. These estimated capacities were reduced by 50 percent at VOC concentrations below 1 ppm. The annualized cost of the carbon adsorber was divided by the tons of VOC removed/year, based on an assumed efficiency of 92 percent, to obtain the cost per ton of VOC removed.

The capital and operating costs estimated include basic installed equipment costs, minimum expected operation and maintenance costs and minimum operating labor requirements. Many other direct or indirect costs associated with groundwater cleanup may be applicable to Superfund site remediation depending on site-specific conditions. Items that were not included in the cost estimates include design, engineering, treatability studies, shipping costs, installation of utilities, groundwater collection systems, auxiliary equipment, heating of gas stream (if required), unscheduled repairs and administrative costs.

It is important to note that if all the above cost factors are considered, the cost of the basic air stripping operation may be a small portion of the total site remediation costs.

TECHNICAL AND ECONOMIC FEASIBILITY OF CARBON REGENERATION OF ADSORBERS TREATING AIR STREAMS WITH LOW VOC CONCENTRATIONS

When treating air streams with low VOC concentrations, carbon adsorbers that make one time use of the carbon (nonregenerative systems) and carbon adsorbers that regenerate the carbon on-site for reuse are competitive from both a cost and technical standpoint. Vendors were contacted in an effort to learn at what VOC concentrations nonregenerative carbon use becomes preferable on both technical and economic grounds. One area of agreement was that boundaries were very situation-specific and the information presented is strictly a generalization.[6,7] The specific comparisons cited are only good for the 10 year operating life.

Economic Considerations

Regenerative systems have a much higher initial capital cost and, therefore, incur large fixed costs due to capital recovery, maintenance, taxes, insurance, etc., whether or not the system operates. Variable costs, i.e., operating labor (the system is essentially automated and small)

and steam for carbon regeneration, are low.

The nonregenerative systems have low initial capital costs, mainly for fans and ductwork, but operating costs are high due to the cost of carbon. Large air flows favor regenerative systems because carbon adsorber costs do not vary linearly with size. For example, a system handling 12,000 cfm has only twice the costs of a system handling 2,300 cfm.

Regenerative systems appear to be less costly at VOC concentrations of approximately 3 ppm at 2,300 and 7,000 cfm and approximately 2 ppm at 12,000 and 16,000 cfm. The technical feasibility of on-site steam regeneration of carbon beds at these low concentrations, however, has been questioned by the carbon system vendors.

The minimum cost of a small (300 to 800 cfm) regenerative carbon adsorber is approximately $80,000. Minimum requirements also include instrumentation and controls and metal fabrication work. Allowing for an additional cost of 50 percent for installation and $5,000 for a steam generator and air compressor, the minimum cost of a regenerative carbon adsorption system of this type is $125,000. Therefore, due to fixed costs such as capital recovery, maintenance, taxes, insurance, etc., a nonregenerative system would be preferable if annualized costs are $35,000 or less.

Technical Considerations

There was agreement among carbon vendors that nonregenerative systems should be considered at concentrations below 10 ppm as well as at higher concentrations. The technical feasibility of a regenerative system was questioned at or below 3 ppm. The dividing line is somewhere between 4 and 10 ppm with the considerations being: (1) the hydrocarbon being adsorbed, (2) the air flow rate and (3) the temperature and relative humidity of the air stream being fed to the adsorber.[6,7] For the purpose of this analysis, if the air concentrations were 4 ppm and below, a nonregenerative system was selected because a regenerative system may not be technically feasible.

In a regenerative system, more VOC is adsorbed on virgin carbon than on carbon that has been regenerated by stream. This operational phenomenon occurs because steam stripping only removes part of the adsorbed VOC, thus reducing the capacity of subsequent cycles. For example, if virgin carbon can adsorb 10 percent of its weight in VOC, then that is considered to be the capacity of the carbon. But steam regeneration may remove only 70 percent of the VOC from the carbon, leaving 0.03 pounds of VOC/pound of carbon still on the carbon. Because the carbon capacity remains at 0.10 pounds of VOC/pound of carbon, the working capacity of the carbon is 0.10 - 0.03 or 0.07 pounds of VOC/pound of carbon. For the purpose of analysis, it was assumed that the regenerative systems lost one-third of their capacity due to the inability to completely regenerate the carbon beds.

RESULTS AND DISCUSSION OF COST ESTIMATES

This section of our paper presents the design results and cost data for air stripping and vapor phase carbon adsorption. The costs per ton of VOC removed by stripping and adsorption are discussed as well as the costs/1000 gallons of groundwater treated.

Air Stripping

Table 3 shows the estimated air stripping costs for the chemicals TCE, DCE and EDC. The stripper dimensions shown are inside packing dimensions. The values reported are based on the results of the Sherwood Holloway packed column model. Other models exist that are more complex and would give somewhat different tower dimensions. In addition, design practice would dictate rounding tower diameters to convenient increments for manufacturing and recalculating packing height and mass transfer rates based on actual dimensions. The total column height used for cost estimates includes five extra feet for internal distribution at column inlet and outlet.

The capital costs, annual operation and maintenance (O&M) costs and annualized costs for air strippers generally increase as the air flow and the inlet water concentrations increase. For TCE the capital costs range from $35,000 to $216,000, and the O&M costs range from $22,000 to $134,000/year. The annualized costs range from $28,000 to $169,000.

For DCE, the air stripper costs are only slightly higher than for TCE by 2 to 4 percent. The air stripper costs for EDC are highest, at 1.2 to 2 times the costs for TCE.

The costs per ton of TCE removed from groundwater by air stripping range from $1900/ton up to $430,000/ton. These unit costs decrease as the quantity of TCE being treated increases and as the size of the air stripper (air flow) is reduced. The costs per ton of DCE and EDC removed are higher as compared to TCE, in the same proportions as the air stripper costs for those chemicals.

Table 3
Estimated Air Stripper Costs for Removal
of Three Chemicals in Groundwater

TRICHLOROETHYLENE (TCE)

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	STRIPPER DIMENSIONS TOWERS	HEIGHT (FT)	DIA. (FT)	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC REMOVED TONS/YR	COST/TON VOC REMOVED
1 TCE	0.05	500	200	2340	1.03	1	7.9	6.3	35000	22000	27695	0.21	130000
2 TCE	0.1	500	400	2340	2.06	1	9.4	8.3	37000	23000	19020	0.43	67000
3 TCE	0.5	500	2000	2340	10.31	1	13	6.3	47000	29000	36847	2.18	17000
4 TCE	1.5	500	6000	2340	30.93	1	15.4	8.3	52000	32000	40460	6.56	6200
5 TCE	3	500	12000	2340	61.87	1	16.9	6.3	54000	33000	41786	13.13	3200
6 TCE	5	500	20000	2340	103.11	1	18	6.3	58000	36000	45437	21.89	2100
7 TCE	0.05	1500	67	7020	0.34	4	5.5	5.4	112000	69000	87722	0.20	430000
8 TCE	0.1	1500	133	7020	0.69	3	7	6.3	103000	64000	80754	0.42	192000
9 TCE	10	1500	13300	7020	68.74	1	17.1	10.9	107000	66000	83409	43.78	1800
10 TCE	0.5	3500	285	16400	1.47	4	8.7	8.3	194000	120000	151584	2.15	70000
11 TCE	1.5	3500	856	16400	4.41	3	11.1	9.6	190000	118000	148913	6.53	23000
12 TCE	3	3500	1712	16400	8.83	2	12.6	11.7	191000	118000	149076	13.10	11000
13 TCE	5	3500	2854	16400	14.71	2	13.7	11.7	199000	123000	155377	21.88	7100
14 TCE	10	3500	5707	16400	29.42	2	15.3	11.7	216000	134000	189143	43.76	3900

DICHLOROETHYLENE (DCE)

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	STRIPPER DIMENSIONS TOWERS	HEIGHT (FT)	DIA. (FT)	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC REMOVED TONS/YR	COST/TON VOC REMOVED
1 DCE	0.05	500	200	2340	1.39	1	16.3	6.3	36000	22000	27857	0.21	130000
2 DCE	0.1	500	400	2340	2.79	1	10.2	6.3	38000	24000	30183	0.43	70000
3 DCE	0.5	500	2000	2340	13.93	1	13.9	8.3	48000	30000	37610	2.18	17000
4 DCE	1.5	500	6000	2340	41.78	1	16.5	6.3	53000	33000	41823	6.56	6300
5 DCE	3	500	12000	2340	83.55	1	18.1	6.3	58000	36000	45437	13.13	3500
6 DCE	5	500	20000	2340	139.26	1	19.3	8.3	59000	37000	46599	21.89	2100
7 DCE	0.05	1500	67	7020	0.46	4	6	5.4	114000	71000	89548	0.20	447000
8 DCE	0.1	1500	133	7020	0.93	3	7.6	8.3	105000	65000	82084	0.42	195000
9 DCE	10	1500	13300	7020	92.84	1	18.4	10.9	111000	69000	87060	43.78	2000
10 DCE	0.5	3500	285	16400	1.99	4	9.4	8.3	200000	124000	156540	2.15	73000
11 DCE	1.5	3500	858	16400	5.98	2	12	11.7	185000	115000	145282	6.53	22000
12 DCE	3	3500	1712	16400	11.92	2	13.8	11.7	198000	123000	155215	13.10	12000
13 DCE	5	3500	2854	16400	19.87	2	14.8	11.7	207000	126000	161879	21.88	7400
14 DCE	10	3500	5707	16400	39.74	2	16.4	11.7	224000	139000	175445	43.78	4000

1,2-DICHLOROETHANE (EDC)

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	STRIPPER DIMENSIONS TOWERS	HEIGHT (FT)	DIA. (FT)	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC REMOVED TONS/YR	COST/TON VOC REMOVED
1 EDC	0.05	500	200	2340	1.36	1	16.3	6.3	53000	33000	41823	0.21	195000
2 EDC	0.1	500	400	2340	2.73	1	20.6	6.3	63000	39000	49250	0.43	114000
3 EDC	0.5	500	2000	2340	13.64	1	30.7	8.3	78000	48000	60091	2.18	28000
4 EDC	1.5	500	6000	2340	40.93	1	37.7	6.3	93000	58000	73131	6.56	11000
5 EDC	3	500	12000	2340	81.87	1	42.1	6.3	100000	62000	78270	13.13	6000
6 EDC	5	500	20000	2340	136.44	1	45.3	8.3	105000	65000	82084	21.89	3700
7 EDC	0.05	1500	67	7020	0.45	2	10	7.7	95000	59000	74457	0.20	367000
8 EDC	0.1	1500	133	7020	0.91	1	13.9	10.9	90000	58000	70643	0.42	168000
9 EDC	0.5	1500	666	7020	4.55	1	23.6	10.9	134000	83000	104802	2.17	48000
10 EDC	1.5	1500	2000	7020	13.64	1	30.7	10.9	159000	99000	124869	6.55	16000
11 EDC	3	1500	4000	7020	27.29	1	35.1	10.9	176000	109000	137635	13.12	10000
12 EDC	5	1500	6700	7020	45.48	1	38.3	10.9	195000	121000	152727	21.88	7000
13 EDC	10	1500	13300	7020	90.86	1	42.8	10.9	213000	132000	168655	43.78	3800
14 EDC	0.5	3500	285	16400	1.95	2	13.8	11.7	249000	154000	194512	2.15	90000
15 EDC	1.5	3500	856	16400	5.84	1	25.3	16.6	265000	164000	207118	6.53	37000
16 EDC	3	3500	1712	16400	11.68	2	29.7	11.7	348000	218000	272620	13.13	26000
17 EDC	5	3500	2854	16400	19.47	2	33	11.7	374000	232000	292850	21.86	13000
18 EDC	10	3500	5707	16400	38.94	2	37.4	11.7	439000	272000	343425	43.78	7800

Carbon Adsorption

Table 4 shows estimated costs for the carbon adsorption controls for the chemicals TCE, DCE and EDC. The costs presented are additional control costs to be added to the cost of air stripping. Both regenerative and nonregenerative carbon systems were used in this study. The regenerative systems were more economical for treating highly concentrated outlet air streams. For cases where the outlet air concentrations were lowest, the nonregenerative systems were found to be more economical. Nonregenerative systems were used in all cases at or below 4 ppm air concentration because of the performance concerns regarding regenerative systems as previously discussed.

The capital costs for the carbon adsorbers are the same for all three chemicals under the same operating parameters. The nonregenerative capital costs range from $14,000 to $24,000, while the regenerative capital costs range from $207,000 to $453,000. The operating costs for the nonregenerative systems depend mainly on the carbon replacement costs. The nonregenerative operating costs/year for TCE range from $24,000 to $475,000. For DCE the range is $62,000 to $547,000. For EDC the range is $51,000 to $443,000. The operating costs for

regenerative systems depend on fixed costs and steam and vary by 5 to 20 percent between different chemicals. Annual operating costs for regenerative systems for the three chemicals range from $20,000 to $54,000. The total annualized costs for controlling TCE range from $26,000 to $479,000. The range for DCE is $54,000 to $551,000 and the range for EDC is $53,000 to $446,000. Except for the cases where nonregenerative systems were chosen over regenerative systems for technical reasons, costs are reduced when the system size is reduced and the quantity of VOC treated is reduced.

Table 4
Estimated Carbon Adsorber Costs for Controlling Air Stripper Emissions

TRICHLOROETHYLENE(TCE):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	SYSTEM TYPE	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC ADSORBED TONS/YR	COST/TON VOC ADSORBED
1 TCE	0.05	500	200	2340	1.03	N/R	14000	24000	26278	0.20	134000
2 TCE	0.1	500	400	2340	2.06	N/R	14000	39000	41278	0.40	104000
3 TCE	0.5	500	2000	2340	10.31	REGEN	207000	20000	53679	2.01	27000
4 TCE	1.5	500	6000	2340	30.93	REGEN	209000	21000	55004	6.04	9100
5 TCE	3	500	12000	2340	61.87	REGEN	212000	21000	55492	12.08	4600
6 TCE	5	500	20000	2340	103.11	REGEN	212000	21000	55492	20.14	2800
7 TCE	0.05	1500	67	7020	0.34	N/R	17000	38000	40766	0.19	219000
8 TCE	0.1	1500	133	7020	0.69	N/R	17000	69000	71766	0.39	185000
9 TCE	10	1500	13300	7020	68.74	REGEN	339000	31000	86155	40.28	2100
10 TCE	0.5	3500	285	16400	1.47	N/R	24000	163000	166905	1.98	84000
11 TCE	1.5	3500	856	16400	4.41	N/R	24000	475000	478905	6.01	80000
12 TCE	3	3500	1712	16400	8.83	REGEN	452000	36000	109540	12.05	9100
13 TCE	5	3500	2854	16400	14.71	REGEN	452000	37000	110540	20.11	5500
14 TCE	10	3500	5707	16400	29.42	REGEN	453000	40000	113703	40.26	2800

DICHLOROETHYLENE(DCE):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	SYSTEM TYPE	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC ADSORBED TONS/YR	COST/TON VOC ADSORBED
1 DCE	0.05	500	200	2340	1.39	N/R	14000	62000	64278	0.20	327000
2 DCE	0.1	500	400	2340	2.79	N/R	14000	117000	119278	0.40	300000
3 DCE	0.5	500	2000	2340	13.93	REGEN	207000	21000	54679	2.01	27000
4 DCE	1.5	500	6000	2340	41.78	REGEN	209000	23000	57004	6.04	9400
5 DCE	3	500	12000	2340	83.55	REGEN	212000	24000	58492	12.08	4800
6 DCE	5	500	20000	2340	139.26	REGEN	212000	25000	59492	20.14	3000
7 DCE	0.05	1500	67	7020	0.46	N/R	17000	110000	112766	0.19	605000
8 DCE	0.1	1500	133	7020	0.93	N/R	17000	219000	221766	0.39	572000
9 DCE	10	1500	13300	7020	92.84	REGEN	339000	39000	94155	40.28	2300
10 DCE	0.5	3500	285	16400	1.99	N/R	24000	547000	550905	1.98	278000
11 DCE	1.5	3500	856	16400	5.96	REGEN	439000	37000	108425	6.01	18000
12 DCE	3	3500	1712	16400	11.92	REGEN	452000	40000	113540	12.05	9400
13 DCE	5	3500	2854	16400	19.87	REGEN	452000	44000	117540	20.11	5800
14 DCE	10	3500	5707	16400	39.74	REGEN	453000	54000	127703	40.26	3200

1,2-DICHLOROETHANE(EDC):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	AIR CONC. (PPMV)	SYSTEM TYPE	CAPITAL COST	O & M COST	ANNUALIZED COST 10YR @ 10%	VOC ADSORBED TONS/YR	COST/TON VOC ADSORBED
1 EDC	0.05	500	200	2340	1.36	N/R	14000	51000	53278	0.20	271000
2 EDC	0.1	500	400	2340	2.73	N/R	14000	95000	97278	0.40	244000
3 EDC	0.5	500	2000	2340	13.64	REGEN	207000	21000	54679	2.01	27000
4 EDC	1.5	500	6000	2340	40.93	REGEN	209000	22000	56004	6.04	9300
5 EDC	3	500	12000	2340	81.87	REGEN	212000	23000	57492	12.08	4800
6 EDC	5	500	20000	2340	136.44	REGEN	212000	24000	58492	20.14	2900
7 EDC	0.05	1500	67	7020	0.45	N/R	17000	90000	92766	0.19	498000
8 EDC	0.1	1500	133	7020	0.91	N/R	17000	177000	179766	0.39	464000
9 EDC	0.5	1500	666	7020	4.55	N/R	17000	443000	445766	2.00	223000
10 EDC	1.5	1500	2000	7020	13.64	REGEN	334000	30000	84342	6.03	14000
11 EDC	3	1500	4000	7020	27.29	REGEN	334000	32000	86342	12.07	7200
12 EDC	5	1500	6700	7020	45.48	REGEN	334000	35000	89342	20.13	4400
13 EDC	10	1500	13300	7020	90.96	REGEN	339000	37000	92155	40.28	2300
14 EDC	0.5	3500	285	16400	1.95	N/R	24000	439000	442905	1.98	224000
15 EDC	1.5	3500	856	16400	5.84	REGEN	439000	36000	107425	6.01	18000
16 EDC	3	3500	1712	16400	11.58	REGEN	452000	39000	112540	12.05	9300
17 EDC	5	3500	2854	16400	19.47	REGEN	452000	42000	115540	20.11	5700
18 EDC	10	3500	5707	16400	38.94	REGEN	453000	50000	123703	40.26	3100

Cost per ton of VOC Adsorbed

The costs per ton of VOC controlled by the carbon adsorber range from a low of $2100/ton to highs of $219,000/ton for TCE, $605,000/ton for DCE and $498,000/ton for EDC. The costs per ton decrease as the quantity of VOC being treated increases and the system size decreases.

As previously noted, Figure 1 shows the cost per ton of VOC adsorbed plotted against the groundwater concentration on a log-log scale. For the regenerative systems at air concentrations greater than 4 ppm, the costs per ton are very similar for the three chemicals. These have been plotted as one set of lines for the 500, 1500 and 3500 gal/min in flow rates. The VOC inlet rates for the regenerative systems are also shown, from 0.5 lb/hr to 10 lb/hr. It can be seen that for a given groundwater concentration, the cost per ton decreases when the water flow rate is increased because the VOC quantity being adsorbed also increases. Below 4 ppm, the nonregenerative systems show different costs per ton for each chemical because of the different carbon use rates. Best-fit lines have been plotted to show the general cost trends for these systems.

Combined System Costs

Table 5 shows the calculated annualized costs for air stripping, carbon adsorption controls and the combined systems. The control costs per ton of VOC adsorbed are shown for the three chemicals.

The annualized costs for the air stripper and the carbon adsorption systems were discussed in the previous sections. In comparing these costs, the additional costs for controls were found to range from 36 percent of the air stripping cost up to 426 percent of the air stripping cost for the extreme case. The smaller percentage additional control costs are generally found in the larger regenerative systems. It can be seen that the total cost of air stripping with controls generally increases as the system size and ground-water concentration increases. These total annualized costs range from $54,000 to $628,000 for TCE, $92,000 to $707,000 for DCE and $95,000 to $637,000 for EDC. Costs for the air stripper, carbon adsorber and the combined system were lowest for TCE. The highest costs for the air stripper and combined system were for EDC, while the highest carbon adsorber cost was for DCE.

Table 5
Estimated Air Stripper/Carbon Adsorption Control System Costs

TRICHLOROETHYLENE(TCE):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	ANNUALIZED COSTS: STRIPPER	ADSORBER	TOTAL	VOC REMOVED TONS/YR	TOTAL COST/TON VOC	COSTS PER 1000 GALLONS: STRIPPING	CONTROL	TOTAL
1 TCE	0.05	500	200	2340	27695	26278	53973	0.21	253000	0.11	0.10	0.21
2 TCE	0.1	500	400	2340	29020	41278	70298	0.43	163000	0.11	0.16	0.27
3 TCE	0.5	500	2000	2340	36647	53679	90326	2.18	41000	0.14	0.20	0.34
4 TCE	1.5	500	6000	2340	40460	55004	95464	6.56	15000	0.15	0.21	0.36
5 TCE	3	500	12000	2340	41786	55492	97278	13.13	7400	0.16	0.21	0.37
6 TCE	5	500	20000	2340	45437	55492	100929	21.89	4600	0.17	0.21	0.38
7 TCE	0.05	1500	67	7020	87222	40766	127988	0.20	632000	0.11	0.05	0.16
8 TCE	0.1	1500	133	7020	80758	71766	152524	0.42	362000	0.10	0.09	0.19
9 TCE	10	1500	13300	7020	83409	86155	169564	43.78	3900	0.11	0.11	0.22
10 TCE	0.5	3500	285	16400	151564	166905	318469	2.15	148000	0.08	0.09	0.17
11 TCE	1.5	3500	856	16400	148913	478905	627818	6.53	96000	0.08	0.26	0.34
12 TCE	3	3500	1712	16400	149076	109540	258616	13.10	20000	0.08	0.06	0.14
13 TCE	5	3500	2854	16400	155377	110540	265917	21.86	13000	0.08	0.06	0.14
14 TCE	10	3500	5707	16400	169143	113703	282846	43.76	6500	0.09	0.06	0.15

DICHLOROETHYLENE(DCE):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	ANNUALIZED COSTS: STRIPPER	ADSORBER	TOTAL	VOC REMOVED TONS/YR	TOTAL COST/TON VOC	COSTS PER 1000 GALLONS: STRIPPING	CONTROL	TOTAL
1 DCE	0.05	500	200	2340	27857	64278	92135	0.21	431000	0.11	0.24	0.35
2 DCE	0.1	500	400	2340	30183	119278	149461	0.43	346000	0.11	0.45	0.57
3 DCE	0.5	500	2000	2340	37810	54679	92489	2.18	42000	0.14	0.21	0.35
4 DCE	1.5	500	6000	2340	41623	57004	98627	6.56	15000	0.16	0.22	0.38
5 DCE	3	500	12000	2340	45437	58492	103929	13.13	7900	0.17	0.22	0.40
6 DCE	5	500	20000	2340	46599	59492	106091	21.89	4800	0.18	0.23	0.40
7 DCE	0.05	1500	67	7020	89548	112766	202314	0.20	998000	0.11	0.14	0.26
8 DCE	0.1	1500	133	7020	82084	221766	303850	0.42	721000	0.10	0.28	0.39
9 DCE	10	1500	13300	7020	87060	94155	181215	43.78	4100	0.11	0.12	0.23
10 DCE	0.5	3500	285	16400	156540	550905	707445	2.15	329000	0.09	0.30	0.38
11 DCE	1.5	3500	856	16400	145262	108425	253687	6.53	39000	0.08	0.06	0.14
12 DCE	3	3500	1712	16400	155215	113540	268755	13.10	21000	0.08	0.06	0.15
13 DCE	5	3500	2854	16400	161679	117540	279219	21.86	13000	0.09	0.06	0.15
14 DCE	10	3500	5707	16400	175445	127703	303148	43.76	6900	0.10	0.07	0.16

1,2-DICHLOROETHANE(EDC):

CASE NO.	VOC FLOW INLET (LB/HR)	WATER FLOW (GPM)	WATER CONC. (PPB)	AIR FLOW (ACFM)	ANNUALIZED COSTS: STRIPPER	ADSORBER	TOTAL	VOC REMOVED TONS/YR	TOTAL COST/TON VOC	COSTS PER 1000 GALLONS: STRIPPING	CONTROL	TOTAL
1 EDC	0.05	500	200	2340	41623	53278	94901	0.21	444000	0.16	0.20	0.36
2 EDC	0.1	500	400	2340	49250	97278	146528	0.43	339000	0.19	0.37	0.56
3 EDC	0.5	500	2000	2340	60691	54679	115370	2.18	53000	0.23	0.21	0.44
4 EDC	1.5	500	6000	2340	73131	56004	129135	6.56	20000	0.28	0.21	0.49
5 EDC	3	500	12000	2340	78270	57492	135762	13.13	10000	0.30	0.22	0.52
6 EDC	5	500	20000	2340	82084	58492	140576	21.89	6400	0.31	0.22	0.53
7 EDC	0.05	1500	67	7020	74457	92766	167223	0.20	825000	0.09	0.12	0.21
8 EDC	0.1	1500	133	7020	70643	179766	250409	0.42	594000	0.09	0.23	0.32
9 EDC	0.5	1500	666	7020	104802	445766	550568	2.17	253000	0.13	0.57	0.70
10 EDC	1.5	1500	2000	7020	124869	84342	209211	6.55	32000	0.16	0.11	0.27
11 EDC	3	1500	4000	7020	137635	86342	223977	13.12	17000	0.17	0.11	0.28
12 EDC	5	1500	6700	7020	152727	89342	242069	21.88	11000	0.19	0.11	0.31
13 EDC	10	1500	13300	7020	166655	92155	258810	43.78	5900	0.21	0.12	0.33
14 EDC	0.5	3500	285	16400	194512	442905	637417	2.15	296000	0.11	0.24	0.35
15 EDC	1.5	3500	856	16400	207116	107425	314541	6.53	48000	0.11	0.06	0.17
16 EDC	3	3500	1710	16400	272620	112540	385160	13.10	29000	0.15	0.06	0.21
17 EDC	5	3500	2850	16400	292850	115540	408390	21.86	19000	0.16	0.06	0.22
18 EDC	10	3500	5707	16400	343425	123703	467128	43.76	11000	0.19	0.07	0.25

Cost Estimates by Volume of Groundwater Treated

In evaluating the costs of groundwater treatment technologies, as well as drinking water and wastewater treatment technologies, the cost/volume of water treated frequently is used as a basis for comparison. Table 5 shows these costs in $/1000 gallons of groundwater treated. It can be seen that the costs range from 8 cents 31¢/1000 gallons for air stripping alone. When carbon adsorption controls are added, the total costs range from 14 to 70¢/1000 gallons.

The costs per 1000 gallons of water treated generally is reduced when the size of the stripping operation is increased and the groundwater concentration is reduced. This trend is opposite from the trend indicated by the cost per ton of VOC treated. The cost/1000 gallons may be a better indicator for evaluating system costs because the treatment rate

for groundwater is constant and variations in groundwater concentration do not drastically affect these costs. The costs per ton of VOC treated, however, are directly affected by the groundwater concentration, which is likely to fluctuate. In many applications, groundwater is moving through an aquifer and it is impossible to accurately predict the quantity of VOC that will be removed over a given period of time. When an air stripping system is only removing a fraction of a ton of VOC/year of operation, the cost per ton of VOC treated becomes a large, abstract number that does not necessarily reflect the actual cost of the system.

DATA LIMITATIONS AND CONCLUSIONS

The cost data generated are based on simplified assumptions and theoretical models and are valid only for the single chemicals in groundwater. The adsorption capacity of carbon actually varies with varying chemical concentration and can vary with different brands of carbon. This variation in treatability can have a significant impact on carbon use and the cost for the nonregenerative units. The design of a practical air stripping system with vapor phase carbon adsorption controls at a specific Superfund site would require a more detailed analysis than was possible to include in this study. For example, the costs generated by PDQ$ for the air stripping columns are for carbon steel. In many cases an FRP (fiberglass reinforced plastic) or a stainless steel column may be more desirable, at a different cost. Most Superfund sites contain a variety of different chemical contaminants. The air stripper must be designed for the chemical with the worst stripping characteristics, while the carbon adsorption system must be designed for chemical com-

binations with potentially complex adsorption relationships. The air stripper also should be designed for the lowest expected operating temperatures.

The cost per ton of VOC removed is extremely sensitive to the tons/year of VOC adsorbed. A minor variation in tons/year of VOC at low concentrations will produce a significant change in the cost per ton of VOC removed. The system with the lowest VOC input and lowest annualized cost can also have the highest cost per ton of VOC removed.

The cost data presented may be used as relative indicators of cost trends for air stripping and carbon adsorption control systems. Real world systems at Superfund sites may vary widely from these numbers depending on a variety of site-specific conditions.

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High Energy Electron Beam Irradiation: Quantitative Evaluation of Factors Affecting Removal of Toxic Chemicals From Aqueous Solution

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ABSTRACT

Irradiation of water with high energy electrons results in the formation of three reactive free radicals: $e^-(aq)$, $H\cdot$ and $OH\cdot$. Once formed, these free radicals react with organic solutes in aqueous solution. Full-scale experiments, conducted at our Electron Beam Research Facility, will be compared to parallel bench-scale studies, conducted at a ^{60}Co facility, for the removal of chloroform and carbon tetrachloride from aqueous solutions. Additional results obtained at the E-Beam facility will describe removal efficiencies obtained for chemicals of interest in site remediation. The results of these studies have led to a better understanding of the factors affecting the removal of the organic compounds of interest to Superfund.

INTRODUCTION

Soils, sediments and groundwater have been contaminated with hazardous compounds in many areas of the country, many of which may persist for considerable periods in the environment. Because of this contamination and the recalcitrant nature of many of the chemicals, it is of interest to develop processes which will effectively and efficiently remove these compounds from aqueous solutions. Effective technology might be defined as that technology which results in the ultimate disposal of the chemicals, not merely a transfer from one environmental compartment to another. Efficiency should consider not only the cost question, but also the overall effectiveness of the process in solving the problem.

High energy electron irradiation is an innovative treatment process which is being developed as an ultimate disposal process for toxic and hazardous organic chemicals. Experiments conducted to date have focused upon their removal from aqueous solutions of varying water quality, i.e., raw wastewater to potable water. Recently, experiments have been initiated which indicate that the process also will work well on sludges.

Table 1 outlines the most frequently found hazardous chemicals at Superfund sites in the United States. Table 2 outlines organic compounds recently added to the list of compounds to be regulated as hazardous. Many of the organic compounds on these lists have been studied at the Electron Beam Research Facility in Miami, Florida. It is possible to use ^{60}Co gamma irradiation to simulate the high energy electron irradiation process. The advantage of conducting studies using gamma irradiation is that smaller volumes can be used and the solutes can be studied in distilled water and in aqueous solutions of defined composition. Reaction byproduct analyses can be conducted much easier in a well-defined aqueous medium and the results confirmed at full-scale and in natural waters.

This paper focuses upon the results of full-scale high energy electron irradiation and batch ^{60}Co gamma irradiation for the removal of chloroform and carbon tetrachloride from aqueous solutions. Studies conducted at both the ^{60}Co and the Electron Beam Research Facility will be compared and a quantitative relationship defined to relate removal efficiency under both conditions.

RADIATION CHEMISTRY OF NATURAL WATERS

The purpose of this section is to provide an overview of aqueous-based radiation chemistry. This brief introduction should assist the reader in understanding the application of high energy electron irradiation to the treatment of toxic and hazardous organic wastes in natural waters.

Table 1
25 Most Frequently Identified Substances At 546 Superfund Sites Adapted from McCoy & Assoc., "Haz. Waste Consult." 3:2(1985))

Rank	Substance	Percent of Sites
1	Trichloroethylene	33
2	Lead and Compounds	30
3	Toluene	28
4	Benzene	26
5	Polychlorinated Biphenyls (PCBs)	22
6	Chloroform	20
7	Tetrachloroethylene	16
8	Phenol	15
9	Arsenic and Compounds	15
10	Cadmium and Compounds	15
11	Chromium and Compounds	15
12	1,1,1-Trichloroethane	14
13	Zinc and Compounds	14
14	Ethylbenzene	13
15	Xylene	13
16	Methylene Chloride	12
17	trans-1,2-Dichloroethylene	11
18	Mercury	10
19	Copper and Compounds	9
20	Cyanides (soluble salts)	8
21	Vinyl Chloride	8
22	1,2-Dichloroethane	8
23	Chlorobenzene	8
24	1,1-Dichloroethane	8
25	Carbon Tetrachloride	8

Table 2
Organic Compounds Recently Added to the List of
Chemicals to be Regulated as Hazardous

Table 2. Organic Compounds Recently Added to the List of Chemicals to be Regulated as Hazardous.	
Compound	Regulatory Level (mg L^{-1})
Benzene	0.5
Carbon Tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Heptachlor	0.008
Hexachlorobenzene	0.13
Hexachloro-1,3-butadiene	0.13
Hexachloroethane	3.0
Methyl Ethyl Ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Tetrachloroethylene	0.7
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
Vinyl Chloride	0.2

The literature relating to radiation chemistry most often reports experiments conducted in pure water. The extrapolation of pure water data to natural waters is complicated by the presence of inorganic and organic matter (primarily humic substances) found in natural waters. These compounds may interact with the reactive species formed during irradiation and lead to side reactions not observed in pure water. Examples of these processes are the reactions of hydroxyl radical with carbonate and halide ions.

Irradiation of pure water with fast electrons has been studied extensively with numerous excellent reviews on the subject.[1-3] The fast electrons can be generated either by ^{60}Co or by electron accelerators. It is thought that the initial radiation process (10^{-16}-10^{-14} sec) results in the formation of excited molecules H_2O^*, H_2O^+ and e^- [4] As these excited state molecules and electrons interact and transfer their energy, several secondary reactive species are formed:

$$H_2O -/\backslash /\backslash /\backslash-> e^-(aq) (2.6), H\cdot (0.55), OH\cdot (2.7), H_2 (0.45), H_2O_2 (0.71), H_3O^+ (2.7) \quad (1)$$
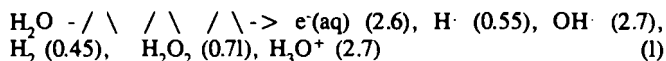
The efficiency of the conversion of energy from ionizing radiation to chemical energy is described by G values. G is defined as the number of radicals, excited states or other products, formed (or lost) in a system absorbing 100 eV of energy. The G value for the formation of the secondary products of irradiation are indicated in parenthesis in Equation (1).

The three free radicals formed are the most reactive species. The $e^-(aq)$ and H· are reducing radicals and the OH· is an oxidizing radical.[5-8] Of these radicals, the aqueous electron and hydroxyl radical account for greater than 90% of the reactive species. Thus, the chemistry of primary interest in this process is that of these two species. However, it is possible that the presence of H_2O_2 may also contribute to the removal of organic toxic and hazardous wastes.

Aqueous Electron

The reactions of the aqueous electron, $e^-(aq)$, with specific organic and inorganic compounds has been studied extensively.[4-6,9] The $e^-(aq)$

is a powerful reducing reagent with an $E°$ ($e^-(aq) + H \longrightarrow \frac{1}{2}H_2$) of 2.77. The reactions of the $e^-(aq)$ are single electron transfer, the general form of which is:

$$e^-(aq) + S^N \longrightarrow S^{N-1} \quad (2)$$

The $e^-(aq)$ reacts with numerous organic chemicals and of particular interest to the field of toxic and hazardous wastes are the reactions with halogenated compounds. A generalized reaction is shown below:

$$e^-(aq) + RCl \longrightarrow R + Cl^- \quad (3)$$

Thus, reactions involving the $e^-(aq)$ may result in the dechlorination of organohalogen compounds. Further reaction of the organic radical formed could result in the complete destruction of the compound and specific examples are given below. The $e^-(aq)$ also reacts with other organic compounds and would contribute to the removal of these compounds from aqueous solutions. Examples of the rate constants of reactions of interest in this area are presented later in this paper.

Hydrogen Radical

The reactions of H· with organic and inorganic compounds have also been summarized.[10] The hydrogen atom accounts for approximately 10% of the total free radical concentration in irradiated water. The H· undergoes two general types of reactions with organic compounds, hydrogen addition and hydrogen abstraction.

An example of a typical addition reaction with an organic solute is that of benzene:

$$H\cdot + C_6H_6 \longrightarrow \quad (4)$$

The second general reaction involving the H· is hydrogen abstraction:

$$H\cdot + CH_3OH \longrightarrow H_2 + CH_2OH \quad (5)$$

Since most natural waters likely to be encountered will be oxygenated, the predominate reaction for H· will be:

$$H\cdot + O_2 \longrightarrow HO_2 \quad (6)$$

This reaction has a second order rate constant of 2.1 x 10^{10}/m. sec. Therefore, it is assumed that the H· is of minimal importance in the removal of toxic and hazardous organic compounds from oxygenated aqueous solutions.

Hydroxyl Radical

Reactions of the hydroxyl radical, OH·, with inorganic and organic compounds has been well-documented.[6] Compilations of rate constants have been published.[7,10] OH· can undergo several types of reactions with chemicals in aqueous solution. The types of reactions that are likely to occur are addition, hydrogen abstraction, electron transfer and radical-radical recombination.

Addition reactions occur readily with aromatic and unsaturated aliphatic compounds. The resulting compounds are hydroxylated radicals:

$$OH\cdot + CH_2=CH_2 \longrightarrow HOCH_2-CH_2 \quad (7)$$

Hydrogen abstraction occurs with saturated and many unsaturated molecules, e.g., aldehydes and ketones:

$$OH\cdot + CH_3-CO-CH_{33} \longrightarrow CH_2COCH_3 + H_2O \quad (8)$$

Reactions involving halogen ions (X⁻) may also be significant:

$$OH\cdot + X^- \longrightarrow X + OH^- \quad (9)$$
$$X + X^- \longrightarrow X_2^- \quad (10)$$

The X_2 can further react with organic molecules possibly forming halogenated organic compounds. The halogens of most interest are Cl⁻ and Br⁻.

Another inorganic radical likely to be involved is the carbonate radical, CO_3^-. CO_3^- is formed by OH· reaction with CO_3^{2-}. The importance of the carbonate radical is as yet unknown, but because of its relatively

low reactivity with organic compounds, it probably will play a relatively unimportant role in their removal from aqueous solution. However, the presence of high concentrations of CO_3^{2-} may have a positive effect on the effective concentration of $e^-(aq)$ by removing OH^- from solution. This situation would result in an increased removal efficiency of compounds which primarily react with $e^-(aq)$.

Hydrogen Peroxide

In oxygenated aqueous solutions, the reactions of O_2 with $e^-(aq)$ and H^- occur and compete for the reactive intermediates formed in Equation 1. Both of these reactions result in the formation of reduced oxygen:

$$e^-(aq) + O_2 ----> O_2^- \tag{11}$$
$$H^- + O_2 ----> HO_2 \tag{12}$$

The products of Equation (11) and (12) are in equilibrium, with a pK_a = 4.5. These products also lead to the formation of additional H_2O_2:

$$2O_2^- + 2H^+ ----> H_2O_2 + O_2 \tag{13}$$
$$2HO_2 ----> H_2O_2 + O_2 \tag{14}$$
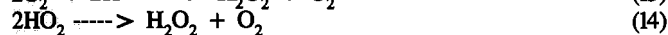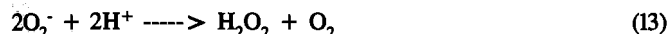
One of the interesting reactions that has been studied is the following:

$$e^-(aq) + H_2O_2 ---> OH + OH^- \tag{15}$$

with a second order rate constant of 1.2-1.4×10^{10}/m. sec. In our study, with the high and continuous radiation dose, it appears that H_2O_2 might serve as a secondary source of OH^-.

ELECTRON BEAM RESEARCH FACILITY

Plant Description

The Electron Beam Research Facility is located at the Virginia Key (Central District) Wastewater Treatment Plant. It was originally installed as a substitute technology for heat-treatment disinfection of sludge and was declared operational on September 25, 1984. The actual project construction costs at that time were approximately 1.7 million dollars.

The accelerator is a horizontal 1.5 MeV electron beam, rated at 50 mA. The beam current is continuously variable from 0 to 50 mA, providing doses of 0 - 850 krads.

The research facility was designed to treat 460 L/min (120 gpm); however, experiments have been conducted using flows of up to 610 L/min. The minimum flow is approximately 380 L/min (100 gpm). Originally designed to disinfect digested sludge, 2-8% solids, the present configuration allows for several influent streams. The influent streams directly connected to the plant are potable (drinking) water, a secondary wastewater effluent and anaerobically digested sewage sludge. The secondary wastewater is the effluent of an extended (pure oxygen) aeration process. The effluent is chlorinated immediately (0.5 - 1 min.) prior to the intake of the electron beam.

In addition to the three flow streams described above, we have the capacity to conduct large-scale (22,400 L) batch experiments using tank trucks. Batch experiments may be used for groundwater and any other source of contaminated water for which treatability studies are desired. The minimum batch experiment is 7,600 L.

The electron beam (E-Beam) research facility has been instrumented to continuously monitor and record various operating parameters; accelerating voltage, beam current, water flow and absorbed dose. The absorbed dose is measured using five resistance temperature devices (RTDs). The five RTDs are mounted in the influent (2 sensors) and effluent (3 sensors) stream immediately before and after the beam. All of the variables are connected via an interface board (Strawberry, Inc.) to a portable computer (Compaq, Inc.) which continuously reads and records temperatures.

Measurement of Absorbed Dose

Absorbed dose is a measure of energy transfer to the irradiated material, in this case, water. In a continuously flowing aqueous system, the absorbed dose can be estimated by measuring the temperature difference of the water stream before and after irradiation as follows:

$$1000 \text{ Krad} = 1.0 \times 10^8 \text{ erg/g} = 2.39 \text{ cal/g} \tag{16}$$

By converting cal/g to temperature in degrees centigrade, 1000 Krads is equivalent to a temperature change of 2.39°C. Therefore, the total absorbed dose (D_t) in pure water is calculated using the equation:

$$D_t = K(t_2 - t_1) \tag{17}$$

where t_1 and t_2 are the before and after irradiation water temperature of the flowing stream in °C, respectively; and K is the constant of proportionality:

$$K = 418 \text{ krads/°C} \tag{18}$$

The measurement of D_t provides an estimate of absorbed dose in natural waters. A slight error results from the deviation from unit density (pure water) of the natural waters. The application of temperature difference to estimate the absorbed dose in irradiated sludges would result in an error which would increase with increasing solids content.

Electron Utilization Efficiency

It is possible to estimate the electron utilization efficiency of the system at the Electron Beam Research Facility described above. Assuming that the system is operated at full power, i.e., 1.5 MeV and 50 mA, total beam power of 75 kW and a flowrate of 470 L/min, then the efficiency may be determined as follows:

$$1 \text{ W} = 860 \text{ cal/hr} \tag{19}$$
$$75 \text{ kW} = 6.45 \times 10^7 \text{ cal/hr} \tag{20}$$

Assuming that 1 cal results in a 1.0 C increase in temperature per gram, complete conversion of electrical energy (beam power) to heat would result in a D_t of:

$$D_t = 6.45 \times 10^7 \text{ cal/hr} / 2.73 \times 10^7 \text{ mL/hr} = 2.36°C \tag{21}$$

We observed a 1.54°C increase in temperature (645 krads). Therefore, the efficiency of the conversion of beam energy to heat was:

$$\text{efficiency (\%)} = 1.54°C/2.36°C \times 100 = 65.3 \% \tag{22}$$

In limited experiments at high water flowrates, 610 L/min the dose was unchanged, i.e., 645 krads or 1.54°C increase in temperature and the efficiency approached 86%. The reasons for the increase in efficiency probably were related to the more complete absorption of the fast electrons in the solution (increased depth of the water) and at the higher flowrate, the water cascaded over the weir nearer to the electron gun window, reducing energy losses in the air between the window and the water.

^{60}Co GAMMA SOURCE RESEARCH FACILITY

More than 20 years of research have demonstrated the reduction of chemical and microbiological contaminants from aqueous-based systems with ^{60}Co-Gamma radiation.[11,12] ^{60}Co represents an unstable nucleus of cobalt. ^{59}Co, when placed in a reactor, will absorb a neutron and become ^{60}Co:

$$^{59}\text{Co} + {}^1\text{n} ----> {}^{60}\text{Co} \tag{23}$$

As the ^{60}Co returns to a stable condition, it releases mass-energy in the form of one beta particle and two gamma rays. This process results in the stable isotope ^{60}Ni.

$$^{60}\text{Co} ----> {}^{60}\text{Ni} + \beta^- + 2\tau \tag{24}$$

Beta (β) particles are electrons and have very little penetrating ability when released from ^{60}Co.[13] When ^{60}Co is encapsulated in stainless steel, all of the beta particles are stopped and only the highly penetrating gamma rays escape into the surrounding medium. Gamma rays are not deflected by an electric or magnetic field and have no charge. They are electromagnetic waves with extremely short wavelengths and are very penetrating.

Gamma rays in water produce a decomposition of water similar to that observed with high-energy electrons. Interaction of gamma rays and water is on the molecular level and not on the nuclear level. Gamma

rays must possess at least 1.50 MeV of energy to enter a nucleus and even at this elevated energy level, photonuclear cross sections are extremely small.[14] Because gamma rays from ^{60}Co are emitted at energies of 1.17 and 1.33 MeV, residual nuclear activity in the water or wastewater is not observed.

^{60}Co Reactor Description

The ^{60}Co reactor is a 5000 Ci gamma source located at the University of Miami Radiation Control Center. The gamma source is located at the center of concentric circles of 10, 20, 30, 40, 50, 60, 70 and 100 cm. A linear regression of a ln/ln plot of distance versus dose rate was generated to determine the dose rate at any distance from the ^{60}Co source:

$$\ln \text{(dose rate)} = -1.958 \times \ln \text{(distance)} + 13.356 \qquad (25)$$

REMOVAL OF SELECTED ORGANIC CHEMICALS IN AQUEOUS SOLUTION

We have conducted numerous experiments on organic chemicals that may be of interest in: water treatment, trihalomethanes; groundwater contamination, halogenated ethanes and ethenes; leaking underground storage tanks, benzene and substituted benzenes; as well as other organic chemicals now regulated as hazardous wastes. Before presenting removal efficiencies, a brief discussion and summary of the rate constants is presented for the compounds that have been studied or are of interest in the area of toxic and hazardous wastes.

Rate Constants

The rate constants of interest are those for the reaction of the reactive intermediates formed when water is irradiated (Equation 1), e^-(aq), H· and OH·. with toxic and hazardous organic chemicals and inorganic chemicals likely to be found in natural waters. A review of the literature[10] for selected rate constants applicable to toxic and hazardous wastes is summarized in Table 3.

Removal Efficiencies

Most of the results shown below, conducted on a large-scale treatment facility, appear to be qualitatively explained using available rate constants. However, other results do not fit the available rate data. These differences are not surprising given that the rate data reported in the literature usually are obtained in pure solutions under controlled experimental conditions. Thus, there may be several reasons for the apparent discrepancies. First, all of the experiments have been conducted in raw or secondary treated wastewater or potable water. These waters are of widely varying (water) quality and present a complex matrix for detailed examination of removal data. Secondly, not all of the applicable rate constants are known for the compounds of interest.

To date, the only compound which has been studied at both the Electron Beam Research Facility and the ^{60}Co Research Facility is chloroform. Chloroform is listed as the sixth most frequently identified substance at 546 Superfund Sites (Table 1). Others have reported studies using electron and gamma irradiation of aqueous solutions of chloroform.[15,16] We have observed removal efficiencies of CHCl$_3$ of approximately 99.9% in distilled water (Figs 1 and 2) using ^{60}Co irradiation. This removal was not affected by the initial concentration of CHCl$_3$ when it was varied from 125 to 1250 ug/L. At the electron beam research facility, similar studies were conducted using potable water (Figs. 3 and 4). Experiments not shown in secondary and raw wastewater have shown removal efficiencies of 85 - 95%.

A proposed mechanism for the decomposition of CHCl$_3$ and the formation of reaction byproducts has been suggested:[16]

$$e^-(aq) + CHCl_3 \quad \longrightarrow \quad Cl^- + CHCl_2 \qquad (26)$$
$$H + CHCl_3 \quad \longrightarrow \quad H_2 + CCl_3 \qquad (27)$$
$$\longrightarrow \quad HCl + CHCl_2 \qquad (28)$$
$$OH + CHCl_3 \quad \longrightarrow \quad H_2O + CCl_3 \qquad (29)$$
$$CHCl_2 + H_2O \quad \longrightarrow \quad CHO + 2HCl \qquad (30)$$
$$CCl_3 + 2H_2O \quad \longrightarrow \quad COOH + 3HCl \qquad (31)$$
$$COOH + COOH \quad \longrightarrow \quad HOOC\text{-}COOH \qquad (32)$$

$$\longrightarrow \quad HCOOH + CO_2 \qquad (33)$$
$$CHO + HCCl_3 + H_2O \longrightarrow CHCl_2 + HCOOH + HCl \quad (34)$$
$$H + CHCl_3 \quad \longrightarrow \quad CH_2Cl_2 \qquad (35)$$
$$CHCl_2 + CHCl_2 \quad \longrightarrow \quad CHCl_2CHCl_2 \qquad (36)$$
$$CCl_3 + CHCl_2 \quad \longrightarrow \quad CCl_3CHCl_2 \qquad (37)$$
$$CCl_3 + CCl_3 \quad \longrightarrow \quad CCl_3CCl_3 \qquad (38)$$
$$H + CHO \quad \longrightarrow \quad HCHO \qquad (39)$$
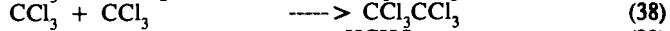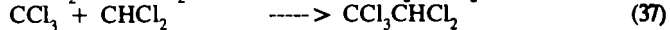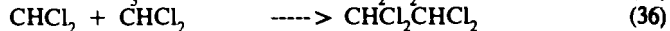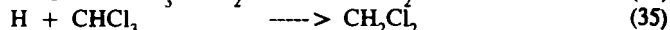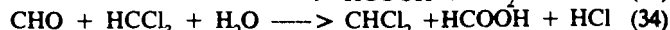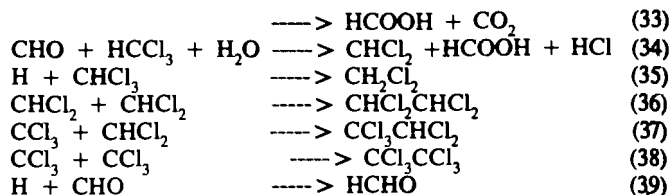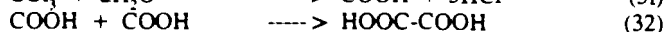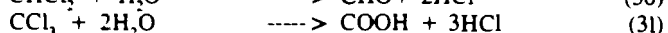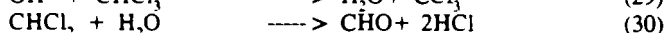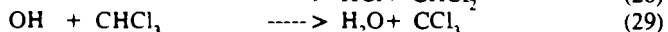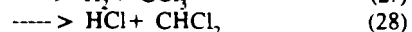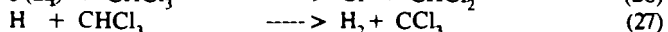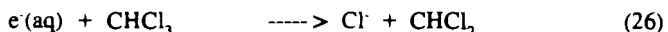
and in solutions with high O_2 concentrations the following reactions are also possible:

$$CHCl_3 + O_2 \quad \longrightarrow \quad O_2CHCl_3 \qquad (40)$$
$$CCl_3 + O_2 \quad \longrightarrow \quad O_2CCl_3 \qquad (41)$$
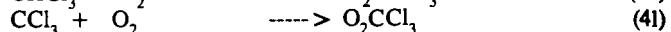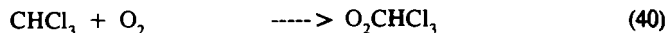
with the exact fate of these radicals unknown.

The major differences between the work which resulted in the above reaction mechanism[16] and our work are: (1) the concentration of the CHCl$_3$ was 70 mm, whereas the concentration range we have been studying is 1000-fold less and (2) the irradiation doses we use are up to 100-fold higher. In our studies, conducted at low solute concentrations, none of the halogenated reaction byproducts have been observed. The liquid-liquid extraction method used for the quantification of the CHCl$_3$ would also have determined the presence of the chlorinated ethanes at detection limits of 0.01 μL. The authors[12] found that the presence of O_2 enhanced the decomposition of the CHCl$_3$. This finding is important because many of the systems in which this process potentially will be used involve solutions which will have been aerated or at least contain some O_2.

Table 3
Rate Constants (1/m. sec.) of Selected Organic Chemicals and the Free Radicals Formed in Irradiated Aqueous Solution[10]

Compound	$e^-_{(aq)}$	$H\cdot$	$OH\cdot$
Benzene	9.0×10^8	9.1×10^8	7.8×10^9
Bromodichloromethane	NF	NF	NF
Bromoform	NF	NF	NF
Carbon Tetrachloride	1.6×10^{10}	3.8×10^7	NF
Chlorobenzene	5.0×10^8	1.4×10^9	5.5×10^9
Chloroform	3.0×10^{10}	1.1×10^7	5×10^6
o-Cresol	NF	NF	1.1×10^{10}
m-Cresol	NF	NF	1×10^{10}
p-Cresol	4.2×10^7	NF	1.2×10^{10}
Dibromochloromethane	NF	NF	NF
1,2-Dichlorobenzene	4.7×10^9	NF	NF
1,3-Dichlorobenzene	5.2×10^9	NF	NF
1,4-Dichlorobenzene	5.0×10^9	NF	NF
1,1-Dichloroethane	NF	NF	NF
1,2-Dichloroethane	NF	NF	NF
1,1-Dichloroethylene	NF	NF	NF
trans-1,2-Dichloroethylene	7.5×10^9	NF	6.2×10^9
2,4-Dinitrotoluene	NF	NF	NF
Ethylbenzene	NF	NF	7.5×10^9
Hexachlorobenzene	NF	NF	NF
Hexachloro-1,3-butadiene	NF	NF	NF
Hexachloroethane	NF	NF	NF
Methylene Chloride	NF	NF	NF
Methyl Ethyl Ketone	NF	NF	NF
Nitrobenzene	3.7×10^{10}	1.0×10^9	3.9×10^9
Pentachlorophenol	NF	NF	NF
Phenol	2.0×10^7	1.7×10^9	6.6×10^9
Pyridine	1.0×10^9	7.8×10^8	3.1×10^9
Tetrachloroethylene	1.3×10^{10}	NF	2.8×10^9
Toluene	1.4×10^7	2.6×10^9	3.0×10^9
1,1,1-Trichloroethane	NF	NF	NF
Trichloroethylene	1.9×10^9	NF	4.0×10^9
2,4,5-Trichlorophenol	NF	NF	NF
2,4,6-Trichlorophenol	NF	NF	NF
Vinyl Chloride	2.5×10^8	NF	1.2×10^{10}
o-Xylene	NF	2.6×10^9	7.5×10^9
m-Xylene	NF	2.0×10^9	6.7×10^9
p-Xylene	NF	3.2×10^9	7.0×10^9

Many experiments conducted at low pH.
NF = not found.

Whether the above mechanism describes the actual breakdown process in natural waters will never be known quantitatively. The importance of the above mechanism (Equations 26-41) is that it provides a point of departure for determining other possible reaction products. We have observed, in preliminary research, that oxidized organic compounds, such as formaldehyde, are formed. Continuing research is underway using analytical methods for the determination of very low concentrations of aldehydes and carboxylic acids.

Another group of organic chemicals that have been studied at our treatment facility are the halogenated solvents. The compounds most commonly found are trichloroethylene (TCE) and tetrachloroethylene (PCE). Radiation-induced decomposition of TCE in aqueous solutions has been the subject of several recent studies.[17-22] An example of the removal efficiency we have obtained in raw wastewater is shown in Figure 5. In most of the referenced studies conducted to date, the complete destruction of TCE was observed. Although the preliminary data indicated a relationship between removal efficiency and second order reaction rate constants of OH·, it is also possible that the e⁻(aq) may be in part responsible for the removal of TCE. We have also conducted studies on the removal of tetrachloroethylene in secondary chlorinated wastewater (Figure 6).

POTABLE WATER

Figure 3
Removal of CHCL$_3$, using ^{60}Co, at several irradiation doses in distilled water at an initial concentration of approximately 100 ug/L (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point)
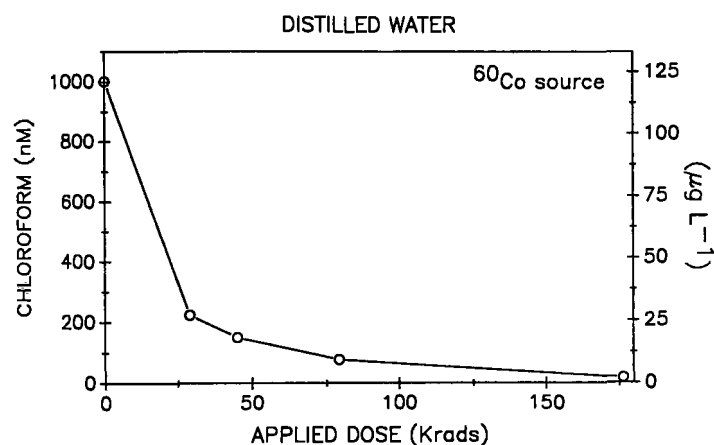
DISTILLED WATER

Figure 1
Removal of CHCL$_3$, using ^{60}Co, at several irradiation doses in distilled water at an initial concentration of approximately 125 ug/L (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point)

POTABLE WATER
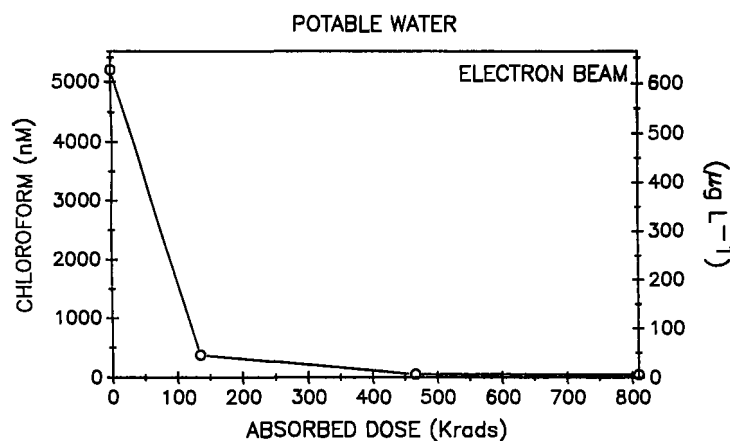
Figure 4
Removal of CHCL^3, using the Electron Beam Research Facility, at several irradiation doses indistilled water at an initial concentration of approximately 600 ug/L error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point)

DISTILLED WATER

Figure 2
Removal of CHCL$_3$, using ^{60}Co, at several irradiation doses in distilled water at an initial concentration of approximately 1250 ug/L (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point)
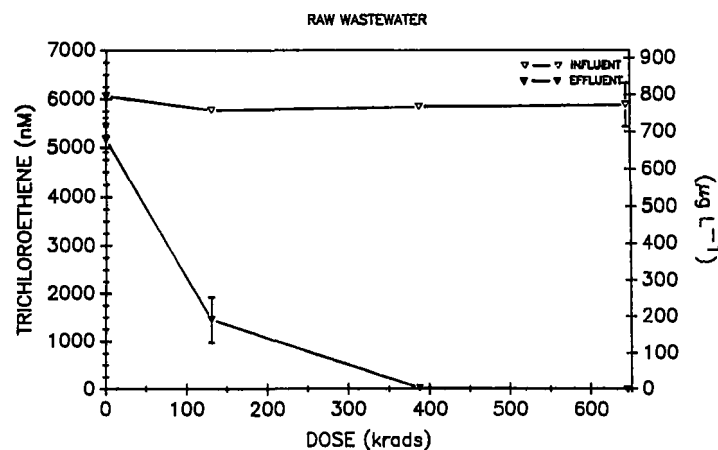
RAW WASTEWATER

Figure 5
Removal of TCE at several irradiation doses in raw wastewater (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point)
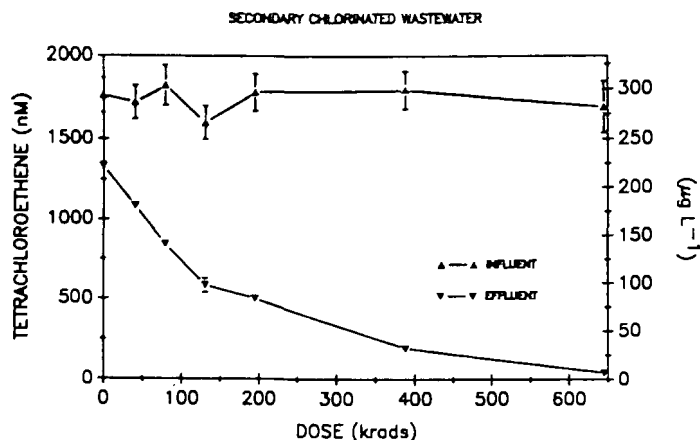
Figure 6
Removal of PCE at several irradiation doses in
secondary wastewater (error bars indicate one standard
deviation from mean, where no error bars are seen the error
is within the data point)

Considerable research has also been reported on the irradiation of aqueous solutions of PCE.[17-20, 22-25] As with TCE, it appears that complete destruction occurs as evidenced by chloride ion mass balance. This observation, insofar as loss of the parent compound PCE, has been confirmed in our studies in potable water. In secondary wastewater, removal was < 95% while in raw wastewater the removal was > 95% (Fig. 6). It is remarkable that there is little, if any, difference in the removal efficiency of PCE in raw and secondary wastewater. A possible explanation of this phenomenon is that the presence of relatively high concentrations of organic compounds in these two waters results in less recombination of the e⁻(aq) and OH⁻. By reducing the recombination of these two species, their effective concentrations in solution increase and result in similar removal efficiencies. Mechanisms for the destruction of both TCE and PCE have been proposed and presently are under investigation in continuing studies.

Another example of a removal efficiency using high energy electron irradiation is shown in Figure 7 for carbon tetrachloride. This chemical is persistent in subsurface environments and is not effectively treated using other oxidation processes. High energy electron irradiation appears to be an excellent choice for its destruction.
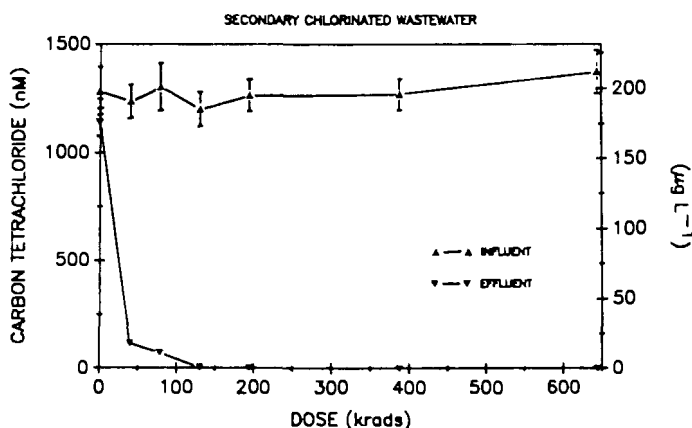
Figure 7
Removal of carbon tetrachloride at several irradiation doses in
secondary wastewater (error bars indicate one standard
deviation from mean, where no error bars are seen the error
is within the data point)

A third group of compounds which we have studied are benzene and substituted benzenes. Numerous studies have been reported on the effect of irradiation of aqueous solutions of benzene.[26-33] In other studies

we have also shown that benzene is very effectively removed from an oxygenated secondary wastewater effluent. Shown in Figures 8 and 9 are the removal efficiencies of chlorobenzene and ethylbenzene in secondary wastewater. We have shown that at low irradiation doses, phenols are formed. However at higher doses, these compounds are removed with a net removal of total phenols of approximately 50%. We also were able to identify formaldehyde and glyoxal in sub-μM concentrations in several samples. Several other aldehydes were observed, but the structures of these reaction products have not yet been determined. Additional studies are underway to determine all of the reaction byproducts.
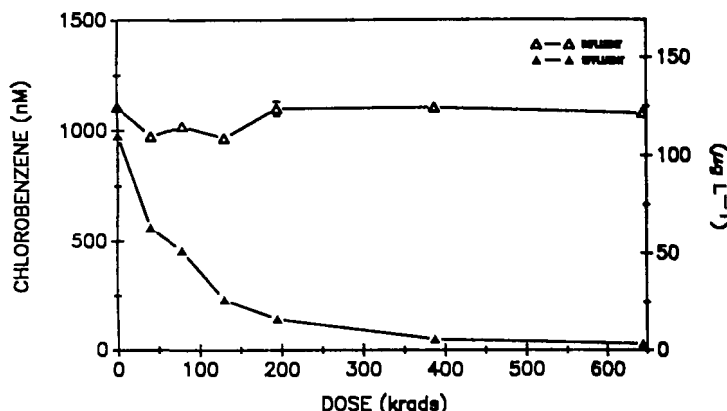
Figure 8
Removal of chlorobenzene at several irradiation doses in
secondary wastewater (error bars indicate one standard
deviation from mean, where no error bars are seen the error
is within the data point)
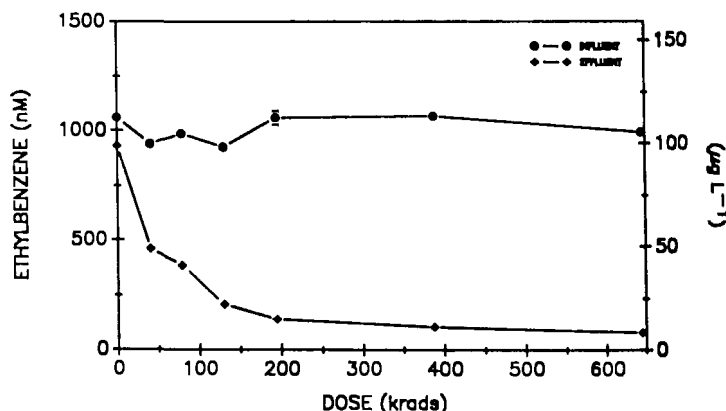
Figure 9
Removal of ethylbenzene at several irradiation doses in
secondary wastewater (error bars indicate one standard
deviation from mean, where no error bars are seen the error
is within the data point)

CONCLUSIONS

The results reported here are part of an ongoing project which will extend the data base to other chemicals of concern to Superfund. The use of high energy electron beam irradiation appears to be an efficient process for the destruction of all organic compounds of interest in site remediation.

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U.S. EPA's Mobile Volume Reduction Unit for Soil Washing

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ABSTRACT

This paper discusses the design and initial operation of the U.S. EPA's Mobile Volume Reduction Unit (VRU) for soil washing. Soil washing removes contaminants from soils by dissolving or suspending them in the wash solutions (which can be treated later by conventional wastewater treatment methods) or by volume reduction through simple particle size separation techniques. Contaminants are primarily concentrated in the fine-grained (0.0025 inches) soil fraction. The VRU is a pilot-scale mobile system for washing soil contaminated with a wide variety of heavy metal and organic contaminants. The unit includes state-of-the-art washing equipment for field applications.

The VRU equipment was originally conceived by the U.S. EPA. It was designed and fabricated by Foster Wheeler Enviresponse, Inc. under contract to U.S. EPA's Risk Reduction Engineering Laboratory (RREL) in Edison, New Jersey, with the following objectives:

- To make available to members of the research community and to the commercial sector the results of government research on a flexible, multistep, mobile, pilot-scale soil washer capable of running treatability studies on a wide variety of soils
- To demonstrate the capabilities of soil washing
- To provide data that facilitate scale-up to commercial size equipment

The design capacity of the VRU is 100 lb/hr of soil, dry-basis. The VRU consists of process washing equipment and utility support services mounted on two heavy-duty semitrailers. The process trailer equipment accomplishes material handling, organic vapor recovery, soil washing, coarse soil screening, fine particle separation, flocculation/clarification and steam generation via a boiler. The utility trailer carries a power generator, a process water cleanup system and an air compressor. The VRU is controlled and monitored by conventional industrial process instrumentation and hardware.

Shakedown operations are currently in progress, and future plans include testing U.S. EPA-produced synthetic soil matrix (SSM) spiked with specific chemical pollutants. The addition of novel, physical/chemical treatment processes, such as sonic/ultrasonic cleaning and acid leaching, will expand the VRU's extraction capability in soil decontamination.

INTRODUCTION

Section 121(b) of the CERCLA mandates the U.S. EPA to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants and contaminants as a principal element."

In most cases, soil washing technologies are used in conjunction with other remedial methods for the separation/segregation and volume reduction of hazardous materials in soils, sludges and sediments. In some cases, however, the process can deliver the performance needed to reduce contaminant concentrations to acceptable levels and, thus, serve as a stand-alone technology. In treatment combinations, soil washing can be a cost-effective step in reducing the quantity of contaminated material to be processed by another technology, such as thermal, biological or physical/chemical treatment. In general, soil washing is more effective on coarse sand and gravel; it is less successful in cleaning silts and clays.

A wide variety of chemical contaminants can be removed and/or concentrated through soil washing applications. Removal efficiencies depend on both the soil characteristics (e.g., soil geology and particle size) and the processing steps contained within the soil washer. Experience has shown that volatile organics can be removed with 90+% efficiency. Semivolatile organics are removed to a lesser extent (40-90%). They usually require the addition of surfactants to the washwater. Surfactants are surface-active or wetting agents that reduce the surface tension at the interface between the hydrophobic contaminants and the soil, thereby promoting release of the contaminants into the aqueous extraction medium.

Metals which are less soluble in water often require acids or chelating agents for successful soil washing. A chelating agent, such as ethylenediaminetetraacetic acid (EDTA), bonds with the metal and facilitates solubilization in the extraction medium.

The VRU process can be applied to the treatment of soils contaminated with hazardous wastes such as wood preserving chemicals (pentachlorophenol and creosote), electroplating residues (cyanides and heavy metals), organic chemical production residues and petroleum/oil residues. The applicability of soil washing to general contaminant groups and soil types, which is shown in Table 1, has been reproduced from a U.S. EPA report, "Treatment Technology Bulletin - Soil Washing," dated May 1990.

The U.S. EPA has developed the VRU to meet the following objectives:

- To make available to members of the research community and to the commercial sector the results of government research on a flexible, multistep, mobile, pilot-scale soil washer capable of running treatability studies on a wide variety of soils
- To demonstrate the capabilities of soil washing
- To provide data that facilitate scale-up commercial size equipment

The U.S. EPA plans to investigate other extraction processes which may be added to the VRU at a later data. The addition to the VRU of novel physical/chemical treatment processes, such as sonic/ultrasonic

cleaning and acid leaching, will expand its overall extraction capability in soil decontamination.

Table 1
Applicability of Soil Washing to General
Contaminant Groups for Various Soils

Contaminant Groups		Matrix	
		Sandy/ Gravelly Soils	Silty/Clay Soils
Organic	Halogenated volatiles	■	▼
	Halogenated semivolatiles	▼	▼
	Nonhalogenated volatiles	■	▼
	Nonhalogenated semivolatiles	▼	▼
	PCBs	▼	▼
	Pesticides (halogenated)	▼	▼
	Dioxins/Furans	▼	▼
	Organic cyanides	▼	▼
	Organic corrosives	▼	▼
Inorganic	Volatile metals	■	▼
	Nonvolatile metals	■	▼
	Asbestos	□	□
	Radioactive materials	▼	▼
	Inorganic corrosives	▼	▼
	Inorganic cyanides	▼	▼
Reactive	Oxidizers	▼	▼
	Reducers	▼	▼

■ Good to Excellent Applicability: High probability that technology will be successful

▼ Moderate to Marginal Applicability: Exercise care in choosing technology

□ Not Applicable: Expert opinion that technology will not work

SYSTEM DESCRIPTION

The VRU is a mobile, pilot-scale washing system for stand-alone field use in cleaning soil contaminated with hazardous substances. The VRU is designed to decontaminate certain soil fractions using state-of-the-art washing equipment. The total system consists of process equipment and support utility systems mounted on two heavy-duty, semitrailers.

Figure 1, General Block Diagram, shows the VRU basic pilot plant subsystems as follows:

- Soil handling and conveying
- Organic vapor recovery
- Soil washing and coarse screening
- Fines/floatables gravity separation
- Fines flocculation/water clarification and solids disposal
- Water treatment
- Utilities - electric generator, steam boiler and compressed air unit

The generator, air compressor, water heater, water filters/carbon adsorbers, recycle water pump, gasoline tank (for the generator) and delisting tank are located on the utility trailer. All remaining equipment is located on the process trailer. The VRU system is controlled and monitored by conventional industrial process instrumentation and hardware, including safety interlocks, alarms and shutdown features.

PROCESS DESCRIPTION

Figures 2, 3 and 4 present the Process Flow Diagram for all VRU subsystems in terms of their process equipment functions.

Soil Handling and Conveying

Raw soil is delivered from battery limits to a vibrating grizzly that separates the particles greater than 0.5 inches into a drum for redeposit and collects the smaller particles (-0.5 inches +0) for transfer to the feed surge bin. (The maximum particle size that can be handled in the miniwasher is 0.5 inches, but smaller screen sizes may be selected.) From this bin, the soil less then 0.5 inches in size is conveyed through a steam-jacketed screw conveyor where the volatile organics and water are vaporized. Both live steam and jacketed steam can be introduced so that the efficiency of the steam extraction can be determined. The conveyor flow is adjusted by a speed controller on the conveyor motor. The solids pass through a motor-operated rotary valve (which prevents air infiltration), then into the feed hopper of the mini-washer.

Organic Vapors Recovery

Volatiles stripped from the soil in the screw conveyor are either collected in the VOC condenser and fall by gravity into the process condensate seal tank or are adsorbed in vapor-phase activated carbon containers located upstream of the vent blower.

The spent carbon will be periodically replaced based on vent gas analyses. The vapor train is maintained under vacuum by an induced draft blower. The vacuum level is adjusted by manual admittance of atmospheric air upstream of the blower to maintain a slight negative pressure on the vapor system. Clean vapors, leaving the blower, vent to the atmosphere.

Soil Washing and Coarse Screening

Soil is fed to the miniwasher at a controlled rate of approximately 100 lb/hr by the screw feeder. Filtered washwater, which can be heated to 150 °F (maximum), is added to soil in the feed hopper and also sprayed onto an internal slotted trommel screen (with a 10-mesh (0.079 inches) slot opening) miniwasher. Five manually controlled meters can control the flow up to approximately 10:1 overall weight ratio water to soil. Hot water should be more efficient in extracting contaminants, but heating is optional. When required, dilute surfactant/detergent and/or caustic can be metered at a controlled rate into the feed hopper.

Two vibrating screens, equipped with antiblinding devices, are provided to continuously segregate soil into various size fractions. These screened fractions can be collected to measure the effectiveness of contaminant removal for each soil fraction recovered and to determine the effectiveness of soil washing in cleaning a particular contaminated soil fraction to achieve sufficient volume reduction.

Miniwasher overflow, containing the coarser solids, falls onto the first 10-mesh (0.079 in/2 mm) vibrascreen. First vibrascreen overflow (-0.5 inches + 10 mesh) solids flow by gravity down to a recovery drum. The underflow is pumped at a controlled rate, using a progressing cavity pump, onto the second 60-mesh (0.0098 in/0.25 mm) vibrascreen where it is joined by the miniwasher underflow.

The overflow from the second vibrascreen (- 10-mesh + 60-mesh), is gravity fed to another recovery drum. Second vibrascreen underflow (a fines slurry) drains into an agitated tank. The VRU is designed with the following flexibility:

- The mesh sizes for both the miniwasher and vibrascreens can be varied [i.e., the screen size could be 20- or 30-mesh (0.033 inches or 0.023 inches)].
- Additional soil cleaning by use of water sprays or steam sprays will be evaluated for each vibrascreen.
- Screened soil fractions, collected in the recovery drums, can be redeposited if sufficiently cleaned or further cleaned by addition of rinse water, followed by reslurrying and pumping the slurry back over the screens (recycle mode). In the future, these soil fractions will be sent for treatment by various extraction units currently under development by U.S. EPA's RREL in Edison, New Jersey.

Fines/Floatables Gravity Separation

Slurry from the second screen (fines slurry) tank, containing particles less than 60-mesh (0.0098 inches/0.25 mm) in size, is pumped to a Corrugated Plate Interceptor (CPI). Material lighter than water
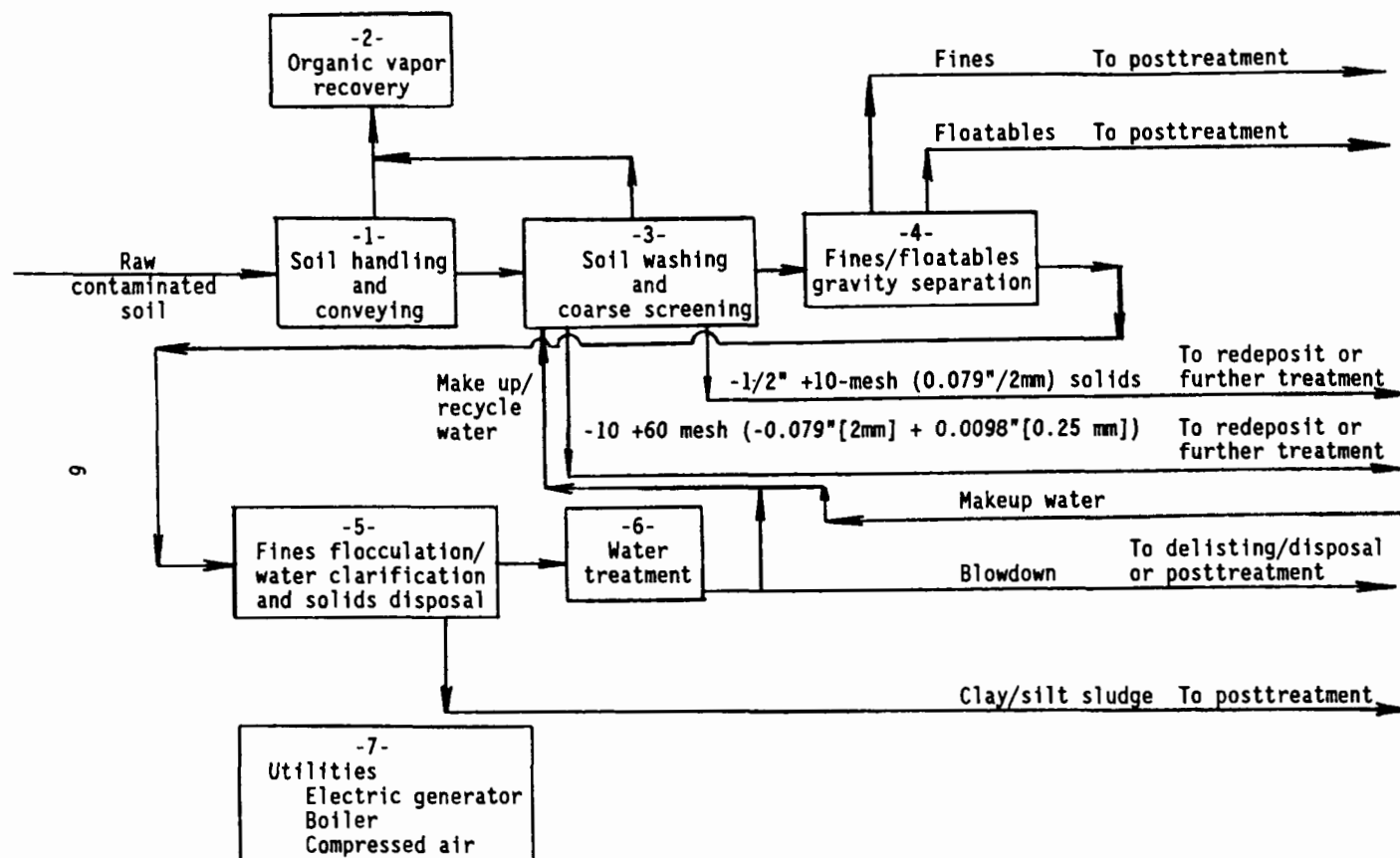
Figure 1
General Block Diagram

(floatables such as oil) will overflow an internal weir, collect in a compartment within the CPI and drain by gravity to a drum for disposal. CPI-settled solids [soil particles - 60- to about 400-mesh (- 0.0098 inches to about 0.0015 inches)] will be discharged by the bottom auger to a recovery drum. The VRU has the flexibility to redeposit or further clean these settled soils, if required, by addition of rinse water followed by pumping the slurry back through the CPI. As mentioned above, these soils could also be sent, in the future, to an extraction unit.

Fines Flocculation, Water Clarification and Solids Disposal

Aqueous slurry, containing fines less than about 400-mesh (34 um/0.0014 inches), overflow the CPI and gravity feed into an agitated tank. The slurry is then pumped to a static flash mixer located upstream of the floc clarifier's mix tank. Flocculating chemicals are introduced into this static flash mixer. Typically, liquid alum and aqueous polyelectrolyte solutions are metered into the static flash mixer to neutralize the repulsive electrostatic charges on colloidal particles (clay/humus) and promote coagulation. The fines slurry is discharged into the floc chamber which has a varispeed agitator for controlled floc growth (sweep flocculation). Sweep flocculation refers to the adsorption of fine particles onto the floc (colloid capture) and continuing floc growth to promote rapid settling of the floc and its removal from the aqueous phase. The floc slurry overflows into the clarifier (another corrugated plate unit). Bottom solids are gravity fed by an auger to a drum for disposal, or to the sludge slurry tank (depending on solids concentration) for subsequent concentration in a filter package unit. Concentrated cake from the filter is discharged to another drum for disposal. This system has the ability to clarify the process water and dewater the sludge. The efficiency of solids dewatering can be determined and cost savings estimated, for trucking waste sludge to a disposal/treatment site.

Water Treatment

Clarified water is polished with the objective of reducing suspended solids and organics to low levels that permit recycle of spent washwater. Water is pumped from the floc settler overflow tank at a controlled rate through cartridge-type polishing filters operating in parallel, in order to remove soil fines greater than 10-um (3.94×10^{-4} inches). One um (3.9×10^{-5} inches) cartridges are available, if required.

Water leaving the cartridge filter flows through activated carbon drums for removal of hydrocarbons. The carbon drums may be operated either in series or parallel and hydrocarbon breakthrough monitored by sampling. A drum will be replaced when breakthrough has been detected.

In order to recycle water and maintain suitable dissolved solids and organic levels, aqueous bleed (blowdown) to the boiler delisting tank may be initiated at a controlled rate. Delisted material will be sealed in drums and sent for disposal in accordance with respective state and local regulations. Treated recycle (recovered) water is sampled for analysis before it flows into the process water storage tank. Supplementary water is fed into this tank from a tank truck. Recovered and added water is pumped by the water recycle pump (and optionally fed to the water heater) for subsequent feed to the miniwasher. A side stream from the water recycle pump is utilized as cooling water in the VOC condenser and either returned to the process water storage tank or sent to the sewerage system.

Utilities Systems

The VRU is equipped with a steam boiler, electric generator and a compressed air system.

Field Operations

While in the field, the VRU would be supported by a decontamina-

Figure 2
Process Flow Diagram
U.S. EPA Mobile Volume Reduction Unit for Soil Washing

Figure 3
Process Flow Diagram
U.S. EPA Mobile Volume Reduction Unit for Soil Washing
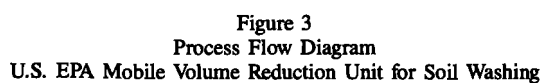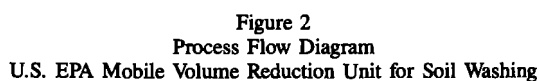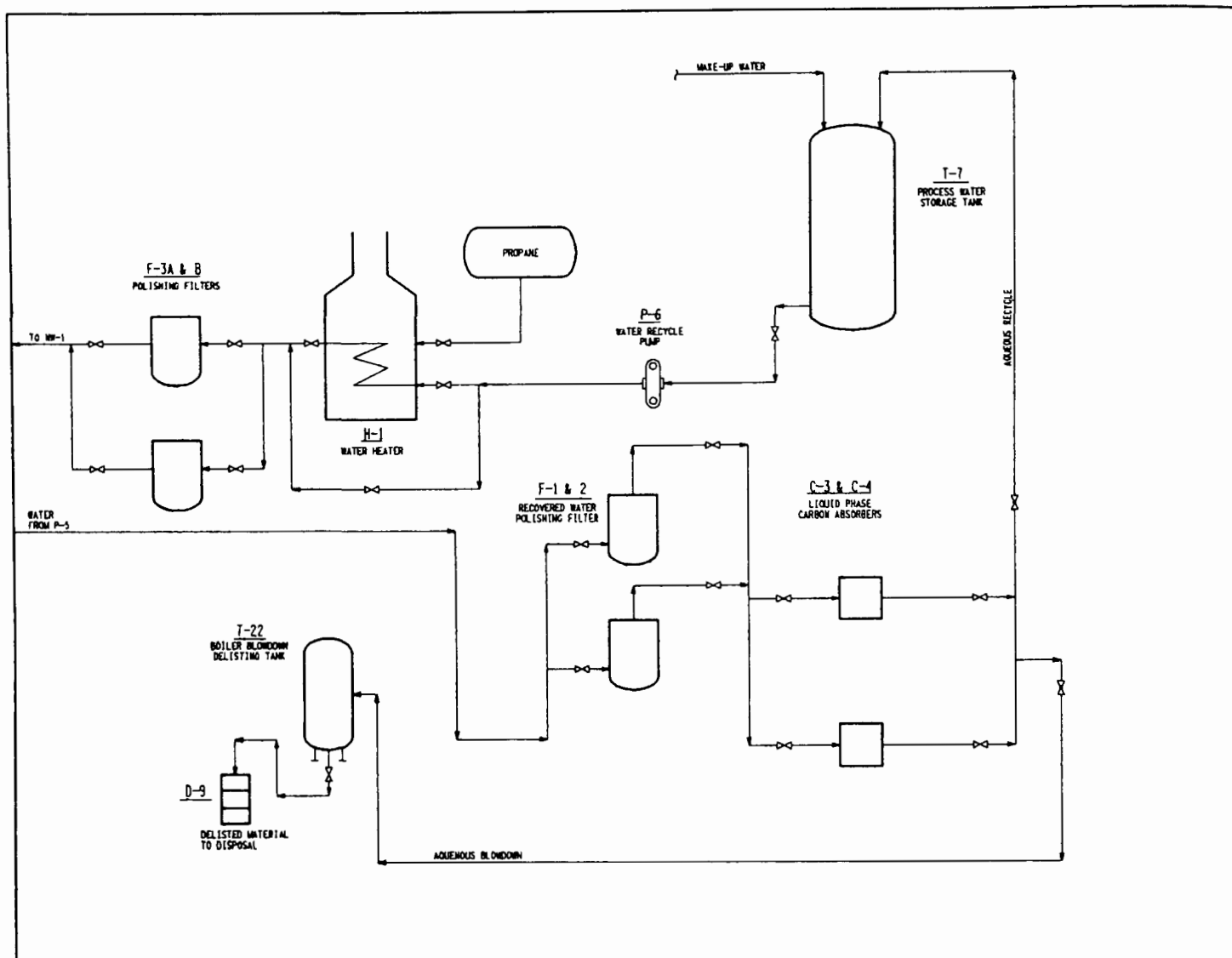
Figure 4
Process Flow Diagram
U.S. EPA Mobile Volume Reduction Unit for Soil Washing

tion trailer, a mobile treatability laboratory/office and a storage trailer for supplies, spare parts, miscellaneous tools, etc.

SUMMARY OF VRU FEATURES

Listed below are the various features, operational parameters and capabilities of VRU:

- The VRU is a mobile, pilot-scale washing system for field use in cleaning soil contaminated with hazardous materials, using state-of-the-art washing equipment and support utilities.
- The unit has the ability to remove VOCs by steam heating and stripping.
- It is capable of washing with water (in combination with surfactants/detergents) up to a 10:1 water to soil ratio while also varying water temperature from ambient to 150°F.
- The miniwasher screen and vibrascreens can be varied in mesh size. Additional use of soil cleaning by water or steam sprays on the vibrascreen decks can be evaluated.
- Four screened soil fractions (including CPI-settled solids) can be further cleaned by slurrying with the addition of rinse water and recycling the slurry over the vibrascreens or the CPI.

- The floc-clarifier system has the ability to clarify the process water and dewater the sludge.
- Additional treatment of the clarified process water through polishing filters and activated carbon should allow, in most cases, reuse of this water as recycle to the washing circuit.
- Side streams from the VRU will be treated using various physical/chemical extraction units currently under development by U.S. EPA.
- The VRU offers a unique method for conducting treatability studies on various contaminated soils.

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Baird and McGuire Superfund Site:
Design of a GWTP Fume Collection and Treatment System

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ABSTRACT

A groundwater extraction system and treatment plant has been designed by Metcalf and Eddy to restore groundwater quality at the Baird and McGuire Superfund Site in Holbrook, Massachusetts. The site, which formerly housed chemical mixing and batching operations, currently ranks 14th of 989 sites on the NPL.

The groundwater at the site has been contaminated with metals, (including arsenic and lead), volatile and semivolatile organics and pesticides. Included among the VOCs found in the groundwater are vinyl chloride, methylene chloride, trans-1, 2-dichloroethane, benzene, toluene and xylenes. The groundwater treatment plant will treat 200 gpm of contaminated groundwater by a series of unit operations including metals precipitation, biological treatment, filtration and granular activated carbon adsorption.

Due to the high concentration of VOCs present in the groundwater, the need for collection and treatment of contaminated air from the process tanks located inside the treatment plant building and from the biological aeration tanks located outside was assessed to ensure the safety of the treatment plant operators and the surrounding community. In order to determine whether collection and treatment of the air would be necessary, the OSHA permissible exposure limits (PELs) of the contaminants and Henry's Law constants were reviewed. Additionally, samples of air emissions were collected during bench-scale treatability testing and submitted to an analytical laboratory for VOC analysis by GC/MS. Test results confirmed the need for collection and treatment of air from all process tanks through the treatment train up through biological aeration.

Two methods of off-gas treatment were considered; fume incineration and vapor-phase carbon adsorption. Fume incineration was selected since this process provides essentially complete destruction of the VOCs without producing a waste byproduct. An air collection system was designed to collect the contaminated air from the plant and aeration tanks and feed it to a 1,000-cfm incinerator. The incinerator will be fueled by natural gas and operate at a minimum temperature of 1,400°F.

INTRODUCTION

The Baird and McGuire Superfund site currently ranks 14th of 989 sites on the NPL. Baird and McGuire, Inc., operated a chemical mixing and batching facility in Holbrook, Massachusetts, for more than seventy years. Operations at the facility included production of household and industrial products such as floor waxes, wood preservatives, pesticides and solvents,[1] and resulted in widespread contamination of the Baird and McGuire property, and the surrounding property by numerous toxic organic and inorganic compounds. In September, 1986, following a number of investigations, the U.S. EPA issued the ROD for the Remedial Alternative for the site. Included in the ROD was remediation of con-

taminated groundwater by metals precipitation, biological treatment and carbon adsorption. The ROD also included remediation of soil by incineration.

Site Contamination

Investigations have been conducted at the Baird and McGuire site by several parties including consultants for Baird and McGuire, Inc., the town of Holbrook, the U.S. EPA, the Massachusetts Department of Environmental Quality Engineering, Goldberg-Zoino Associates[2] and GHR Engineering Associates. Most recently, Metcalf and Eddy conducted a comprehensive groundwater sampling effort to provide support for design activities. The analytical data from this sampling round documented extensive groundwater contamination by metals, semivolatile and VOCs and pesticides.

VOCs were of special interest in the design of the groundwater treatment plant since the need for fume collection and treatment, as well as removal of these constituents from the groundwater, had to be assessed. The VOCs detected in the groundwater during the most recent phase of sampling are shown in Table 1.

Table 1
VOCs Found in Groundwater at
the Baird and Mcguire Site[3]

Parameter	Concentration (ug/l)		
	Detection Limit	Maximum	Ave (*)
Chloromethane	<5	550	14
Vinyl Chloride	<5	130	13
Methylene Chloride	<5	490(1400B)	133
Acetone	<25	740	78
1,1-Dichlorethane	<2	7.5	2.3
Trans-1,2-Dichlorethene	<2	3700	315
1,1,1-Trichloroethane	<2	5.7	2.2
Trichlorethene	<2	130	5.4
Benzene	<2	1100	62
Toluene	<2	1500	127
Ethylbenzene	<2	1200	153
Total Xylenes	<2	9000	870

* Based on not detected = detection limit
B - Compound found in blank

DESIGN OF THE GROUNDWATER TREATMENT PLANT

As part of the Baird and McGuire site remediation, Metcalf and Eddy designed a groundwater treatment plant (GWTP). The plant was designed to produce an effluent which will meet drinking water stan-

dards as is required for infiltration to the aquifer. The standards are specified by the federal Safe Drinking Water Act (SDWA) Maximum Contaminant Levels (MCLs) or the Massachusetts Groundwater Quality Standards, whichever is lower. The plant was designed to treat 200 gpm of groundwater contaminated with metals, volatile and semiVOCs and pesticides. Treatment processes include two-stage metals precipitation, biological treatment by activated sludge process, filtration and granular activated carbon adsorption.

During predesign activities conducted by M and E to confirm or develop design parameters, it was determined that the need for controls to eliminate volatile emissions during GWTP operations had to be assessed. This measure was not required to comply with the ROD since, unlike off-gas from an air stripper, off-gas from a biological aeration tank does not require treatment under Massachusetts regulations.

Predesign Activities

The predesign activities, which were conducted as part of the design effort, included a groundwater pumping test and a bench-scale treatability study. These investigations developed data for the design of the groundwater extraction system and confirmed the ability of the proposed treatment processes to meet the discharge limitations; the treatability study developed treatment system design data. Water produced during the pumping test was temporarily stored on-site in an open 300,000-gallon above ground tank. Due to past odor problems, community concern and the potential for health impacts, a review of the need for temporary controls to prohibit release of VOCs from the tank to the atmosphere was conducted at this time.

The review was conducted to evaluate airborne VOC concentrations in the vicinity of the tank and at the property boundary. Henry's Law was used to estimate the concentration of contaminants in the air at the air/water interface, and a simple U.S. EPA dispersion model was used to estimate contaminant concentrations at the property boundary. The estimated air concentrations were then compared with OSHA permissible exposure limits (PELs) and what was then called Massachusetts proposed allowable ambient levels (AALs). Only organic contaminants that had been defined as critical in the public health risk assessment, conducted as part of the Feasibility Study,[4] and which had been detected in the groundwater were included in the evaluation. Conservative assumptions were used in this comparison, including maximum measured contaminant concentrations, high ambient temperature for the time of year the pumping test would run (77 °F) and low wind speeds (1 m/sec to 2 m/sec). In addition, comparing a water/air interface concentration with an OSHA PEL is very conservative, since the concentration where workers are exposed should be lower.

The evaluation determined that five contaminants were greater than the OSHA PELs indicating the potential to exceed PELs in the vicinity of the tank and that 12 to 14 of the compounds exceeded the AALs. The estimated property boundary concentrations were as high as 1,000 times the state AAL. This evaluation was based on very conservative assumptions; however, concentrations up to 1000 times the state's AALs indicate the potential for contaminants to volatilize from an uncovered tank at concentrations above AALs even under less conservative conditions than those used in the models. The results of this evaluation, as well as the concern for potential odors, indicated the need to install a floating cover on the 300,000-gallon tank. The evaluation also indicated a need to incorporate emissions controls into the design of the full-scale treatment plant. A program for measuring loss of volatiles from the groundwater to the air was incorporated as part of an ongoing bench-scale treatability testing program. The goal of the sampling program was to quantify volatile contaminants that would pose a threat to the operators of the proposed GWTP and the surrounding community.

Two methods were used to determine quantities of volatiles being transferred from the water to the air. The first calculation involved a simple mass balance around a batch aerated tank. Loss of volatiles to the air was determined by measuring VOCs in the waste before and after aeration over a 4-hour test period.

The second method involved the collection of air samples from two covered tanks, one unaerated and one aerated, over a measured period

of time. An aeration tank containing biomass from activated sludge test was used as the aerated test vessel. The biomass was added to the tank in order to help account for loss of VOCs due to biodegradation. Contaminated groundwater was added to the tank and a sample of the contaminated air was collected using a volatile organic sampling train (VOST).

The VOST consists of a series of vapor traps, condensers and a vacuum pump that allow vapor to flow through the apparatus and capture organic contaminants in a trap containing a carbon medium. The apparatus was set up to draw samples from an exhaust stack stemming from each of the enclosed tanks. Air was sampled for 0.5 rh at a rate of 1 L/min, which equaled the diffused air flow rate into the test aeration tank. A vent in the tank cover allowed the flow of air into the test apparatus.

The results of the mass balance around the aerated tank are shown in Table 2. These data indicate that at an air flow rate of 1 L/min, 15 L of waste yield 82.5 mg of volatile compounds over the 4 hour test period. This amount equals 344 mg/m³ of VOCs leaving the aeration tanks. Analytical results could not be obtained for the samples collected by the VOST method since VOC concentrations on the carbon collection media were higher than the GC/MS calibration limits for the test. This result indicated that the air VOC concentrations were extremely high.

Table 2
VOCs Concentrations in Groundwater
Before and After Aeration

Parameter	Concentration (ug/l)(*)	
	Raw Groundwater	Aerated Groundwater
Trans-1,2-dichloroethane	1100	21
Benzene	160	1.6
Toluene	900	9.6
Ethylbenzene	660	4.5
Total Xylene	2700	33
Total Volatiles	5520	69.7

* Only volatile organics detected in the test sample have been reported.

Test Conclusions

Results of the mass balance indicated that loss of VOCs to air would be high enough to warrant the collection of fumes off the GWTP aeration tanks and the application of Best Available Control Technology to the contaminated air collected from the tanks. In addition, since all process tanks that precede the activated sludge process were to be located inside a building, a decision was made to cover the tanks and collect the contaminated air in the tank head-space for treatment as well, in order to ensure operator safety.

Design of the Fume Collection and Treatment System

Based on the test results and the sampling data presented in Table 1, a fume collection and treatment system was designed. Two methods of off-gas treatment were considered for the full-scale GWTP; fume incineration and vapor-phase carbon adsorption.

The two alternatives were evaluated based on their ability to remove or destroy the contaminants of concern, their applicability to the Baird and McGuire site and cost. A technical evaluation of the two alternatives indicated that carbon has low adsorption capacity for several of the contaminants of concern, including methylene chloride and vinyl chloride. This finding was of particular concern due to the potential for high concentrations of some of these organics in the air. Incineration, under proper operating conditions, will result in virtually complete destruction of all the organics of concern, regardless of concentration.

An additional consideration evaluated was community reaction to the two alternatives. Due to the low adsorption capacity of carbon for some of the contaminants and the potentially high concentrations expected in the air stream, frequent carbon replacement or on-site steam regeneration would be required. Replacement or regeneration would result in additional traffic to and from the site through the bordering residential area, either delivering and removing carbon, or removing the concen-

trated solvent waste that would result from regeneration. The community's reaction to another incinerator on the site was of concern.

Table 3
Cost Comparison

	Carbon Adsorption	Incineration
Design Basis:	1,000 cfm 1,000 lbs carbon/adsorber	1,000 cfm 1,400 °F
Capital Cost	$110,000[1]	$ 90,000
Annual Operating Cost	$ 45,000	$ 20,000
Net Present Value[2]	$452,000	$242,000

1. Includes adsorbers and steam regeneration system
2. Present value assumes an annual interest rate of 10% over a 15 year project life.

However, it was found that any increase in traffic, particularly if the vehicles would be transporting hazardous materials, seemed to be of

groundwater into the air, the tendency of some of the VOC contaminants found in the groundwater to deplete the capacity of carbon at a high rate and the need for disposal or on-site regeneration of carbon with regenerant disposal, the fume incineration option was selected. This option will provide essentially complete VOC destruction without producing a waste byproduct requiring disposal.

All process tanks preceding and including the biological aeration tanks and clarifiers were covered, and exhaust gas from these tanks were vented at a rate of 800 to 1000 cfm through FRP ductwork and fans to a fume incinerator located outside the treatment plant building. FRP was selected due to the presence of chlorinated organics. Vents were included in the tank covers to allow air to be drawn by two induced-draft fans to the incinerator. A process flow diagram is shown in Figure 1.

Due to the low BTU value of the contaminated air and aeration tank off-gas, an air-to-air heat exchanger was included to recover heat from the incinerator stack gas to preheat the incoming air to approximately 700 °F. The VOC contaminants will be thermally oxidized in the incinerator at a minimum temperature of 1400 °F. The system is design to achieve 99.99% destruction of organics. The incinerator burner will be fueled by natural gas.
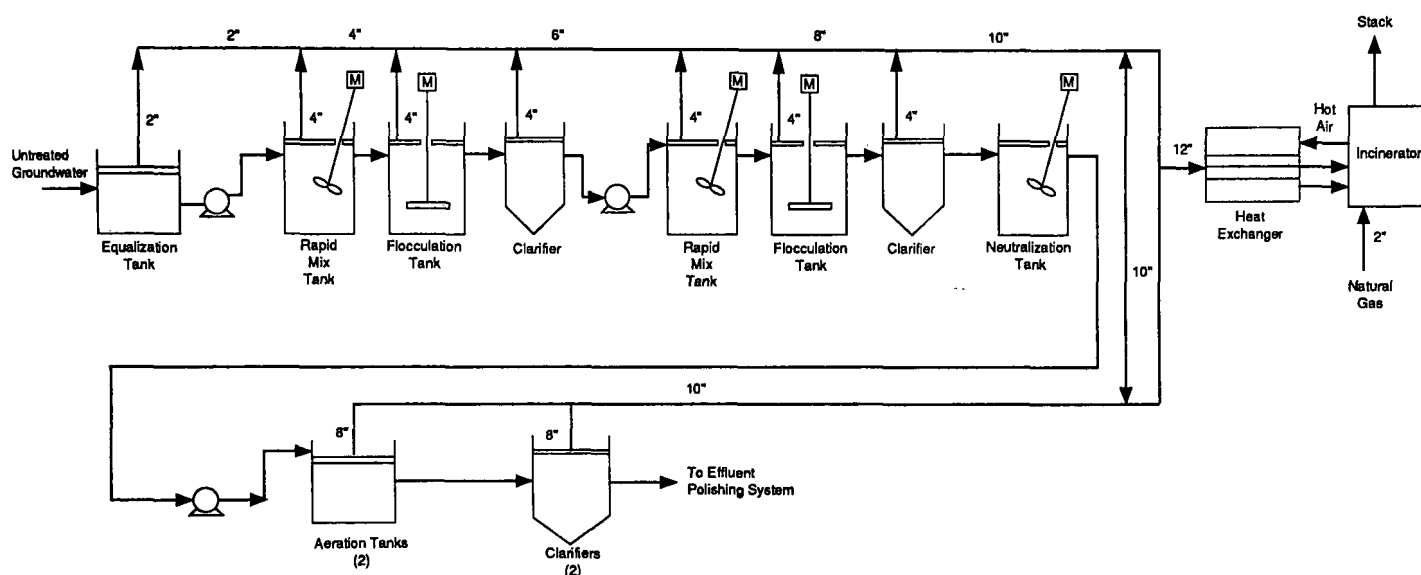
Figure 1
Process Flow Diagram

greatest concern to the surrounding community.

Finally, incineration was found to be the more economical solution for treating the contaminated air at this site. Although equipment costs of the two proposed alternatives are comparable and both use fairly low maintenance equipment, the need to frequently replace or regenerate the carbon drives up the operating cost of this process. A cost comparison is presented in Table 3.

CONCLUSIONS

Due to the potentially high concentration of VOCs removed from the

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Chemical Oxidation of Dissolved Organics Using Ultraviolet-Catalyzed Hydrogen Peroxide

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INTRODUCTION

The development of the perox—pure™ UV/Peroxidation process was started in the late 1970s. Today, while there are more than 30 full-scale treatment units in operation or in the final stages of design and installation, the development and improvement of the process is continuing.

This advanced oxidation process using ultraviolet (UV) light-catalyzed hydrogen peroxide is a cost-effective treatment for a wide array of organic compounds found in contaminated groundwater, toxic waste leachates and industrial wastewaters. Recent improvements in the perox-pure™ Process have reduced the operating cost for total destruction of these toxic organics by up to 50%. In addition, the oxidation rate of many of the "difficult to oxidize" compounds such as 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), chloroform (CHCl₃) and methylene chloride (MeCl) have been increased up to three-fold. These advances increase the cost-effectiveness of on-site destruction processes versus transfer technologies and broaden the applicability of chemical oxidation as the technology of choice.

perox-pure™ PROCESS

In this process, UV light converts the hydrogen peroxide (H_2O_2) in solution to hydroxyl radicals (HO·) and "activates" many of the organic molecules to make them easier to oxidize. The photolysis reaction which forms HO· can be shown as follows:

$$H_2O_2 \xrightarrow{\text{UV}} 2\,HO\cdot \tag{1}$$
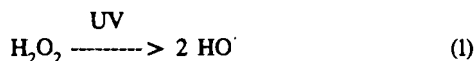
The activation of the organic molecules can range from direct oxidation by UV absorption and disassociation to the formation of organic radicals or other reactive intermediates. With enough time and reactants, organic compounds can be completely destroyed to CO_2, H_2O and, if present, the appropriate inorganic salt.

Most early UV oxidation processes used low pressure mercury vapor lamps combined with ozone (O_3). The perox-pure™ Process utilizes a proprietary high intensity UV lamp combined with H_2O_2. This provides a number of advantages for chemical oxidation of aqueous solutions.

Three process considerations which manifest advantages include:

- *UV Intensity* - The higher intensity allows for a more compact equipment design as well as lower capital cost. In addition, the higher UV intensity gives better penetration in wastewater or high concentration waters and allows for treatment of a wider range of applications.
- *UV Spectra* - Since activation of organic compounds plays a key role in the destruction process, the broad spectra of the high intensity lamps are better suited for most applications than the narrow spectrum low pressure mercury lamps.
- *Hydrogen Peroxide* Because H_2O_2 is completely miscible with water, it can easily be added in any desired concentration. This wide range of permissible concentrations combined with high intensity lamps allows for simplicity of reactor design and short reaction times for both groundwater and wastewater applications. In addition, there are no toxic gas emissions or stripping of volatile organics into the air.

BENCH-SCALE TESTING

Over the last 5 years, Peroxidation Systems, Inc. (PSI) has tested hundreds of water and wastewater samples from clients using bench-scale equipment. In addition, an ongoing research and development program has contributed to the large body of information available on the oxidation of organic compounds by UV peroxidation. These data are stored in a computerized data base that can be used to generate preliminary process design and cost estimates for a given set of influent and effluent specifications. Table 1 is a partial listing of the compounds in the data base.

Table 1
perox-pure™ Data base
Organic Compounds Listing

Acenaphthene	
Acenaphtylene	2,4-Dichlorophenol
Acetic Acid	Dichloropropane
Acetone	Dichloropropene
Acetonitrile	Dinitrophenol
Acrolein (Propenal)	Dieldrin
Acrylic Acid	EDTA
Acrylonitrile	Endrin
Alachlor	Ethylbenzene
Alcohols	Ethylene Diamine
Aldicarb	Fluoranthene
Aldrin	Fluorene
Aniline	Formaldehyde
Anthracene	Formic Acid
Benzene	Hexachlorobenzene
Benzoic Acid	Hydrazines
Benzyl butyl phthalate	Isophorone
Bis (2-chloroisopropyl) ether	Methyl ethyl ketone (MEK)
Bis (2-ethylhexyl) phthalate	Methyl isobutyl ketone (MIBK)
Bromodichloromethane	Methylene chloride
Butyric Acid	MTBE
Butyl Acrylate	Napthalene
Butylbenzene	Nitroglycerine
Carbon tetrachloride	Nitrophenol
Chloroaniline	Nitrosamine
Chlorobenzene	PCBs
Chlorodane	Pentachlorophenol
Chloroethane	Phenanthrene
Chloroform	Phenol
Chloromethane	Tetrachloroethane
2-Chloronaphthalene	Tetrachloroethene
	Tetrahydrofuran

Chlorophenol	Toluene
Cresol	Trichlorobenzene
Chlorotoluene	1,1,1-Trichloroethane
Cyanide	1,1,2-Trichloroethane
Cyclohexanone	Trichloroethene
1,2-Dibromo-3-	Trichlorofluoromethane
chloropropane	2,4,6-Trichlorophenol
Dibromochloromethane	Trichlorophenols
1,2-Dibromoethane	Vinyl chloride
Dichlorobenzene	Xylene
Dichlorobenzidine	
Dichlorodifluoromethane	
1,1-Dichloroethane	
1,2-Dichloroethane	
1,1-Dichloroethene	
1,2-Dichloroethene	

PROCESS CONSIDERATIONS

Like most other chemical oxidations, the UV/Peroxidation process is dependent upon a number of reaction conditions which can affect both performance and cost. Some process variables are inherent to the properties of the contaminated water while other process variables can be controlled by the treatment system design and operation. Some of the more important process variables are summarized in Table 2.

Table 2
UV/Peroxidation Process Variables

* Variables related to the contaminated water:
    * type and concentration of organic contaminant
    * light transmittance of the water
      (color/suspended solids)

* Variables related to treatment process design and operation:
    * UV and H2O2 dosages
    * pH and temperature conditions
    * Use of catalysts

TREATMENT EQUIPMENT

While the UV/Peroxidation process is based on well-known chemistry, the equipment and the use of a high intensity UV source such as is embodied in the perox-pure™ equipment is a more recent development. Figure 1 presents data which illustrates the relationship between the UV power employed and the oxidation rate for trichloroethylene (TCE).

As is shown, the reaction rate improves significantly and is more than 10 times faster for the high output UV sources employed in the perox-pure™ equipment than for the older conventional sources. In practice, for UV/Peroxidation reaction, this relationship results in a four-lamp 80-gallon reactor being able to provide equivalent treatment to a system requiring 200 lamps in a 1500-gallon reactor. The increased lamp power costs are more than off-set by the much simpler and lower capital cost equipment.

This smaller, simpler design has significance with regard to space requirements, the number of potential replacement parts and the corresponding maintenance costs. A schematic design of a high intensity UV/Peroxidation system is shown in Figure 2.

In practice, H_2O_2 stored on-site in polyethylene or aluminum tanks at 50% concentration is fed via small chemical metering pumps directly into the incoming water. The solubility of H_2O_2 in water obviates any need for mixing or dispersion devices other than the inlet piping. The mixture passes into the bottom of the oxidation chamber and then upward over horizontally mounted UV lamps. Mechanical design and hydraulic principles ensure mixing during the oxidation process. The unit contains no moving parts, further minimizing maintenance problems.

Individual oxidation chambers can contain up to 15 lamps which can be controlled in increments which match the UV dosage to the treatment needs based on the incoming flow and organic concentration. As treatment flow increases or higher concentrations are treated, the modular oxidation chambers are mounted in series or parallel depending on whether longer contact times or higher flow capacities are required.

Modular systems have been constructed which have hydraulic capacities up to 1500 gpm. As shown schematically in Figure 2, the majority of equipment on each skid-mounted system is devoted to the electrical feed and control system which provides output readings on lamps, power controls, alarm readouts and the option for remote and automatic operation and control.

EFFECT OF UV INTENSITY ON DESTRUCTION RATE
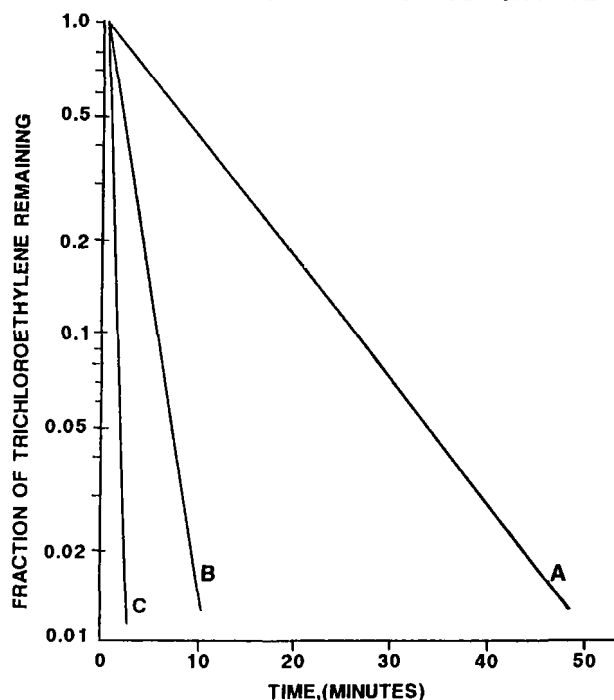
LINE A - DATA FROM SUNDSTROM⁵ AT 2.5 WATTS @ 254 NM/LITER
LINE B - DATA FROM HAGER⁴ AT 230 WATTS TOTAL UV/LITER
LINE C - DATA FROM RECENT PEROXIDATION SYSTEMS TESTING AT OVER 500 WATTS TOTAL UV/LITER

Figure 1
Effect of UV Intensity on Destruction Rate

FULL-SCALE OXIDATION

Of the 30 full-scale perox-pure™ systems in operation or final construction/installation, approximately 10 are treating wastewaters with organic concentrations between 10 mg/L and 1%. The remainder of the 30 on-line units are treating groundwater. Table 3 shows a partial list of the organic compounds being treated by these installations. Operating costs for these treatment systems range from approximately $0.25/1000 gallons for low concentration groundwater containing TCE and DCE to approximately $0.12/gallon for the highest concentration wastewaters.

APPLICATION OF THE PROCESS

Examples of treatment systems and their performances are presented below to illustrate the application of the process.

Because of the low flow estimated for treatment (25-50 gpm) and the bench-scale success, the smallest perox-pure™ production model, an LV 60, was chosen for the on-site demonstration. Specifications for the LV 60 are shown in Table 4. Other process components included an air stripper, equalization tank, piping and well pumps.

In order to make maximum use of both air stripping and the UV/Peroxidation system, the treatment system was plumbed to allow UV/Peroxidation first followed by the air stripper. Data from this treatment sequence are presented in Table 5. As is shown, the UV/Peroxidation destroyed virtually all contaminants with the exception of TCA which is subsequently reduced to below 2 μg/L by the air stripper. The result of this sequence is higher quality effluent water as well as much lower atmospheric emissions of chlorinated hydrocarbons.
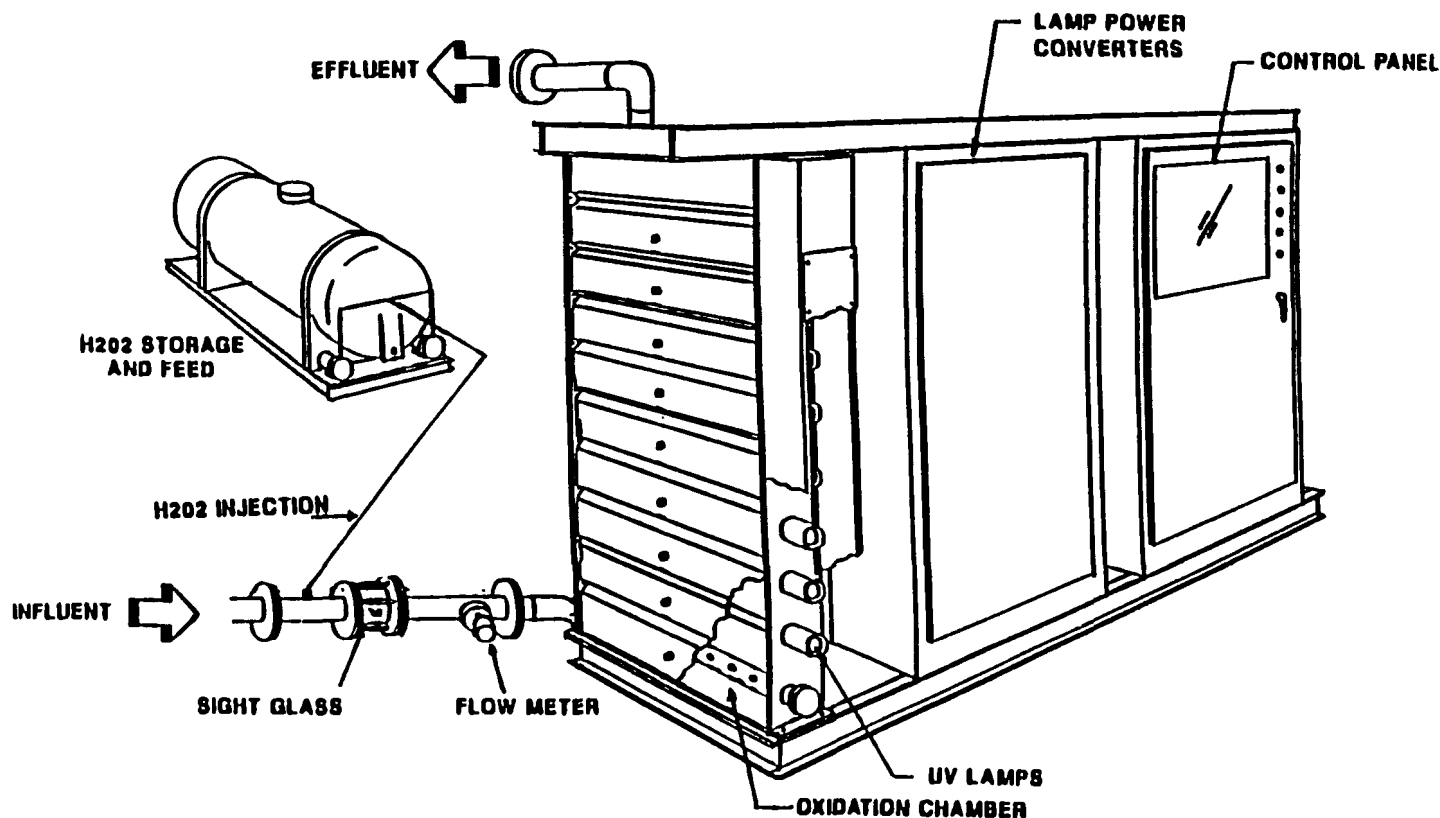
Figure 2
Equipment Arrangement and Process Water
Flow for the UV/H$_2$O$_2$ System

Table 3
perox-pure™ Operating Systems
Organic Chemicals List

Acrylic Acid	Ethyl Benzene
Aniline	Hydrazines
Benzene	Isopropanol
Bis 2-ethylhexyl	MeCl
phthalate	PCE
Butyl Acrylate	Pentachlorophenol
Chlorinated phenols	1,1,1-TCA
Chlorobenzene	TCE
Chloroform	Total Toxic Organics
1,1-DCA	Vinyl Chloride
1,1-DCE	Xylene
1,2-DCE	
Dimethyl Nitrosamine	

Table 4
Specifications for the perox-pure™ LV 60

Maximum GPM:	160
Inlet:	2 1/2" 150# Flange
Outlet:	2 1/2" 150# Flange
Power Supply:	3/60/360-480/60 KW, 70 KVA
Electrical Enclosure:	NEMA 3R
Material	
Wetted Parts:	316 SS, Quartz, Viton, TFE
External Parts:	Enamelled Steel
Weight:	3000 lbs.
Size:	2'1"w x 8'l x 6'h
No. of Lamps:	4 individually controlled

Table 5
UV/Peroxidation Performance Ahead of
Air Stripper

Contaminant	Influent (ug/l)	Effluent (ug/l)
MeCl	75	3.8
1,2-DCE	3480	ND
1,1,1-TCA	1980	1430
TCE	1480	ND
PCE	4990	ND

Table 6
Contaminated Groundwater Treatment

Contaminant	Influent (ug/l)	Effluent (ug/l)
Hydrazine	180,000	<10.0
Acetone	41	<1.0
Phenol	14	<1.0
Aniline	730	<1.0
Bis. 2-ethyl hexyl phthalate	170	<2.0
TOC	31,000	2,000

Oxidation time: 18 min.
H202: 300 mg/l

Table 7
Comparison of UV/H$_2$O$_2$ and GAC

Contaminant	GAC[1] Influent (ug/l)	GAC[1] Effluent (ug/l)	GAC[2] Influent (ug/l)	GAC[2] Effluent (ug/l)
TCE (Ave. 6 Mos)	756	3.8	4016	<1

1. GAC usage 1.2 lbs./100 gal., Contact time 50 min.
2. H202 usage 50 mg/l, oxidation time <1 min.

The perox-pure™ system on this site is being operated on a Full Service Contract which eliminates capital expenditure and includes regular service, all parts and labor for maintenance, delivery of H_2O_2 and a guarantee of system performance. The cost to destroy the organics as shown with the perox-pure™ system is approximately $2.69/100 gallons treated including capital amortization, chemicals, electricity and all maintenance parts and labor, but excluding air stripping costs.

OTHER EXAMPLE INSTALLATIONS

In order to illustrate the range of treatment applications, two more sets of performance data are presented. Table 6 shows treatment of water principally contaminated with hydrazine with other trace organics present.

While it is notable that all treatment objectives were met, it also is interesting to note that the total organic carbon (TOC) content of the water was reduced more than 93% indicating that most of the organics have been converted to CO_2.

Table 7 is a comparison of 6 months of averaged data on a TCE-contaminated site which operated both a granular activated carbon (GAC) and UV/Peroxidation system.

The principal difference in the operation was that while the GAC system was operated on a production well, the UV/Peroxidation system operated on a monitoring well with nearly six times higher concentration. Twelve months of operating data showed the UV/Peroxidation

system capable of producing a significantly better effluent at an operating cost of $0.83/1000 gallons compared to $3.05/1000 gallons for GAC.

CONCLUSION

The use of chemical oxidation and particularly the use of ultraviolet light-catalyzed hydrogen peroxide systems, is a proven, very effective technology for removal of organic contamination from water. It is economically competitive with adsorption and operationally simpler than other technologies which may produce sludges, air emissions or other secondary disposal problems. The UV/Peroxidation process is relatively easy to evaluate and demonstrate and should be included in any evaluation of treatment technology alternatives.

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Hazardous Material Control Versus "End of Pipe" Disposal

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ABSTRACT

This paper describes current industrial interest in the subject of pollution prevention, gives some historical perspectives on it and then addresses, as a case study, a program of the U.S. Navy to reduce hazardous waste by 50% during the next five years. An overview of the specifics of key elements of the Navy's Hazardous Material Control and Management Program is presented as an example of one approach that brings together all the elements of environment, safety and health by a life-cycle approach to management.[1]

INTRODUCTION

This paper presents a brief overview of the regulatory maze governing pollution control, the resulting philosophies of regulatory action and compliance and associated economic implications. It then addresses concepts and approaches developed by the U.S. Navy to reduce the amounts and costs associated with using hazardous materials and the disposal of their ultimate waste.

At the outset it must be understood that in both industry and in the defense establishment there always will be processes, systems and operations that require the use of materials with properties hazardous to human health safety and/or the environment. As J. Clarence Davies stated in his remarkable text almost twenty years ago, "We can not stop all the activities which introduce potentially dangerous substances into the environment, because to do so would be to sacrifice most of the benefits of modern society."[3] He also pointed out that the prevailing philosophy then was we could build treatment plants and install control devices if money and political power were brought to bear on the problem. From an economic viewpoint, it is interesting to note that in 1970 it was estimated that the control costs to bring down air, water and solid waste pollution to the then acceptable levels was $300 billion in 1970 dollars over a thirty year period.

Events and costs have overtaken the political, social and engineering/technical philosophies that national environmental goals can best be met through control technology. Environmental control procedures have been based on the premise that the best solution will come from ever increasingly stringent codes, standards and regulations directed at requiring achievement of the best available technology. A recent article on occupational hazard illustrates that this approach is rapidly being recognized as bad policy.

A rethinking of these traditional approaches began in the early 1980s. Waste minimization as an alternative to disposal has rapidly become a recognized industry objective. That process is defined by DuPont as "reducing the quality and toxicity of materials to be wasted by end-of-the-pipe treatment."[2] While large companies and government agencies have been committed to source reduction and waste minimization, the large outlay of funds that may be involved results in many small and medium size companies concentrating on treatment and disposal procedures with all of the associated permit requirements.

Beginning in 1986, the U.S. Navy began to address the questions of both hazardous material control and hazardous waste minimization. After extensive study of ongoing efforts in several naval activities, including the Naval Aviation Depot Pensicola, Florida, broad-scale investigations led to the development and issuance of the Navy directive on Navy Hazardous Material Control and Management. This approach has been recognized by the General Accounting Office as being a unique approach worthy of being emulated by other Federal agencies. The principles and procedures are applicable to the private sector as well as the Defense and Aerospace community.

BACKGROUND OF REGULATORY REQUIREMENTS AND ECONOMIC IMPLICATIONS

Among the driving forces affecting the widening recognition that a true preventive management and engineering approach is needed for hazardous materials and hazardous waste is the high cost of complying with the wide variety of Federal, State and local regulations. Significant also are the regulations' indirect impacts.

Among these indirect impacts are the costs of training the people working with hazardous materials to meet the Hazardous Communication Standard of OSHA; the costs associated with installation of ever increasingly complex new equipment to meet such requirements as Fossil Organic Compound Controls; medical examinations for personnel routinely working with hazardous materials and hazardous waste; and the sharply increasing costs of storage facilities. The General Accounting Office has estimated that it costs the Defense establishment approximately $1.10 for waste disposal for each $1.00 actually spent in procuring a hazardous material. Thus economic implications begin to take a major role in a search for alternatives to pollution control technology.

FUNDAMENTAL CONCEPTS OF HAZARDOUS MATERIAL CONTROL AND MANAGEMENT

As envisioned by the U.S. Navy, Hazardous Material Control and Management is not waste minimization alone. Waste minimization is an element of a multifaceted approach bringing together all of the requirements associated with environment, safety and health. As shown in Figure 1, it is a program which provides for policy, action and followup by all of the interested and affected elements of the Navy structure. It recognizes that there is a relationship between the life-cycle control and management of acquisition procurement and use of hazardous materials and the control and waste minimization efforts and procedures. Highlights of the most important elements of the Navy policy embodied in its directive, OPNAV Instruction 4110.2, Hazardous Material Control and Management, are provided below.[6]
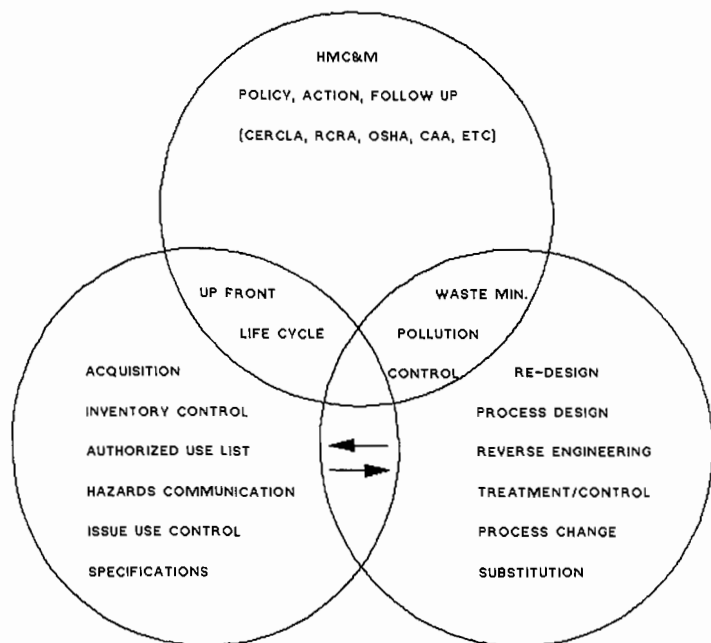
Figure 1
HMC&M Concept/Inter Relationship

Figure 2
Life Cycle of System and Requirement

Policy and Goals

The basic Navy policy is that the Navy will control and reduce the amounts of hazardous material used and hazardous waste generated through a life-cycle approach. A central element of the policy is the establishment of an integrated effort encompassing the health and safety of Navy workers and procedures to protect the environment. A firm goal of achieving a 50% reduction in weight of hazardous waste generated by the Navy by 1992 is also established. In view of the fact that some observers are looking at a 25% reduction of waste from most generators by the year 2000, this goal may seem overly optimistic, but at least it represents a reasonable target.

The Life-Cycle Approach

In essence, the Navy program calls for institution of hazardous material control and management procedures and actions throughout two related life-cycles of Navy systems and equipment. The first of these relates to the life-cycle of systems and equipment as shown in Figure 2. Consideration of the need for use of hazardous material and resulting hazardous waste reduction must begin from the time of conception to the new system of procedure throughout its research, engineering development, production, installation, use and ultimate disposal. The systematic application of hazardous material control and management studies and analyses as part of system development is intended to result in inputs to the Navy's authorized use list discussed later in this paper.

There is another life-cycle which is also recognized in the Navy process. It is described in Figure 3. A second life-cycle is at the activity or installation level. It involves the local facilities' ordering of materials, their receipt, storage, distribution, use and ultimate disposition. In a manufacturing installation or other similar commercial facility, this same life-cycle exists. It involves raw materials, transportation and handling; plant and process operations; storage, distribution and transportation of the finished product; and use by an ultimate consumer. It also includes final disposition of the waste streams in the manufacturing process and of the finished products distributed in commerce.

In effect, in both the military installation and the civilian situation, there are two distinct phases in controlling a hazardous material. The first control phase is the in-plant one involving exposures of personnel, equipment and facilities to the hazards associated with the materials. The second control phase involves the external environment using a systems engineering process. These process must be addressed con-

currently. The approach taken by the Navy and its Hazardous Material Control and Management Plan clearly recognizes these interfaces and provides for them in a cohesive fashion.
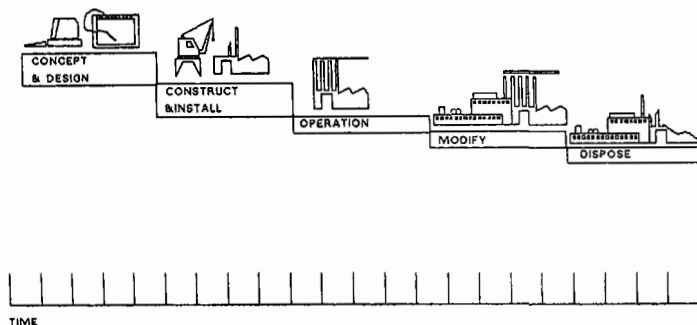
Assignments of Actions and Responsibilities

Any program for comprehensive hazardous material control bringing together environmental safety and health concerns requires a clearly defined assignment of actions and responsibilities from the top level of management to the lowest operating level. The Navy directive does this in unmistakable terms. Responsibilities are assigned commanders of systems command and fleet commanders in chief, and additional specific assignments are provided to those elements concerned with systems development, acquisition and research for education and training and to commanders of Navy facilities.

A key element to ensure the program's success is to assign the Naval Inspector General to make the project a special interest item. Past experience has indicated that this action will result in the necessary responsiveness at all echelons of the organizational structure.

Authorized Use List Concept

The OSHA Hazard Communications Standard (29 CFR 1910.1200) requires that employers (and the Navy, as well as other Federal agencies, is considered an employer) must maintain inventories of hazardous materials in the workplace and provide workers with material safety data sheets on those materials. Literally tens of thousands of hazardous materials are currently in use throughout American industry and the Navy is no exception.

As in industry, many of the materials used by the Navy used are specified by plant process, production and operational design staff. Far too often, little or no consideration has been given or had to be given to whether or not a less hazardous material than the one called for might be more suitable.

Instead of approving the use of hazardous materials on an uncontrolled basis or operational need, the Navy is now changing its method of dealing with this problem. It is requiring an "up front" analysis and control at the earliest possible moment. The objective is to help the Navy avoid excessive costs associated with hazardous waste disposal and the acquisition of hazardous materials.

To that end, the Navy directive calls for the establishment at activity level and at the Navy level of "Authorized Use List." Such a program has been adopted by the Navy for its forces afloat and is now being carried over into the entire Navy establishment. Accomplishment of hazards analysis, risk assessment and economic analysis of an appropriate level of detail to the intended usage is required as part of the decision process involved in the selection and use of hazardous materials.

Recognizing that there are many specifications and standards calling for the use of hazardous materials applicable to existing systems and equipment, the Navy program provides for a 36 month time period for the establishment and implemention of plans to take the necessary actions to review these and develop plans and procedures for the substitution of less hazardous materials as appropriate. One unique procedure now being investigated by the Navy is the use of reverse engineering/value engineering techniques to determine if existing

requirements for the use of hazardous materials can be changed or modified.

Plan of Action Requirement

In addition to the inspection program through the Naval Inspector General, an important feature of the Navy's program which is directly applicable in a civilian sector is the requirement for a formal plan of action and milestones for implementation of the program and overview of progress in meeting the requirements by the "Corporate Headquarters," namely the office of the Chief of Naval Operations.

PERCEIVED OUTPUTS/BENEFITS

Although the primary objective of the Navy program is to reduce hazardous waste by 50% in a finite time period, there are many other perceived outputs and benefits of the Navy program which are applicable to the civil sector as well as to other Federal agencies. Some of these benefits have already been cited in this presentation. In addition, the following are of critical importance:

- Avoidance of both resources (dollars and time) to deal with litigation, citations and fines associated with environmental impacts or violations and/or occupational safety and health requirements.
- Avoidance of the costs of new control equipment to comply with the requirements of the pending Clean Air Act and OSHA permissible exposure limit regulations.
- Reduction in impacts on productivity because of requirements for use of personal protective equipment, preventive measures, etc.
- Reduction in the costs for compensation for occupational injuries and illnesses.
- Cost containment associated with accident and emergency response requirements.
- Lessened technical administrative and management needs to deal with

hazardous materials.
- Reduction in specialized hazardous materials/hazardous waste storage facilities.
- Improve public and worker perception of the organizations policies, procedures and actions.[4]

SELECTION PROCESS FOR HAZARDOUS MATERIALS

One major need associated with the Navy program and similar hazardous material control and management programs in the civilian sector (in this author's view) is the lack of uniformly acceptable procedures for evaluation and selection of the least hazardous material to achieve specific needs. While the concept of substitution of lesser hazardous materials has been a longstanding philosophy of industrial hygiene and environmental engineering, no definitive guidance currently exists. In addition to toxicological and other environmental, occupational health and safety and public health hazard information (for example, fire and explosion potential), such considerations as the number of persons exposed, the frequency and duration of exposure and the circumstances of use need to be taken into account.

While there is a lot of literature relating to "risk analysis" in relation to environmental impacts[5], there is a need to compare the use of one solvent with another in a particular industrial setting. A number of methods currently used to evaluate occupational exposures may be utilized to meet this need. Among these are the procedures for "deriving risk assessment codes for health hazards" developed by the U.S. Army Environmental Hygiene Agency and adaptations to include environmental concerns total Air Force Occupational Safety and Health Standard 161-11,"Work Place Monitoring."[7] These both use numerical rating systems which allow a comparative analysis of the potential hazards and other concerns associated with the specific workplace situation. This is an area which requires much more study within the hazardous materials control community.

REQUIREMENTS
PROCUREMENT ACTION
SUPPLIES
WASTE
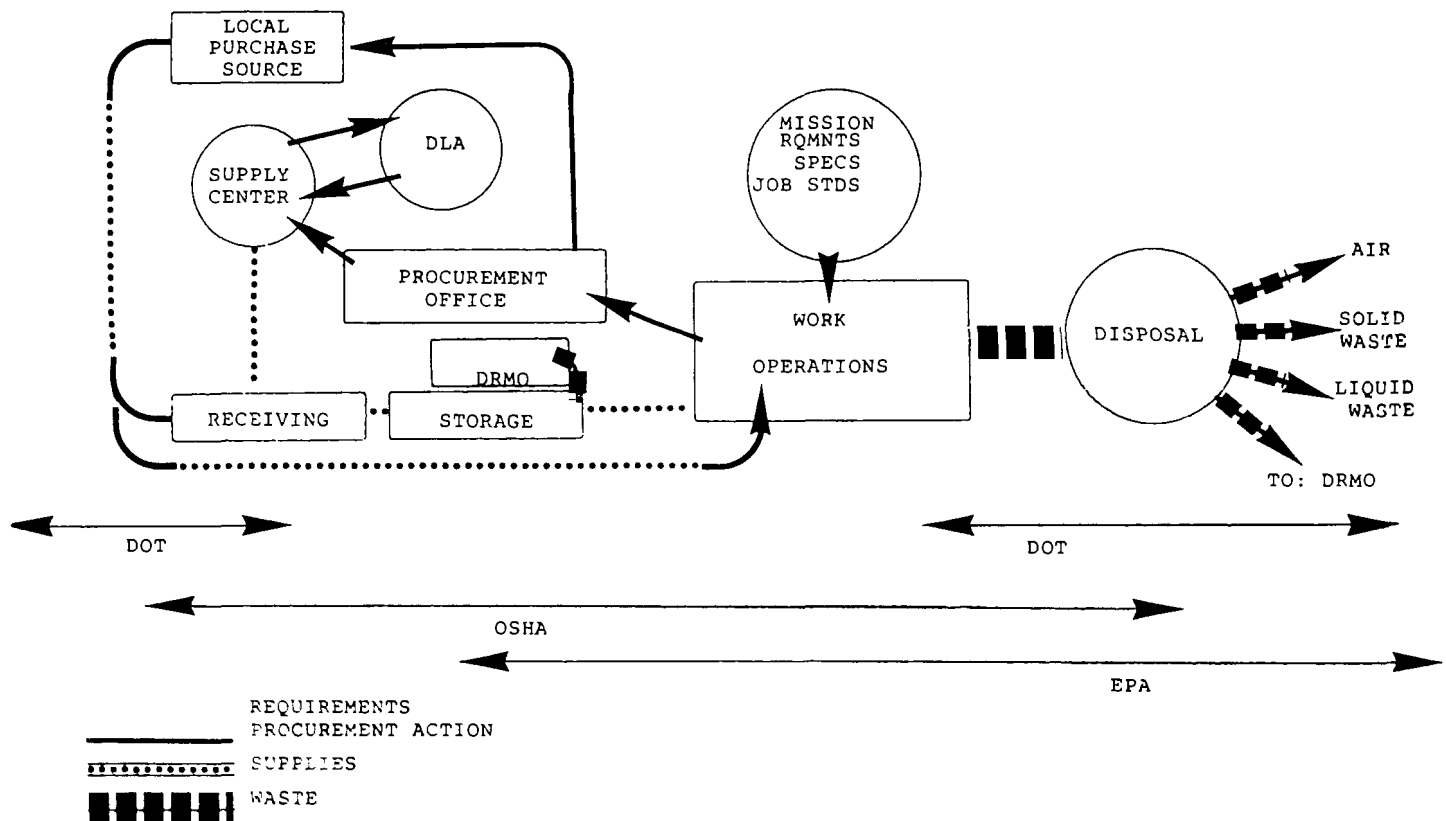
Figure 3
Hazardous Material Management Regulatory
Requirements and Life Cycle Concept

CONCLUSION

The end-of-the-pipe air, water pollution and solid waste control solution still is required for many waste streams. Hazardous materials control by "up-front" procedures is not a panacea, but it is essentially more cost-effective and less wasteful than the former mode of operation. From an overall national economic viewpoint, addressing a requirement for waste minimization and process control, when conducted in conjunction with measures to improve productivity and modernization of production processes, has built-in benefits as an important element in improving American competitiveness.

DISCLAIMER

This paper represents the opinions of the author only and is not an official U.S. Navy view or position.

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Case Study: Degradation of Diesel Fuel With In Situ Microorganisms

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ABSTRACT

Following a diesel fuel spill of approximately 1,400 gallons a portion of the contaminated soils was obtained for studies of bioremediation with an indigenous microbial consortium. These soils were characterized for existing microorganisms and hydrocarbon concentration. The predominant microbial species found in the diesel-contaminated soils consisted of *Pseudomonas putida, P. fluorescens, Acinetobacter calcoaceticus* var. *anitratus, A. calcoaceticus* var. *Iwoffi* and other *Pseudomonas* species. The initial total heterotrophic bacterial population was 2×10^5 CFU/g, the final population was 6×10^8 CFU/g and the soil contained approximately 14,000 $\mu g/g$ of diesel fuel.

In 150 days of treatment, approximately 87% of the hydrocarbons were mineralized to carbon dioxide and water. In another reactor where additional oil-degrading microbes were added along with the nutrients, the degradation of diesel fuel was 84%. A degradation study with oxygen consumption was also conducted with a six-reactor respirometer. Mineralization of 97% of initial concentrations of 100 and 300 ppm of diesel fuel was obtained in 60 days.

INTRODUCTION

Human and animal populations have demonstrated chronic and acute toxicity to organic chemicals.[1-3] Stricter federal and state regulations for organic pollutants have required owners to clean up their toxic wastes from the contaminated environment.[4-6] Although incineration technology often is the optimum choice for destruction of toxic and concentrated organic wastes, it is not economically feasible for organics sorbed to soils over a wide area.

The cleanup of persistent organic contaminants that have been strongly adsorbed to soils is difficult and expensive. One promising and economically feasible approach is through in situ biodegradation of the organic contaminants.[7-11] Theoretically, any organic compound can serve as a carbon source for microorganisms. Metabolism of organics with naturally existing living microorganisms may be encouraged by adding nutrients, oxygen and minerals. When naturally-occurring degradative microorganisms are absent or low in numbers, preacclimatized cultures may be added along with nutrients to the environment.

The specific objectives of the research were: (1) to evaluate the capability of a fertilizer formulation to serve as a nutrient source for promoting indigenous bioactivities, (2) to determine the indigenous microorganisms present in degrading diesel fuel and (3) to compare the biodegrading capability among the indigenous microorganisms, as well as the activated sludges obtained from an industrial wastewater treatment plant and a municipal wastewater treatment plant.

EXPERIMENTAL

In Situ Bioreactor

The soil samples obtained from the site were separated into two portions and placed into two 55-gallon glass reactors called AQUA-1 and AQUA-2. The design of the reactors is shown in Figure 1. AQUA-1 was designed to use naturally existing microbes for degrading the diesel fuel. A mixture of Pseudomonas, Enterobacter, Acinetobacter, Klebsiella and Bacillus was added along with the nutrient during injection into AQUA-2. The nutrients were applied during treatment of the soils in both reactors and the soils were continuously aerated with the PVC pipe. The excess nutrients were recycled back to the container. The nutrient was a fertilizer containing urea as a nitrogen source, phosphoric acid as a phosphorous source and metals.
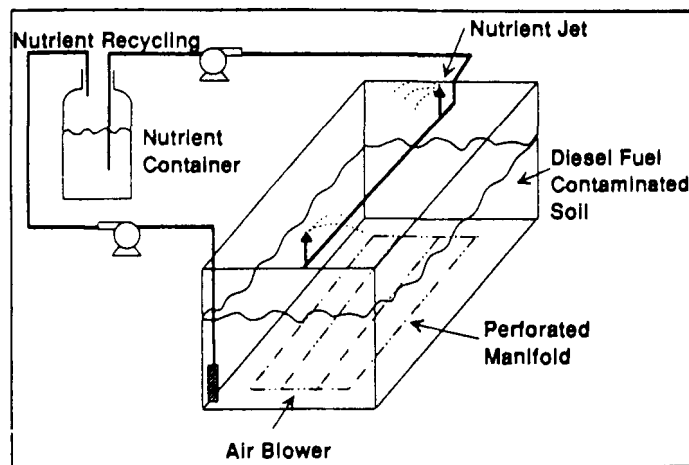
Figure 1
Design of In Situ Bioreactor for Degrading
Diesel Fuel in Contaminated Soil

Closed System Bioreactor - The Electrolytic Respirometer

The reaction vessels used in the study were 1-L flasks with side openings so that septa were easily inserted into them allowing sampling of the reaction mixture. The experiments consisted of duplicate flasks of two concentrations of diesel fuel (100 mg/L and 300 mg/L) in each flask. The indigenous microorganisms were isolated from the contaminated soils. Besides the indigenous microorganisms, mixed con-

sortium inocula also were obtained from an industrial wastewater treatment plant at Kelly Air Force Base, San Antonio, Texas and the San Antonio City Municipal Wastewater Treatment Plant. The seed inocula were suspended in a nutrient mixture containing ammonium chloride, calcium chloride, potassium phosphate, sodium phosphate and trace metals (magnesium sulfate, ferric chloride, sodium molybdate, cobalt chloride, copper sulfate, zinc sulfate) as nutrients. The respirometric control system consisted of (1) nutrient/substrate control (diesel fuel/sterile water/nutrient) and (2) nutrient/substrate/inoculum control (diesel fuel/nutrient/inoculum). At specified times, 25-mL aqueous samples were removed from the respirometer vessels and analyzed for diesel fuel aliphatic, aromatic compounds and related metabolites using gas chromatography/mass spectrometer (GC/MS). When necessary, the pH was adjusted to ensure that the environment remained optimal for microbial growth. The electrolytic respirometer was developed as a means of providing a more accurate and complete measurement of the BOD than normally is obtained by the standard dilution BOD methods. The BOD is determined by precise measurement of the oxygen uptake reaction. This system eliminates many technical problems encountered with other methods for determining oxygen demand and the rate at which it is exerted.

The electrolytic respirometer consists of three basic components: (1) a reaction vessel, (2) an electrolysis cell and (3) an electronic control unit. Together, these components comprise a large-volume respirometer which provides continuous and automatic adjustment of the oxygen pressure within the enclosed reaction vessel.[12]

As oxygen is consumed by the biological reaction within the reaction vessel, metabolically produced carbon dioxide is absorbed in a KOH scrubber solution. A slight vacuum is thereby created, causing a decrease in the electrolytic level in the outer chamber of the electrolysis cell. When an approximate 1-mm change in electrolyte level has occurred, the outer electrolyte surface breaks contact with the switch electrode. This signal activates the electronic control unit and causes a controlled direct current to flow through the electrolyte. Oxygen is produced at the positive electrode according to Faraday's Law. This oxygen is added to the reaction vessel in precise increments until the original internal pressure is reestablished and electrolyte contact is made at the switch electrode. Oxygen production is monitored electronically by counting the increments of input needed to equalize the pressure. Hydrogen produced at the negative electrode is vented to the atmosphere at the outside top of the electrolysis cell.

Microbial Analyses of Soil Samples

Soil samples were collected in sterile vials and refrigerated immediately upon receipt. These diesel fuel contaminated soil samples were used to characterize the indigenous microbial population growth. Serial tenfold dilutions of the soil samples were made using sterile 0.85% saline solution. Aliquots (0.1 mL) of the dilutions were spread plated onto plate count agar, MacConkey's agar, Pseudomonas agar P and Sabouraud dextrose agar plates.

Gram-negative isolates were identified using the API-20E system (Analytab Products, Plainview, New York). The system contains dehydrated chromogenic substrates that are activated with the addition of the bacterial suspension. The reactions are assigned numbers according to the result that occurs, and a seven or eight digit combination of these numbers is then decoded in the data base. The methodology used to detect the other microbial parameters was that described in the latest edition of Bergey's Manual of Systematic Bacteriology, Volumes I and II.[13] The techniques selected for identification were those which should yield the greatest degree of sensitivity for the samples examined.

RESULTS AND DISCUSSION

Oxygen Uptake

Results of the respirometry experiments were based on the oxygen uptake from each reactor vessel (containing 100 and 300 ppm, respectively) and the mineral nutrients.

1) 100 ppm diesel fuel/nutrients in sterilized water
2) 100 ppm diesel fuel/nutrients/industrial aerobic sludge

3) 100 ppm diesel fuel/nutrients/indigenous microbes
4) 300 ppm diesel fuel/nutrients/industrial aerobic sludge
5) 300 ppm diesel fuel/nutrients/indigenous microbes
6) 300 ppm diesel fuel/nutrients/municipal microbes

The oxygen uptakes are shown in Figure 2. The figure displays cumulative oxygen consumption with respect to duration time illustrated by oxygen uptake kinetics. Oxygen uptake in the nutrients with the 100-ppm diesel fuel began after approximately 2 days lag time and leveled off at approximately 180 mg/L through 30 days. In the substrate/nutrient/inoculum control studies, inocula obtained from the industrial wastewater treatment plant showed a better initial bioactivity comparing the indigenous and municipal wastewater cultures. The activity of the industrial inoculum could be traced to the acclimation and selection of the inoculum to hydrocarbons at the treatment plant.
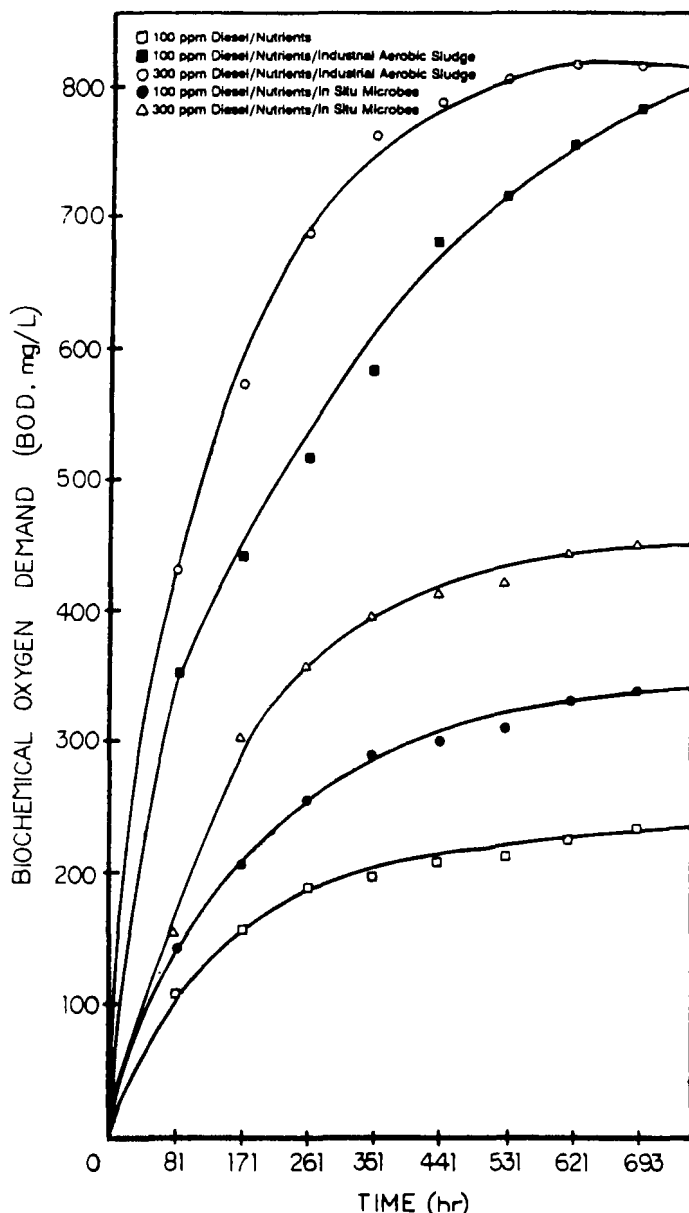
Figure 2
Cumulative Oxygen Consumption in Respirometry Experiments

Oxygen consumption showed a cumulative oxygen uptake plateau at 780 mg/L at a 300-ppm initial diesel fuel concentration in the industrial inoculum culture. The maximum oxygen uptake values for the indigenous soil microbe inoculum were 320 mg/L and 450 mg/L at 100

ppm and 300 ppm initial diesel fuel concentration for 60 days incubation. Figure 2 only shows 30 days of incubation.

Microorganism Analysis

Growth data indicated significant increases of growth of the indigenous oil degrading microorganisms at the end of the 60-day incubation period.

Table 1
Microorganisms Extracted from in Situ Diesel Contaminated Soils and Cultured in the Laboratory

Colonies Count (Plate Count Agar) = 1.2×10^5 cfu/mL

1. *Pseudomonas aeruginosa*
2. *Pseudomonas fluorescens*
3. *Pseudomonas putida*
4. *Acinetobacter calcoaceticus var. anitratus*
5. *Acinetobacter calcoaceticus var. lwoffi*

MICROORGANISMS OBTAINED FROM INDUSTRIAL AEROBIC ACTIVATED SLUDGE

Colonies Count (Plate Count Agar) = 2.8×10^5 cfu/mL

1. *Pseudomonas aeruginosa*
2. *Pseudomonas pseudomallei*
3. *Pseudomonas fluorescens*
4. *Pseudomonas cepacia*

MICROORGANISMS OBTAINED FROM MUNICIPAL AEROBIC ACTIVATED SLUDGE

Colonies Count (Plate Count Agar) = 1.1×10^5 cfu/mL

1. *Pseudomonas pseudomallei*
2. *Enterobacter cloacae*
3. *Aeromonas hydrophila*
4. *Acinetobacter calcoaceticus var. anitratus*

Plate counts demonstrated that the number of organisms increased from 2.1×10^5 cfu/mL on the soil samples to 6×10^8 cfu/mL after 60 days of incubation in the respirometric reactors. The total heterotrophic bacteria count seemed to level off after the first 2-3 weeks of incubation.

hydrocarbons degrading capability in the literature.[7-11] An attempt to characterize the aerobic activated sludges obtained from Kelly Air Force Base, Texas, and the San Antonio Municipal Wastewater Treatment Plant is shown in Table 2.

Gas Chromatographic/Mass Spectrometry Analysis Information

Table 2 illustrates the GC/MS analysis in culture samples obtained from respirometric vessels. This analysis demonstrates almost complete mineralization of the aliphatic and aromatic hydrocarbons in these experimental systems at the end of 60 days incubation in Reactions 2-5. Significant biodegradation of diesel fuel at 100 mg/L and 300 mg/L occurred with inocula obtained from the industrial wastewater treatment plant and acclimated indigenous soil microbiota. This result also shows that higher concentrations of diesel fuel in the inlet stream of municipal treatment plant may upset the activated aerobic sludge of the plant. The blank control experiment in Vessel 1 using the respirometric approach provided evidence that more than 90% of the diesel fuel remained in the sample at 60 days post-inoculum.

The Fourier transform infrared analysis technique was applied to analyze the samples obtained at 60 days. These samples were extracted by Freon 113 and hydrocarbons monitored at 2930 nm.

Biodegradation data for diesel fuel contaminated soils at approximately 14,000 μg/g are shown in Table 3. Control studies were conducted with air aerated at 10 psig throughout the soil for 10 days. Soil samples obtained from the reactors on the 3rd, 6th and 10th days demonstrated that the high molecular weight aliphatic (mle = 57) and aromatic (mle = 91) hydrocarbons are strongly absorbed by the soil matrix. The concentrations remained at a homogeneous level with 2,900 ppm of aliphatic hydrocarbons and 13,000 ppm of aromatic hydrocarbons for reactor AQUA-1 and 3,100 ppm of aliphatic hydrocarbons and 13,000 ppm of aromatic hydrocarbons in reactor AQUA-2.

On the 11th day, sprinkle-type injection systems were set up on both aerated reactors and the soil moistures were controlled to near 40-60%. For reactor AQUA-1, only buffered fertilizer medium was applied to the soils while hydrocarbon preacclimatized microbes were added into the buffered fertilizer medium to enhance the degradation rate of the AQUA-2 soils. During applications, the nutrient conditions were monitored and maintained at pH 7 and room temperature. The samples obtained after 30 days showed a drastic drop in concentrations of the residual diesel fuels. In AQUA-1 60% and 50% of the initial aliphatic and aromatic hydrocarbons, respectively, were degraded; at the same time the soil samples obtained from AQUA-2 demonstrated 74% and 62% degradation of the aliphatic and aromatic hydrocarbons, respectively. In both reactors, the recycled nutrients in the bioreactors do not

Table 2
Respirometer Study with Diesel Fuel Exposed
to Acclimated Inocula

Sample ID	Amount (µg/g)				
	By GC/MS				By FTIR (TPH)
	T=0 Day	T=15 Day	T=30 Day	T=60 Day	T=60 Day
1. 100 ppm Diesel Fuel/Nutrient	100	105	82		120
2. 100 ppm Diesel Fuel/Nutrient/Industrial Wastewater Inoculum	100	113	98		1.3
3. 100 ppm Diesel Fuel/Nutrient/Indigenous Soil Inoculum	100	96	88		3.3
4. 300 ppm Diesel Fuel/Nutrient/Industrial Wastewater Inoculum	300	197	214		20
5. 300 ppm Diesel Fuel/Nutrient/Indigenous Soil Inoculum	300	192	179		7.3
6. Diesel Fuel/Nutrient/Muncipal Wastewater Inoculum	300	392	207		86

As shown in Table 1, the inoculum composition was characterized for the component and microbial species. The contaminated soils contained *Pseudomonas aeruginosa, Pseudomonas fluorescens, Pseudomonas putida, Acinetobacter calcoaceticus var. anitratus* and *Acinetobacter calcoaceticus var. lwoffi. The organisms have established*

contain any hydrocarbons. In the total population counts, a 50% increase in bacteria density was obtained in both reactors. In 150 days of treatment, approximately 87% of the hydrocarbons were mineralized to carbon dioxide and water in AQUA-1. In AQUA-2, the degradation of diesel fuel was 84%. It is anticipated that the soils will be cleaned

up in another 4 months.

Analytical respirometry and the in situ bioreactor technique were shown to be a valuable experimental approach for testing biodegradability of the diesel fuel formulations in contaminated soil matrices.

Table 3
Biodegradation Control Studies with the Diesel Fuel
Contaminated Soils Obtained from a Diesel Fuel Spill Site

CONTROL AQUA-1	m/z = 57 amount		m/z = 91 amount			
T =	% Dry Wt	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry		
3	95.1	2,863	3,011	11,953	12,569		
6	91.6	2,815	3,073	12,362	13,496		
10	93.5	2,972	3,179	12,626	13,504		

CONTROL AQUA-2	m/z = 57 amount		m/z = 91 amount			
T =	% Dry Wt	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry		
3	88.4	2,756	3,118	13,201	14,933		
6	88.6	2,971	3,353	14,774	16,675		
10	91.9	2,804	3,051	14,605	15,892		

SOIL AQUA-1	m/z = 57 amount		m/z = 91 amount		FTIR Amount	
T =	% Dry Wt	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry
30 days	79.5	956	1,203	5,219	6,565		
60 days	76.5	341	450	2,965	3,800		
90 days	75.1	685	912	1,548	2,064	3,247	3,820
150 days						1,548	1,821

SOIL AQUA-2	m/z = 57 amount		m/z = 91 amount		TPH Amount	
T =	% Dry Wt	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry	µg/g Wet	µg/g Dry
30 days	80.0	621	776	3,822	4,778		
60 days	75.7	723	960	3,499	4,600		
90 days	79.3	350	441	1,898	2,393	3,961	4,660
150 days						1,789	2,181

CONCLUSIONS

Respirometric and bioreactor biodegradation data have demonstrated a significant enhancement of biodegradation of diesel fuel with the use of fertilizer and mineral nutrients. In situ stimulation of the growth of indigenous microbes from diesel-contaminated soil with nutrients permitted the mineralization of hydrocarbons to environmentally acceptable products, carbon dioxide and water. Inoculum from an industrial wastewater treatment plant were an alternative source of microbes permitting degradation of hydrocarbons. The results of this experiment have promoted an on-site pilot study of the diesel fuel spill site. We anticipate the cleanup of the contaminants will be accomplished within a year.

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Biodegradation of Aromatic Compounds

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ABSTRACT

An overview of current knowledge on the capacity of microorganisms to degrade polycyclic aromatic compounds (PAH) will be reviewed. Bioremediation of PAH compounds such as pentachlorophenol (PCP), creosote, naphthalene and phenanthrene will be demonstrated through case histories.

A former railroad tie-treating plant on the NPL list is contaminated with creosote in soil and groundwater. PCP, naphthalene and phenol have migrated from site ponds and have contaminated shallow groundwater beneath the site and a nearby river. Contamination at the site ranges from oil-saturated sands and gravel to groundwater containing $\mu g/L$ concentrations of dissolved contaminants.

ECOVA conducted a 20-month treatability study and process development program to evaluate the effectiveness of oil recovery and develop advanced in situ soil washing and bioremediation treatment techniques. Laboratory bench-scale studies provide a thorough analysis of site soils, and a series of micro-column studies determined the effectiveness of bioremediation. The results confirm that the PCP can be rapidly degraded in the highly contaminated soil and water at this site. This study confirmed that the PAHs could be successfully biologically remediated in the contaminated soil and water. The rates of loss are extremely rapid in a soil slurry system, with concentrations reaching nondetectable levels in four weeks in some cases. Similarly, water biotreatment can be extremely rapid and complete. Finally, the compounds can be effectively (90%) removed from soil by simulating in situ soil washing which has tremendous potential for hastening on-site remediation of heavily-contaminated sites.

The Brio Refining Superfund Site has a large volume of soil containing styrene still bottom tars and chlorinated hydrocarbon solvents. The site, located adjacent to a housing development, contains approximately 60,000 yd^3 of waste. VOCs, ethylbenzene, styrene and toluene, were detected at maximum concentrations of 4,400 ppm, 240 ppm and 510 ppm, respectively. The contaminant of particular concern is phenanthrene, detected in ranges from 0.44 to 170 ppm. ECOVA conducted a process development and treatability study to bioremediate the soil.

A site assessment and laboratory study demonstrated that phenanthrene could be degraded to <1 ppm using biological techniques. A four-month pilot demonstration of solid-phase bioremediation was conducted. The treatment area was enclosed into greenhouse-type enclosures to capture vapor emissions during treatment and eliminated the need to control or treat rainwater. An overhead spray system distributed water, nutrients and inocula. Organic vapor emissions were controlled by adsorption on carbon and the greenhouse helped control dust. Approximately 200 yd^3 of contaminated soils were successfully treated during the 94 days of operation. VOCs were reduced by more than 99%. Semivolatile organic compound concentrations were reduced an average of 89%, and phenanthrene concentrations reduced an average of 84%. the average phenanthrene half-life was 33 days, significantly less than reported half-life values of 69-298 days in other solid-phase bioremediation systems. The data indicated that approximately 131 days would be required for the phenanthrene concentration to reach 0.33 ppm, the analytical detection limit using U.S. EPA-approved procedures.

INTRODUCTION

Bioremediation is the controlled use of microbiological agents, commonly bacteria and fungi, to reclaim soil and water contaminated with substances which are deleterious to human health and the environment. The biological agents are often indigenous microorganisms inhabiting the polluted matrix. However they also may be seed organisms which have been isolated from another environment on the basis of their ability to degrade a specific class of substances. It is due to the wide diversity of microbial metabolic potential that bioremediation is possible.

PAHs represent a class of organic compounds which are ubiquitous in the environment. They are present in fossil fuels and are formed during the incomplete combustion of organic material. Creosote has been used extensively to treat wood products against fungal and insect attack or to impart fire resistance. The creosote found in wood treatment wastes is a coal tar distillate boiling from 200 to 400°C. Chemically, creosote is a complex mixture predominantly of PAHs, plus a minor fraction of phenolic substances. The major PAH constituents are 2-, 3-, 4- and 5-ring compounds, including; naphthalene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzopyrene and methyl derivatives of these compounds. PAHs, as a class of organic compounds exhibit low volatility and low aqueous solubility. As the molecular weight of these compounds increases, there is an exponential decrease in both solubility and volatility. PAHs exhibit a strong tendency to adsorb onto soils and sediments due to their hydrophobic character, which is an intrinsic function of molecular size.

The microbial degradation of individual PAHs by pure cultures[1] as well as mixed populations is well documented.[2] In addition, the degradation of PAHs has been evaluated in complex mixtures such as petroleum refining wood preserving wastes. Numerous laboratory studies have been performed which demonstrate the biodegradability of these compounds under a wide range of soil types and environmental conditions.[4,5,6]

Generally, the factors which seemed to have the greatest influence on the rates of biodegradation were moisture content of soils, pH, inorganic nutrients, loading rates, initial concentrations and the presence of an acclimated microbial population.

Feasibility studies are an essential component for the development of a bioremediation strategy. These studies are performed in a phased testing program which is designed to accomplish a number of objec-

tives. These objectives include:

- Establish the existence of an indigenous microbial population with the appropriate degradative potential on-site contaminants
- Define the rate limiting factors for enhanced microbial degradation of the contaminants
- Perform process optimization studies to define the optimal treatment in terms of rates and cleanup levels attainable
- Develop design parameters for field operations

The first half of this paper presents a case study on a feasibility testing program and the implications of the results for the development of a site-specific remediation strategy. The second half will present a review of a pilot-scale demonstration program treating soils containing styrene still bottoms and chlorinated hydrocarbon solvents presented at this conference in 1987.[7]

CASE HISTORY: TREATABILITY STUDY

The site is a former wood treating facility which was in operation for almost 100 years. Wood preserving agents used in the process included zinc chloride, creosote oil and pentachlorophenol. Wastes were disposed of at the plant according to the standards of the era, resulting in approximately 100 acres at the site becoming contaminated by present standards. Contamination consists largely of an immiscible, denser than water mixture of creosote and PCP. The principal compounds of concern are PCP and PAHs. The range of site contamination varies from oil-saturated sands and gravel to groundwater with $\mu g/L$ concentration of dissolved phenols, PCP PAHs and other petroleum hydrocarbon fractions.

The site was secured with a contaminant isolation system installed on-site. Actions over the past three years have focused on cleanup of the site through on-site contaminant removal and biotreatment technologies. Due to the tightness of the bedrock formations and the high porosity of the soils, this site is well-suited to in situ bioremediation techniques.

RESULTS

Phase 1: Microbial Biotreatability Evaluation

A microbiological evaluation was performed to determine whether the microorganisms currently present in the soils and groundwater at the site were capable of degrading the site contaminants under conditions conducive to biodegradation. Soil and water samples were incubated under aerobic conditions with sufficient nutrients for 4 weeks. The loss of contaminants was monitored by GC/MS. Half of the samples received growth factors and a surfactant to determine whether these chemical treatments could enhance biodegradation.

The results indicated that substantial biodegradation of contaminants could be achieved in all of the areas sampled. Contaminant reduction was greatest in the groundwater samples (93%), followed by the saturated soils (80%) and the unsaturated soils (66%). The percent reduction in individual target contaminant levels was not related to the initial concentrations in all samples. However, the total biodegradation was related to total contaminant concentration in all samples. The residual hydrocarbon after a 4-week incubation appeared to be related to the inherent biodegradability of the contaminants present in a given sample. Most of the individual compounds were readily biodegraded. The average loss of 2 - 3 ring polynuclear aromatic hydrocarbons (PNAs) was 80 to 90%. In those sites showing residual hydrocarbon, the compounds were those showing slower rates of biodegradation such as pentachlorophenol (PCP) and the 4 - 6 ring PAHs (approximately 65% loss on average). No effect of the growth factor and surfactant addition was observed.

Although the results indicate substantial biodegradation of contaminants, it was necessary to confirm that microorganisms present at the site are capable of mineralizing the contaminants (i.e., convert organic carbon to carbon dioxide). To confirm mineralization, selected ^{14}C-labeled compounds were incubated with enrichment cultures selected during the previous activity and mineralization was monitored by measuring the evolved $^{14}CO_2$.

The results showed that the 2 - 3 ring PAHs tested (naphthalene,

phenanthrene and fluorene) were rapidly mineralized by most of the enrichment cultures when present as sole carbon source. The 4- and 5- ring PNAs tested (pyrene and benzo(a)pyrene, respectively) were not mineralized when present as the sole carbon source. However, $^{14}CO_2$ was evolved by some enrichments when contaminated soil (containing additional hydrocarbon substrate) was added. This is evidence that mineralization of 4- and 5-ring PNAs may be achieved through cooxidation by stimulating microbial activity on other organic substrates (i.e., microbes are growing related simpler contaminants). PCP was mineralized when present as sole carbon source only by enrichments from some of the surface and unsaturated soil samples. Microorganisms responsible for mineralizing PCP appeared to be lacking from the groundwater and saturated soil samples. The apparent lack of this metabolic potential in these areas probably is due to the lack of oxygen. An acclimated culture capable of PCP mineralization was under development and testing.

The initial studies have shown that the site contains microorganisms capable of extensive biodegradation of all target contaminants. Many of the simpler compounds can be biodegraded as sole carbon source and these apparently can induce the production of enzymes capable of degrading the more complex compounds as well. These bacteria apparently are not distributed evenly throughout the site. Thus, the extent of biodegradation of PCP or more complex PNAs was highly variable between samples and there was no conclusive evidence that the microorganisms present in any one sample could degrade all of the contaminants. However, the results establish the potential for in situ biological treatment for both contaminated groundwater and soils at the site.

The following conclusions can be drawn from this work:

- The total contaminant concentration at the site varies with sampling site (location) and/or medium (groundwater, surface, subsurface soil).
- The potential to biodegrade all of the contaminants present in the soil and water exists in the metabolic capabilities of the microorganisms present at the site.
- The fraction of the total contaminant load which was biodegraded in a given time period was related to the location of the sample (groundwater > saturated soil > unsaturated soil).
- The total contaminant biodegraded in a given time period was related to the total concentrations of contaminants as well as the concentration of 4 - 5 ring PNAs or PCP.
- The amount of contaminant biodegradation achieved was not increased by addition of growth factors or surfactants.
- Inoculation of microorganisms or substrates may be necessary to redistribute the biodegradation potential at the site to achieve total bioremediation.
- Mineralization of most the compounds tested can be achieved by microorganisms present in the site.
- Cooxidation or the addition of specific organic substrates may stimulate the biodegradation of other compounds (4 - 5 ring PNAs and PCP).

Phase 2: Bioremediation Process Optimization

From the Phase 1 studies it was concluded that the indigenous microorganisms possessed the contaminant biodegradation potential required for an effective in situ bioreclamation process. The focus for the Phase 2 studies was on determining how best to use these capabilities in a site-specific bioreclamation process and on preliminarily evaluating the cleanup levels that can be achieved over time.

Several specific in situ bioreclamation processes were developed and tested. These processes include surface bioreclamation, in situ subsurface bioreclamation after free product recovery and in situ subsurface bioreclamation following soil washing using an alkaline polymer surfactant (APS). Each process relies on stimulating the contaminant biodegradation activity of native microorganisms by managing the soil environment. Process specific techniques include altering and maintaining pH and moisture levels within a preferred range, supplementation with inorganic nutrients that would otherwise be present in limiting concentrations and providing sufficient oxygen for optimal aerobic

activity. Laboratory results suggest that surface bioreclamation following primary product recovery and in situ subsurface bioreclamation following soil washing each has potential as a viable, cost-effective remediation technique.

Surface Bioreclamation

Surface bioreclamation is based on the microbial degradation of organic contaminants in soils in a land surface treatment system. Surface bioreclamation essentially consists of stimulating contaminant degradation in a relatively shallow (< 18 inch) surface soil layer. Contaminant biodegradation is stimulated by providing an environment conducive to optimal microbiological activity. Aerobic conditions are maintained by optimizing atmospheric contact and oxygen diffusion through surface soil and may be aided by soil tilling methods. Inorganic nutrients and other soil amendments can also be tilled into the soil while the moisture content is maintained within a range conducive to microbial activity.

The most effective surface bioreclamation methods were evaluated by measuring contaminant reduction in soils treated by different methods in microcosm studies. The surface bioreclamation microcosm studies were carried out in small open pans containing approximately 3 kg of soil spread to a depth of approximately 10 cm. Daily tilling and watering were carried out to maintain soil moisture content at approximately 50% to 70% of the water holding capacity. Treatments evaluated in these studies included the following:

- Soil amendment with inorganic nutrients
- Amendment with various levels of manure
- Inoculation plus amendment with nutrients

Figure 1 illustrates the results obtained for the biodegradation of the PAH fraction in the surface soils under evaluation for surface bioreclamation.
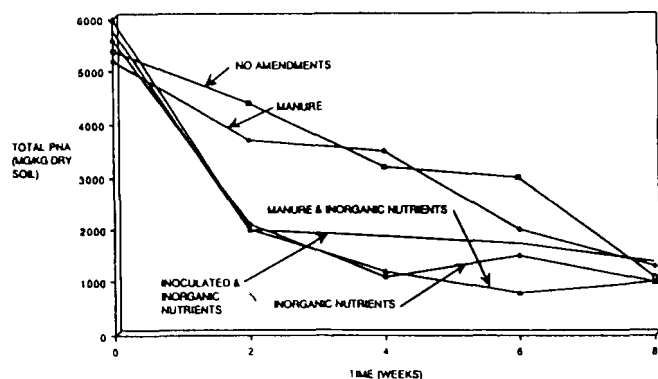
Figure 1
PAH Removal Results for Laboratory Simulation of Surface
Soil Bioreclamation

The contaminant removal kinetics observed in these studies were on the high end of the range obtained in similar studies reported in the available literature. Similar results were observed for the oil and grease component of the site contamination. As observed in other studies, the higher ring PAHs (i.e. > 4-rings) exhibit degradation rates which are lower than for the 2-to 3-ring PAHs. This results in a lower overall biodegradation efficiency of the larger PAHs during the study period (Table 1). Given the limited duration of these studies (i.e., 8 weeks), the rates should be considered initial rates at best for the higher ring PAHs and therefore the residual contaminant levels achievable for these compounds cannot be accurately assessed.

These laboratory simulations suggest a number of factors that may be important for surface bioreclamation pilot studies. For example, it appears that while the addition of manure did not significantly enhance the rate of biodegradation, it did enhance the physical character of the soil making it easier to till. This operational factor alone warrants the use of manure for field pilot studies. The laboratory studies also suggest

Table 1
Residual Contaminant Levels Achieved in Surface Bioreclamation Pan Studies

that it may be beneficial to add nutrients in small multiple increments.

The most important implication of the laboratory soil pan studies is that surface bioreclamation does indeed appear to be a viable means of reducing the contaminant levels in the surface soils. It should be further investigated in field pilot studies.

Soil Washing

Laboratory column studies, which are designed to simulate an in situ treatment process, have provided data on the effectiveness of the APS soil washing process. These studies confirm the contaminant removal effectiveness of the APS soil washing technique as summarized in Table 2. Generally, better removal efficiencies (>89%) were observed in the more heavily contaminated Trench 4 soil.

Table 2
Contaminant Removal in APS Soil Washing Studies

In situ soil washing is a two-step process consisting of delivery of the APS solution followed by an aquifer reequilibration step designed to purge residual polymer and surfactant and to establish base line pH conditions. The high pH values subsequent to the APS wash are not conducive to microbial activity. In addition, the alluvium will contain high residual concentrations of polymer and surfactant. This contamination may contribute to an increased oxygen demand and result in the preferential biodegradation of this material over the target contaminants.

As part of the laboratory studies, various treatment evaluations were performed on soil columns that had been subjected to the APS washing process. One series of columns was treated by flushing the soil with 0.001 N phosphoric acid solution to return the soil to near neutral pH. The other series of columns was treated by flushing neutral pH, oxygenated water through the columns to slowly reequilibrate the soil. As summarized in Table 3, higher concentrations of polymer, surfactant and target contaminants were leached with neutral water solution than with the acid solution. This suggests that aquifer rehabilitation will be most effectively accomplished with non-pH-adjusted water.

Table 3
Contaminant Removal During Simulated Aquifer Rehabilitation

Parameter	Contaminant Concentration After Soil Washing	After Aquifer Rehabilitation			
		Treatment 1[a]		Treatment 2 and 3[b]	
		Concentration	Percent Reduction	Concentration	Percent Reduction
Chemical Oxygen Demand	49,000	10,350	79	27,500	44
Total Petroleum Hydrocarbons	10,208	985	90	1,425	86
Total PNAs	2,406	139	91	185	89
Pentachlorophenol	57	ND[c]	--	ND[c]	--

[a]Flushed with Neutral Water
[b]Flushed with phosphoric acid solution
[c]Not detected at the method detection limit.

Note: Concentrations in mg/kg.

Subsurface Bioreclamation

Subsurface bioreclamation may be implemented in two distinct soil environments. One scenario is implementation immediately following primary oil recovery in which case the soil environment would be heavily contaminated. In the second scenario, primary oil recovery would be followed by in situ soil washing with in situ bioreclamation as the polishing step to achieve final cleanup levels. The soil environment would be characterized by much lower target contaminant levels, the presence of residual polymer and surfactant from the wash step and potentially altered microbial populations and metabolic capabilities.

Laboratory studies were performed to evaluate in situ bioreclamation in both washed and unwashed soils. The discussion of the results from this study is therefore presented in two sections: bioreclamation in unwashed soils and bioreclamation in washed soils.

Studies performed to evaluate in situ bioreclamation in unwashed soils were designed to answer the following questions:

* Considering the toxicity of certain site contaminants, could microbial degradative activity be stimulated in the heavily contaminated soils present after primary oil recovery?
* What specific treatments are required to most effectively stimulate activity in these soils?
* What cleanup levels are achievable as a function of time in the specified process?

The ability to stimulate microbial activity in heavily contaminated unwashed soils was evaluated in column studies designed to simulate in situ subsurface bioreclamation. Soils from two site locations, Trench 1 and Trench 4, were used in these studies. Trench 4 soil had the highest contaminant levels, approximately four times greater than Trench 1 soil. Approximately 400 g of soil were placed in columns 20 cm long with a diameter of 5 cm. Simulated groundwater containing combinations of treatment agents (e.g., oxygen, nutrients, peroxide and inoculum) was then passed through the saturated soil column. Data were obtained
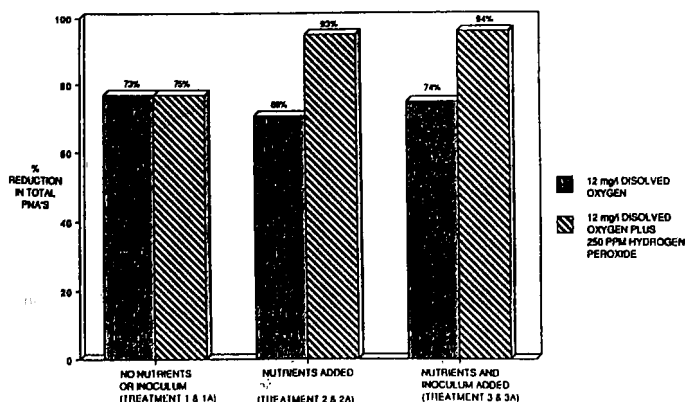
Figure 2
Contaminant Reduction in Trench 4 Soil During Column Studies

through influent and effluent analysis and through analysis of soil from sacrificed columns.

Results from the column studies demonstrated that microbial contaminant degradation could be stimulated in heavily contaminated Trench 4 soils. Oxygen consumption in the columns is indicative of aerobic microbial activity since the aerobic biodegradation of the contaminants will exert an oxygen demand on the system. Oxygen supplied to the columns was generally rapidly and completely utilized in the columns. The data suggested that higher oxygen delivery rates resulted in increased contaminant biodegradation or removal. The greatest degree of contaminant reduction occurred in columns which received elevated oxygen levels and inorganic nutrients. This result is illustrated in Figure 2 which presents a summary of results obtained in studies conducted in the soil columns.

The level of cleanup achievable using in situ subsurface bioreclamation and the time required to attain a given cleanup level will be two criteria that will determine the feasibility of this technique for site cleanup. The most pertinent data generated in the bioreclamation laboratory studies for cleanup levels are the data on contaminant concentrations in column leachates at the conclusion of the tests. These data provide a measure for organic groundwater quality achievable as subsurface contaminants are removed and biodegraded.

Leachate from the columns was evaluated after 15 weeks of delivering oxygen and nutrients to saturated soil columns. No PAHs or PCP were detected in the column leachate at a detection limit of 10 µg/L. Levels of total petroleum hydrocarbon (TPH) were below the detection limit of 1.0 mg/L. Another measure of the degree of cleanup achievable with in situ bioreclamation immediately following primary oil recovery is the degree to which specific contaminant concentrations in column soils are reduced. Table 4 contains data on soil contaminant levels at the beginning and after 15 weeks of treatment in select column studies.

It is apparent from these data that significant reductions in all contaminants were observed; however, this result was not considered representative of the ultimate degree of cleanup attainable. Most of the oxygen being supplied to the columns was still being consumed in the columns at the time these data were collected.

Select columns were operated through 92 weeks of treatment before the columns were sacrificed and analyzing soil samples were analyzed for residual contaminant levels. Generally, oxygen consumption had subsided considerably and nutrient levels in column effluents approached those of the influent. This was taken as an indication that microbial degradative activity had subsided. Trench 1 soils continued to exhibit further reductions in all PAHs. In the more heavily contaminated Trench 4 soil columns, further reductions in contaminant levels were observed only in those columns receiving inorganic nutrients and aerated groundwater. Columns receiving additional oxygen in the form of hydrogen peroxide showed no significant reductions in PAHs after the first 15 weeks of treatment. The indication is that treatment with hydrogen peroxide can substantially reduce the time frame of in situ bioreclamation and achieve the maximum cleanup levels attainable. Table 5 provides a summary of the results obtained for specific bulk contaminant parameters such as COD, oil and grease, TPH and total PAHs. These data suggest that while though peroxide treatment resulted in optimal PAH removal during the first 15 weeks of treatment, further significant reductions in COD and TPH could be achieved through longer treatment times. The data can also be interpreted to indicate that PAHs are preferentially biodegraded in comparison to the total organics. Table 6 provides a summary of the reductions obtained in specific target contaminant levels for Trench 1 (low PAH) and Trench 4 (high PAH) at various treatment times. The results tend to indicate that the use of hydrogen peroxide yielded optimum reduction of all PAHs during in the shortest treatment interval (15 weeks). When treatment consisted of supplying oxygen via aerated groundwater, then both Trench 1 and Trench 4 soils exhibited substantial reductions in PAHs with extended treatment periods.

Laboratory studies were performed to evaluate in situ subsurface biodegradation of contaminated subsurface soil following in situ soil washing with an APS solution. These studies were designed to answer the following questions:

Table 4
Residual Contaminant Levels Achieved in Select
Surface Bioreclemation Studies After 15 Weeks

Parameter	Treatment 1[a]			Treatment 2[b]			Treatment 3[c]		
	Initial	After 15 Weeks	Reduction	Initial	After 15 Weeks	Reduction	Initial	After 15 Weeks	Reduction
Chemical Oxygen Demand	7,900	3,800	52	16,500	11,500	30	13,000	17,250	--
Total Petroleum Hydrocarbons	415	123	70	650	70	90	300	300	0
Oil & Grease Polynuclear Aromatic Hydrocarbons	325	207	36	964	72	92	580	290	21
2 - and 3-Ring PNAs	59.4	ND	100	365	76.4	79	189	62	67
4- and 5 Ring PNAs	70	14.6	79	175	157.4	10	138	81	41
Total PNAs	129.4	14.6	88.7	540	233.8	56	329	143	56

[a] Treated with aerated water.
[b] Treated with aerated water containing inorganic nutrients.
[c] Treated with aerated water containing inorganic nutrients and inoculum.

Table 5
Contaminant Reduction in Representative Subsurface
Bioreclemation Column Studies

Table 6
Residual Contaminant Achieved in Representative Subsurface
Bioreclamation Column Studies

- To what extent will microbial populations and metabolic capabilities be altered by the APS soil washing process?
- What measures are required following soil washing to restore microbial degradative activity towards site contaminants?

- What cleanup levels are achievable using in situ subsurface bioreclamation following in situ soil washing?

A major concern about the in situ soil washing process followed by in situ bioreclamation as a polishing step was the potential adverse effect of the APS solution on microbial populations and metabolic capabilities towards site contaminants. The saline, alkaline, APS solution could drastically reduce microbial numbers and metabolic capacity during the washing cycle. It was hypothesized that a soil washing agent that effectively liberates and displaces oil from the subsurface soils could flush the associated microbial biomass from the soils as well.

The degree to which microbial populations and metabolic capabilities were altered by the soil washing process was evaluated in a series of column experiments. Approximately 400 g of Trench 4 soil were placed in columns 20 cm long with a diameter of 5 cm. Four pore volumes of the APS solution were then passed through the columns. After soil washing, various treatments for rehabilitating the soil were evaluated. Simulated groundwater containing combinations of treatment agents (i.e., phosphoric acid, oxygen, nutrients, peroxide and inoculum) were then passed through the saturated soil column. Data were obtained through influent and effluent analysis and through analysis of soil from sacrificed columns. Evidence of restoration of microbial activity can be divided into three categories:

- Oxygen consumption in the columns
- An increase in microbial numbers during the bioreclamation phase
- Contaminant removal during bioreclamation

After the soil washing process, Trench 4 soil samples exhibited a reduction in microbial populations from 2×10^5 viable heterotrophic bacteria per gram of soil to less than 10^4 gram of soil. Trench 2 soil showed a more drastic reduction in microbial populations from 3×10^7 to 1×10^5/gram of soil (Table 1). Subsequent to cycling water containing oxygen and nutrients through the soil columns, microbial counts increased to 2×10^7/gram of soil. This increase in numbers is another indication that microbial activity can be reestablished in soils after APS washing.

The effect of the simulated soil washing process on microbial biodegradation capabilities was evaluated by measuring phenanthrene mineralization during incubation of soils subjected to the soil washing process. Mineralization was measured using a ^{14}C - radioisotope of phenanthrene and monitoring for the production of $^{14}CO_2$.

As can be seen by the results presented in Table 7, phenanthrene mineralization was reestablished in Trench 4 soils but apparently was not reestablished in Trench 2 soil.

Nearly all oxygen supplied to the columns was consumed during the bioreclamation phase. In columns with an influent dissolved oxygen of 12 mg/L, the effluent dissolved oxygen was always less than 1.5 mg/L.

Table 7
Reestablishment of Biodegradation Potential After APS Soil Washing

Sample	Percent of 14-C as CO2 (mg/kg total phenanthrene)		
	Week 2	Week 4	Week 6
TRENCH 2:			
Unwashed	7.29(18.7)[a]	8.65(22.2)	12.4(31.9)
Washed, untreated	0.17 (0.02)	1.15 (0.15)	ND[b]
Washed + H2SO4(pH 7.0)	ND	ND	ND
Washed + H3PO4(pH 7.0)	ND	0.86(0.11)	ND
Washed + H3PO4+N	ND	ND	ND
Washed + H3PO4 + N + Inoculum	1.01(0.13)	0.71(0.09)	1.17(0.15)
TRENCH 4:			
Unwashed	1.95(12.4)	4.37(27.8)	7.30(46.5)
Washed, untreated	0.79(0.51)	2.93(1.9)	4.27(2.8)
Washed + H2SO4 (pH 7.0)	5.17(3.4)	13.9(9.0)	13.4(8.7)
Washed + H3PO4 (pH 7.0)	3.12(2.0)	7.77(5.1)	14.0(9.1)
Washed + H3PO4 + N	ND	ND	ND
Washed + H3PO4 + N + Inoculum	ND	ND	0.72(0.47)

[b] None detected after subtraction of sterile controls. Sterile controls produced an average of 1.65 percent of the total 14-C as CO2 after 6 weeks.

Table 8
Results of Bioreclamation Column Studies After APS Soil Washing and Restoration

	Soil Concentration		Removal	
	Initial	Final	% Removal	Removal Rate mg/kg/day
Treatment 1: Washed Soil Leached Groundwater				
PNA -				
Total 2-3 Ring	59.4	ND	<95%	0.57
Total 4-5-6 Ring	70.0	14.6	79%	1.05
TOTAL	129.4	14.6	88.7%	2.19
COD	7,900	3,800	52%	39.0
TPH	.415	123	70%	2.8
O&G	325	207	36%	1.1
Plate Count (cfu)	2x10^5	2x10^5		
Treatment 2: Washed Soil Leached with Nutrient Amended Groundwater				
PNAs				
Total 2-3 Ring	365	76.4	79%	2.75
Total 4-5-6 Ring	175	157.4	10%	0.33
TOTAL	539	233.8	56%	5.80
COD	16,500	11,500	30%	48
TPH	650	70	90%	5.5
O&G	964	72	92%	8.5
Plate Count (cfu)	2x10^5	2x10^6		
Treatment 3: Washed Soil Leached with Nutrient Amended, Inoculated Groundwater				
PNAs				
Total 2-3 Ring	189.0	61.7	67%	2.42
Total 4-5-6 Ring	138.4	81.4	41%	1.09
TOTAL	328.4	143.0	56%	3.53
COD	13,000	17,250	--	--
TPH	300	300	0%	--
O&G	580	290	50%	2.7
Plate Count (cfu)	2x10^5	2x10^6		

Although these data suggests that significant microbial activity was restored, there is no certainty whether the target contaminants (PAHs) or residual polymer surfactant were being degraded.

As part of this study, replicate columns were sacrificed and the soil was analyzed at the conclusion of the soil washing and again at the conclusion of the bioreclamation process. Although it is possible to state, based on these data, that aerobic microbial degradative activity was restored in these columns, it is difficult to conclude to what degree the capability of soil microorganisms to degrade target contaminants was affected.

This conclusion is due in large part to the excellent contaminant removal efficiencies attained in the soil washing phase. The concentration of target contaminants (PAHs and PCP) in the column soils at the conclusion of soil washing was generally near nondetectable levels. Some further reduction in target contaminant concentrations was achieved during the bioreclamation phase of the study (Table 8). It is not possible to differentiate between contaminant loss resulting from microbial activity in the column and contaminant loss resulting from the leaching of a mixture of residual polymer, surfactant and target contaminants.

It is important to note that the lowest contaminant levels were attained in the soil columns that were not subjected to rapid pH adjustment with phosphoric acid. These columns were simply treated by cycling oxygenated groundwater through the column.

CONCLUSIONS

The most important conclusion from the bioreclamation column studies described previously is that in situ subsurface bioreclamation is a viable process under either of the following scenarios:

- Directly following primary oil recovery where very high contaminant levels will be present
- Directly following soil washing with an APS solution as a polishing step.

Microbial contaminant biodegradation was stimulated in soils containing relatively high residual contaminant levels. Providing sufficient oxygen appeared to be the most important parameter for stimulating microbial degradative activity. Supplementation with nitrogen and phosphorous as inorganic nutrients was also beneficial, but only if sufficient oxygen was provided.

In situ, subsurface bioreclamation following soil washing also appears to be a viable treatment scenario. Although the APS soil washing process did have some impact on microbial populations, the laboratory study results suggest that microbial contaminant biodegradation activity can be restored and stimulated. In the laboratory column studies, bioreclamation following soil washing successfully lowered the residual concentrations of target contaminants (PAHs and PCP) in the soil to levels near or below the analytical detection limit.

Preliminary indications of the time required to achieve cleanup were obtained in the column studies. It is believed that the time required to achieve cleanup by in situ bioreclamation may be determined primarily by the rate at which oxygen is delivered to the subsurface. The laboratory studies suggest that the subsurface oxygen demand that must actually be met to achieve cleanup may be substantially less than the predicted oxygen demand based on in situ mineralization of the gross organics present. Thus, depending upon the oxygen delivery rate actually achievable under field conditions, actual cleanup times could potentially be lower than theoretical predictions.

As previously stated, the laboratory results suggest that in situ bioreclamation is a viable treatment alternative for the remediation of this site and field pilot testing was recommended. Based on the laboratory results, it was suggested that one of the major objectives of the field program should be the correlation of oxygen delivery with contaminant removal. Developing the correlation will require determining the relative extent of contamination reduction through several mechanisms. Monitoring the following parameters will be critical tasks in field pilot studies:

- Mass of oxygen delivered
- Mass of oxygen consumed and definition of the zone of aerobic treatment
- Contaminant reduction in the aerobic zone
- Contaminant reduction in anoxic zones
- Nature and extent of contaminant removal through leaching from the subsurface

CASE HISTORY: PILOT-SCALE DEMONSTRATION

A pilot-scale, solid-phase air stripping and biological treatment facility was constructed at the Brio Refining Superfund Site, Texas, in order to demonstrate the feasibility of bioremediating affected soils and organic residues on-site. The site has a large volume of affected soils containing

styrene still bottom tars and chlorinated hydrocarbon solvents.

The biodegradability of the site material was determined by Microtox testing. Of 11 areas tested, two areas were found suitable for biodegradation without dilution. Of these two areas, the one with the lowest concentration of volatile organic compounds was selected as the source of material for the pilot-scale biodegradation demonstration. This area was designated as Pit O during the RI/FS. Additional samples of the Pit O backfill were collected in order to conduct a bench-scale evaluation of the biodegradability of the organic compounds present in the backfill. This testing indicated that the ketones, short-chain chlorinated hydrocarbons, chlorinated aromatic hydrocarbons and aromatic hydrocarbons found in the pit backfill could be removed by air stripping or biologically destroyed by indigenous microorganisms. On this basis, the decision was made to undertake a pilot-scale demonstration of biodegradation of backfill material from Pit O.

The treatment facility consisted of an enclosed, lined treatment bed containing 200 yd^3 of affected soil from one of the backfilled storage lagoons located at the site. The liner was an 80-mil HDPE synthetic membrane with heat-welded seams. A sand drainage layer was placed on top of the liner and a 6-inch thick layer of affected soil was placed on top of the sand. Nutrients and inoculum were applied to treatment bed through an overhead spray system. The treatment bed was tilled daily to increase soil surface area and provide aeration. Volatile emissions from the treatment bed were contained by a plastic-film greenhouse and routed to carbon adsorption units.

Following construction of the treatment facility, approximately 200 yd^3 of soil were transferred to the treatment facility. The excavated soil was placed on top of the prepared treatment bed. Due to the cohesiveness of the clay soil, the pit backfill material was allowed to dry before final grading. For several days the tracked front-end loaders were run back and forth over the pit backfill to break up large blocks of soil and distribute material evenly over the treatment bed. After 3 days of manipulation, the clay was amendable to tillage by a power rototiller attached to a tractor. Soil moisture content was low enough after 6 days to add nutrients.

The soil treatment bed was divided into four lanes so that different methods of optimizing microbial activity and biodegradation rates could be evaluated. A control lane, which received only tilling and water additions, was established to provide a base line for evaluating the effectiveness of the following three treatment processes: (1) nutrient addition, (2) single microbial inoculation and (3) multiple microbial inoculations.

The pilot-scale treatment facility was operated for 94 days. The soil in the treatment facility was tilled daily to optimize contact between microorganisms and the organic constituents present in the pit backfill material and to ensure adequate aeration for microbial activity. Tilling also facilitated the air stripping of VOCs. Soil moisture content, soil temperature and soil pH were monitored to ensure that they remained within ranges conducive to microbial activity. Water, nutrients and inocula were added as required to the treatment bed through the overhead spray system.

Sample Collection Analysis

Soil samples were collected on Day 0, Day 21, Day 58 and Day 94. Soil samples were analyzed for volatile and semivolatile organic compounds in order to determine the rate of organic compound degradation and measure the effectiveness of the three treatment processes. In addition, the soil samples were analyzed for soluble ammonium, nitrate and phosphate to determine if the concentrations of these nutrients were sufficient to ensure maximum microbial growth and organic compound degradation.

Removal of Volatile Organic Compounds

The predominant VOCs detected in the Pit O backfill material placed in the treatment facility were ethylbenzene, styrene and toluene. These compounds were detected at maximum concentrations of 4,400 ppm, 240 ppm and 510 ppm, respectively. Methylene chloride and 1,1,2-trichloroethane were also detected but at lower concentrations. Methylene chloride concentrations ranged from 0.53 ppm to 20 ppm.

while 1,1,2-trichloroethane concentrations ranged from 0.52 ppm to 110 ppm. Acetone; 2-butanone; chlorobenzene; 1,1-dichloroethane; methylene chloride; 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane; and xylene were detected at concentrations ranging from 3.1 to 88 ppm; 3.7 to 54 ppm, 3.4 to 26 ppm; 2.3 to 200 ppm; 0.53 to 20 ppm; 4 to 5.1 ppm; 0.52 to 110 ppm and 0.55 to 180 ppm, respectively.

The concentrations of the volatile organic compounds in the treatment facility were reduced by more than 99% over the 94 day period of operation (Table 9). Most of this reduction occurred within the first 21 days of operation and was predominantly due to air stripping. Volatile compounds of both high and low volatility were removed with equal efficiency. For example, the concentrations of methylene chloride and 1,1,2-trichloroethane, both highly volatile compounds, were reduced by more than 99%. The concentrations of ethylbenze and styrene, both low volatility compounds, also were reduced by more than 99%.

Two methods were used to estimate the amount of volatile organic compounds removed from the affected soils by air stripping: (1) concentration of volatile compounds adsorbed in the activated carbon units and (2) air emissions data collected during facility operation. The amount of volatile compounds air stripped from the affected soils ranged from 137 kg to 159 kg, a removal rate of approximately 7 kg per day.

Table 9
Volatile Organic Compound Removal, Pilot-Scale Bioremediation, Brio Refining Site, Friendswood, Texas

Total Volatile Organics (PPB)

Lane	Day 0	Day 21	Day 58	Day 94	Reduction*
Control	25,972	81	17	29	99.69%
Nutrient Adjusted	39,460	40	14	12	99.90%
Single Inoculation	273,184	13	16	25	99.99%
Multiple Incoluation	101,868	10	19	27	99.9%
* Reduction After 21 Days of Operation					

Degradation of Semi-Volatile Organic Compounds

Phenanthrene was the predominant semivolatile organic compound detected in the Pit O backfill material placed in the treatment facility. Phenanthrene concentrations ranged from 0.44 to 170 ppm and the average phenanthrene concentration was 36.3 ppm. 2-Methylapthalene concentrations ranged from 6.2 to 170 ppm, with an average concentration of 50. ppm. Naphthalene concentrations ranged from 0.13 to 96 ppm and the average concentrations was 19.5 ppm. Over the 94 day operation of the pilot-scale biological treatment facility, semi-volatile organic compound concentrations were reduced an average of 89% (Table 10).

Table 10
Semi-Volatile Organic Compound Degradation, Pilot-Scale Bioremediation, Brio Refining Site, Friendswood, Texas

Total Semi-Volatile Organic Compounds (PPB)

Lane	Day 0	Day 21	Day 58	Day 94	Reduction
Control	18,900	9,346	6,078	2,928	84.51%
Nutrient Adjusted	16,100	6,999	5,325	1,402	91.29%
Single Inoculation	56,983	4,610	3,967	2,023	96.45%
Multiple Inoculation	18,496	6,028	6,611	2,800	83.03%

Phenanthrene Degradation

Due to its predominance in the affected soil from Pit O, phenanthrene was used to determine the effect of the various treatment processes on the degradation rate of semivolatile organic compounds. Over the 94 days of facility operation, phenanthrene concentrations were reduced an average of 84% (Table 11). During the first 21 days of operations, phenanthrene degradation occurred at a relatively rapid rate. For the remainder of the demonstration project, the phenanthrene degradation rate was approximately 124 μg/kg/day. At this degradation rate, approximately 131 days would be required for the phenanthrene con-

centration to reach 0.33 ppm, the analytical detection limit using the U.S. EPA-approved procedure.

Table 11
Phenanthrene Degradation, Pilot-Scale Bioremediation, Brio Refining Site, Friendswood, Texas

Phenanthrene Degradation, Pilot-Scale Bioremediation, Brio Refining Site, Friendswood, Texas				
Phenanthrene Concentration (PPB)				
Lane	Initial Day 0	Final Day 94	Reduction	Half-life (Days)
Control	27,850	5,725	79.44%	40.8
Nutrient Adjusted	19,400	2,712	86.02%	33.0
Single Inoculation	73,600	5,750	92.19%	25.7
Multiple Inoculation	24,360	5,275	78.35%	43.3

Phenanthrene half-life values for the control, nutrient-adjusted, single inoculation and multiple-inoculated lanes were 40.8, 33.0, 25.7 and 43.3 days, respectively. A statistical analysis of the data demonstrated that there was no significant difference in the rate of phenanthrene degradation in the different treatment lanes; the initial phenanthrene concentration was apparently the parameter controlling the rate of phenanthrene degradation. The data collected during this demonstration project suggested that aeration and the amount of contact between the microorganisms and the affected soil also were parameters that governed the rate of phenanthrene degradation.

Since there was no significant difference in the rate of phenanthrene degradation observed in the different treatment lantes, all of the date were pooled to determine the rate of phenanthrene biodegradation in the treatment facility. The average half-life was 33 days, significantly less than reported half-life values of 69 to 298 days in other solid-phase biodegradation systems.

CONCLUSION

The pilot-scale biological treatment facility constructed at the Brio Refining Superfund Site conclusively demonstrated that target compounds such as 1,2-dichloroethane, 1,1,2-trichloroethane and phenanthrene could be removed effectively from soils using an on-site treatment technology other than incineration. The process removed volatile organic compounds by air stripping and destroyed semivolatile organic compounds by biodegradation.

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Biotreatment of Red Water with Fungal Systems

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ABSTRACT

Red water generated during the manufacture of trinitrotoluene (TNT) is an environmental concern because it contaminates ground surfaces and groundwaters. Past methods for the management of this hazardous waste stream either did not meet pollution compliance or were not cost-effective. Biodegradation of TNT by bacteria has been reported, but no conclusive evidence supports its biotransformation to harmless products or its complete mineralization to CO_2 and H_2O. The lignin peroxidase (ligninase) secreted by the white rot fungus (*Phanerochaete chrysosporium*) has been shown to degrade a broad spectrum of organic pollutants. In this study, the efficacy of treating red water with the *P. chrysosporium* system was investigated.

INTRODUCTION

Red water is a waste stream generated during the manufacture of explosives. During TNT purification, a red colored waste water is produced that is rich in sodium sulfite (sellite) and sulfonates of various isomers of TNT. Red water has been classified by the U.S. EPA as hazardous and has been an environmental concern not only to U.S. Army ammunition plants, but also to the general public because it can contaminate ground surfaces and groundwaters.

Disposal of untreated red water by direct discharge into waterways and sewer systems is not acceptable. Tighter pollution regulations have prevented paper mill companies from recycling the red water for its sodium and sulfur content for use in pulping operations.[1] The conventional method of disposal by incineration is expensive and energy-intensive, and the ash accumulated from incineration can cause a leachate problem when it is landfilled.[2] The Sonoco process,[3] which converts red water into a sellite solution for reuse in TNT purification, has been tried in several operations, but the capital cost of the equipment and the cost of plant operation are astronomical. In addition, the quality of the recovered sulfite remains questionable.

An average Army ammunition plant, such as the Joliet Army Ammunition Plant (JAAP), generates red water at rates of approximately 80,000 gal of liquid per day and 250,000 lb solids per day during full operation. Samples taken from different sites at JAAP indicated that past operations have caused contamination of the soils, sediments, surface water and groundwater. Until a solution for effective red water treatment is found, all United States ammunition plants must be maintained in a standby mode, and no TNT may be produced.

One of the most cost-effective methods for on-site remediation is microbial biodegradation. However, the effectiveness of this treatment depends heavily on the survival, adaptability and activity of the microorganisms. Initial efforts at biological treatment of wastewater containing TNT were not satisfactory. Bacteria generally reduce nitro groups of the TNT, but no conclusive evidence exists that they cleave the aromatic ring. In addition, the bacterial transformation created a sludge disposal problem and produced an effluent that was more toxic to fish than the untreated samples.[4] Therefore, an economical and environmentally safe method needs to be developed to treat red water.

Direct enzyme treatment of hazardous compounds and environmental contaminants is a relatively new concept. Lignin peroxidase (ligninase) secreted by a white rot fungus has been shown to nonspecifically break many aromatic and substituted aromatic rings.[5] Ligninases play a key role in the degradation of a broad spectrum of organic pollutants including DDT, polychlorinated biphenyls, benzopyrene, pentachlorophenol and dioxins.[6] In this study, red water samples were treated with ligninase prepared from the fungal culture or with the fungal culture itself, under various conditions. Different analytic and toxicologic parameters were tested to evaluate the efficacy of the various treatment protocols. The best biotreatment protocol can be used as the basis for further development of field application and on-site, large-scale demonstrations.

EXPERIMENTAL

The red water samples obtained from Canadian Industries, Limited (McMasterville, Quebec) are representative of waste streams from continuous production lines in the U.S. Army ammunition plants. The "as received" (AR) red water was refrigerated, and the solid precipitate (identified as Glauber's salt, $Na_2SO_4 \cdot 10\ H_2O$) formed upon refrigeration was removed to yield the salt-reduced (SR) form.[7] Both AR and SR red water samples were treated with the fungal system.

The white rot fungus *P. chrysosporium* (BOK-f-1767, ATCC 24725) originally from T.K. Kirk (U.S. Department of Agriculture, Forest Products Laboratories, Madison, Wisconsin) was cultured according to the procedures of Tien and Kirk.[8] The ligninase activity secreted into the fungal culture media during the ligninolytic phase of fungal growth was extracted. The ligninase activity was measured at room temperature by monitoring the increase in absorbance at 310 nm.[9] One unit of ligninase activity (U) is defined as that which catalyzes oxidation of one micromole of veratryl alcohol to veratryl aldehyde (which absorbs intensely at 310 nm) per minute under specified conditions.

The extracted ligninase preparation was concentrated by Amicon CH2PRS and 8200 concentrators (Amicon Division, W.R.

Grace & Co., Danvers, Massachusetts) using a membrane with a cutoff at 10,000 molecular weight. Dialysis of the concentrated ligninase preparation (CLP), removal of mucilagenous materials after the CLP was frozen or partial purification of the extracellular enzyme followed, depending on the experimental design. The stability of the ligninase activity was evaluated at various temperature to ensure that the storage and activity of the enzyme preparation were proper for laboratory use or for long-term field application.

The CLP collected from several batches of shake flask culture of *P. chrysosporium* was used in various biotreatment incubations. Both the AR and the SR red water, undiluted and diluted (1:10 - 1:20), were incubated with CLP at 25° C. The whole fungal culture was sampled when peak ligninase activity was observed. The peak fungal broth (PFB) was used to treat the SR red water sample at 39° C. The biodegradation rate of the whole fungal culture treatment was compared to that of the direct enzyme (CLP) treatment. Biotreatment controls (with no CLP or no red water) were also set up for proper comparison.

An aliquot of the SR red water was preexposed (at room temperature) for three days to a Philips back-light lamp (with greater than 96% of its energy peaked at 365 nm) from four directions in a sealed structure made in-house. Ultraviolet light (UV) exposure is known to cause photolysis and to weaken the structure of the organic ring. The effects on biodegradation of UV pretreatment and the addition of veratryl alcohol (known to stabilize the ligninase activity) were also tested in the SR red water.

Treated sample aliquots were taken from the incubation mixture at 4 hr, 1 day, 3 days and 7 days. These samples were stored at −20° C until the time of assay. Samples collected from various biotreatment plans were analyzed for decolorization and ligninase activity and by UV spectral analysis, high-performance liquid chromatography (HPLC) metabolite analysis and Microtox™ bacterial toxicity screening.[10]

Two different HPLC column systems with UV detection (230 nm) were developed to analyze specific reactants in the red water and their biodegradation products. The Supelcosil LC-8 column (4.6 mm x 33 mm, 3-um packing, from Supelco, Inc., Bellefonte, Pennsylvania) was heated at 30° C. Sample (20 ul) was injected onto the column through a 0.5-um pore stainless steel precolumn frit filter. Standards of structures similar to the organic compounds commonly found in red water were chosen to calibrate the column. The standards, used in 95% glacial acetic acid (GAA) were 2,4,6-trinitrobenzenesulfonic acid (picrylsulfonic acid, PSA), TNT, 2,4-dinitrotoluene (2,4-DNT) and 2,6-DNT. The column was eluted for the first 4 min with 100% 1 mM GAA (at 0.5 mL/min) and for the next 10 min with a solvent system consisting of 30% of 1 mM GAA (at 2 mL/min).

The second HPLC system, developed to analyze biodegradation metabolites, used a longer column (Beckman Ultrasphere Octyl 5-um column, 4.6 mm x 250 mm, from Beckman Instruments, Inc., San Ramon, California) and a longer elution time (30 min) for better resolution of the earlier peaks derived from the treated samples. Samples (20 uL), diluted in 1 mM GAA, were injected onto the column at 40° C. From 0 to 7 min, a 10% solution 2% THF in methanol in 90% water was used as mobile phase at a flowrate of 0.3 mL/min. From 7 to 30 min, the mobile phase was changed to 30%:70% and the flowrate increased to 2.5 mL/min.

To get even better resolution of the major sample peaks, samples were run isocratically on the Beckman column at 40° C for 25 min. The mobile phase used was a 10% solution of 2% THF in methanol in 90% water at a flowrate of 0.3 mL/min.

Samples collected at different time points of the biotreatment incubation were screened for biotoxicity with the Microtox bioassay (Microbics Corporation, Carlsbad, California). This assay involves exposing luminescent bacteria to red water and measuring any decrease in light output, which is indicative of the degree of sample toxicity. When the treated red water is subjected to the same test, an increase in light output over that for the untreated

sample reflects degradation and detoxification of the red water. The Microtox test was conducted on a Luminescence Biometer (DuPont Instruments, E.I. DuPont deNemours & Co., Wilmington, Delaware).

RESULTS AND DISCUSSION

Stability of Ligninase

In vitro stability of ligninase is important in determining the economic and technical feasibility of its application in bioremediation or industrial uses. The ligninase activity of two different CLPs was compared at 25° C. The high-activity (3580 U/L preparation, without mucilagenous material, showed a slow decrease in activity, finally staying at 70% of its original activity at 7 days. However, the low-activity preparation (750 U/L), containing mucilagenous material, dropped to only 3% of its original activity in 24 hr. Ligninase activity of a CLP (1540 U/L, mucilates removed) first decreased and then stayed at 70 to 80% of its initial activity over a period of 7 days when it was stored at 25° C (Fig. 1) or 39° C (Fig. 2). When the original enzyme activity (1540 U/L, 1X) was diluted to 0.2X, 0.1X or 0.02X, the stability pattern remained the same. The same ligninase stability pattern was also observed with a CLP of 1050 U/L (mucilates removed) stored at −70° C, −20° C or 4° C for 28 wk. If the mucilagenous material is removed from the crude enzyme preparation, the ligninase activity apparently will remain at 70 to 80% of its original value at starting activity levels ranging over two orders of magnitude (30 to 3500 U/L). The polysaccharides or protease present in the mucilates may have detrimental effects on the ligninase activity.

Decoloration and UV Spectral Analysis

The red color intensity was measured in all samples by absorbance at 400 nm. A loss of red color suggests that biotransformation of the red water has occurred. The red color intensity was
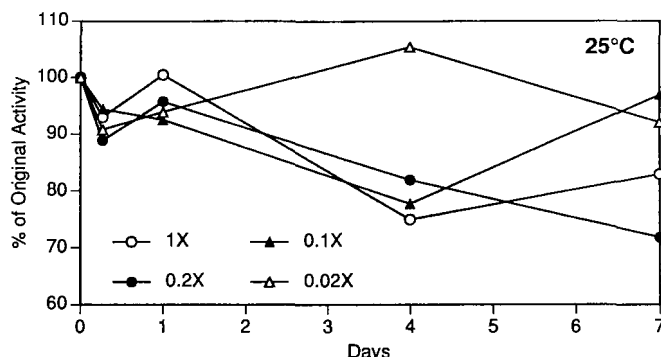
Figure 1
Stability of Ligninase Activity at 25° C (1X = 1540 U/L).
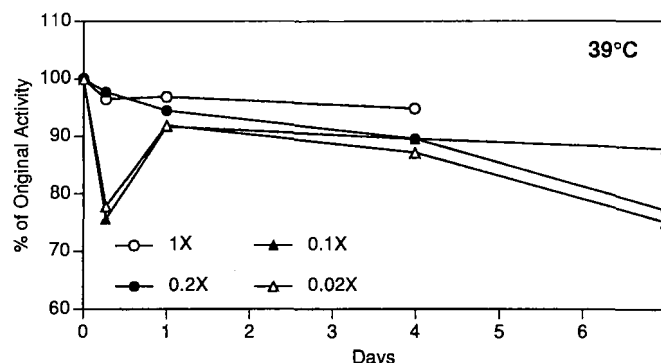
Figure 2
Stability of Ligninase Activity at 39° C (1X = 1540 U/L).
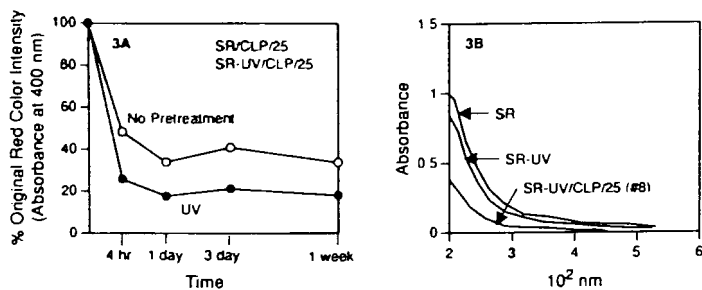
Figure 3
Effect of UV Pretreatment on Enzyme-Treated SR Red Water
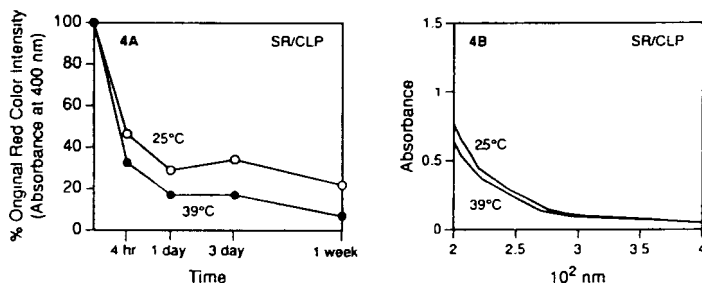
Figure 4
Effect of Temperature (25 ° C vs. 39 ° C) on Enzyme-Treated
SR Red Water
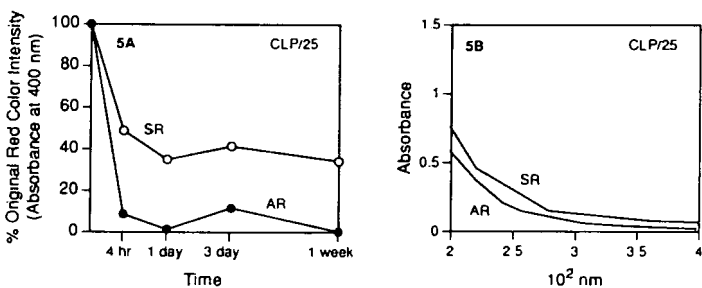
Figure 5
Effect of Enzyme (Ligninase) Treatment on AR Red Water
and SR Red Water

Figure 6
Comparison of Direct Enzyme (Ligninase) Treatment with
Whole Fungal Culture Treatment
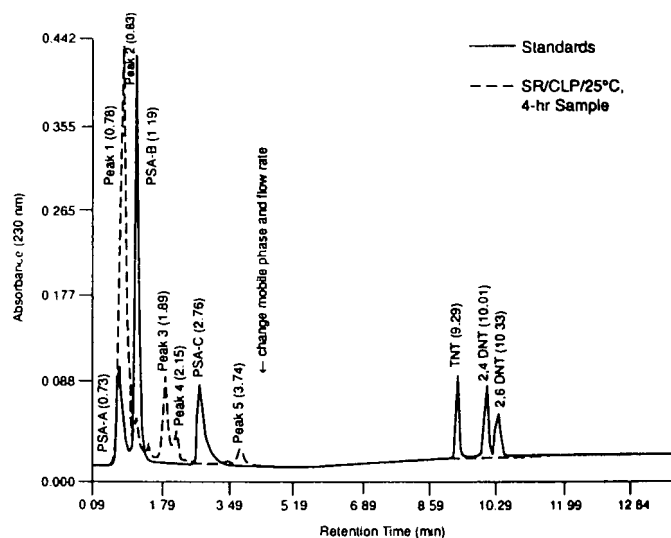
Figure 7
HPLC (Supelcosil LC-8 column) Profile of CLP-Treated
SR Red Water Sample (4-hr Time Point) Spiked with Standards

reduced in all samples from 30 to 0% of the original value after only 1 day of treatment with the fungal system. The diminished absorbance in the region 200 to 300 nm may result from UV spectral changes associated with the reduction of NO_2 groups of TNT isomers, a general bathochromic shift and the degradation of aromatic rings by enzyme hydrolysis. The decoloration of treated red water (Figs. 3A, 4A and 5A) corresponds with changes in the UV spectral profile (Figs. 3B, 4B and 5B). Figure 3 (A and B) shows that red color and UV absorbance (at 200 to 300 nm) were reduced when SR red water received UV treatment before enzyme (CLP) treatment. When SR red water was treated at two different temperatures, the 39° C incubation caused more biodegradation than the 25° C incubation as decoloration (Fig. 4A) and UV spectral results (Fig. 4B) demonstrate. Both red color intensity data (Fig. 5A) and UV spectral analysis (Fig. 5B) demonstrated that the fungal enzyme degrades AR red water more effectively than SR red water.

More decoloration was observed (Fig. 6) when SR red water was treated with whole fungal culture (PFB) than with the fungal enzyme (CLP). The addition of veratryl alcohol (V-OH), a substrate for ligninase, further reduced the red color.

The decoloration and UV spectral results both suggested that SR red water is more toxic (see following toxicity data) and less biodegradable than AR red water. The UV pretreatment makes the SR red water more amenable to fungal biotreatment. The salt

that was removed from the AR red water may be important to the enzyme activity and the biotreatment regime.

HPLC Analyses of Red Water Biodegradation Metabolites

Data from HPLC analyses revealed that biotreatment with fungal enzymes altered red water components. An aliquot from the 4-hr sampling of the CLP-treated (at 25° C) SR red water was spiked with 0.1% PSA, 77 mg/L TNT, 109 mg/L 2,4-DNT and 93 mg/L 2,6-DNT and the mixture was applied to the Supelcosil column. The elution profile with its respective retention time (min) is given in Figure 7. Five distinct peaks were recovered from the treated red water sample. The applied PSA standard was resolved into three earlier peaks (PSA-A, PSA-B and PSA-C) which were mingled with the five peaks derived from the treated sample. The TNT, 2,4-DNT and 2,6-DNT peaks appeared toward the end of the elution.

The calibrated Supelcosil column system was used to analyze samples taken from biotreatment incubations. The results are summarized in Table 1. All samples initially had low levels (less than 0.5% of the total peak height) of TNT isomers. After CLP
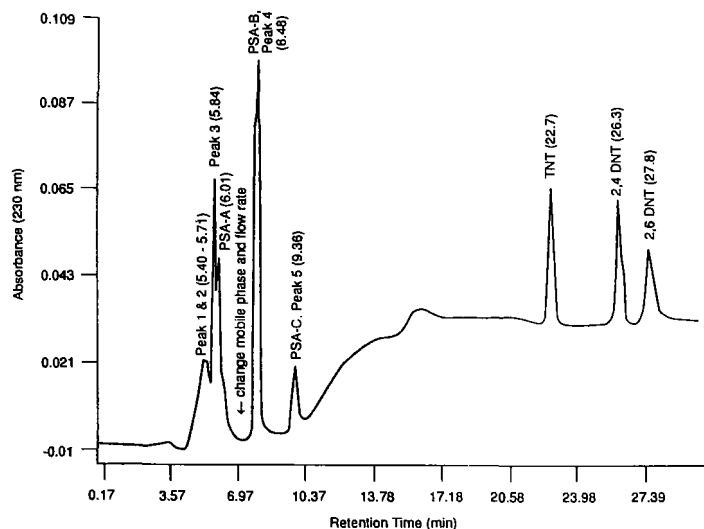
Figure 8
HPLC (Beckman Ultrasphere Octyl column)
Profile of AR Red Water Spiked with Standards

Table 1
Changes of HPLC (Supelcosil Column) Peak Profile (% Peak Height) in Different Biotreatment Protocols

Biotreatment Protocols[b]	Pk1[a]	Pk2	PSA-B	Pk3	Pk4	Pk5
A. SR red water	–	53	25	13	6	4
SR/CLP/25-4hr	33	39	15	8	3	2
SR/CLP/25-1wk	29	43	15	9	3	2
B. SR/UV	–	54	25	12	6	2
SR/UV/CLP/25-1wk	30	43	14	8	3	1
C. SR/CLP/25-1wk	29	43	15	9	3	2
SR/CLP/39-1wk	31	44	12	8	3	1

[a]Retention times are 0.78, 0.83, 1.19, 1.89, 2.15, and 3.74 min, respectively, for peaks Pk1-Pk5.

[b]Abbreviations: SR, salt-reduced red water; CLP, concentrated ligninase preparation; 25, 39, red water sample treated at 25°C or 39°C; 4 hr, 1 wk, sample aliquots taken at 4 hr or 1 week of red water biotreatment incubation; UV, SR red water subjected to UV pretreatment for 3 days before biotreatment.

Table 2
Changes of HPLC (Beckman) Peak Profile (% Peak Height) in Different Biotreatment Protocols

Biotreatment Protocols[b]	Pk[a]	Pk2	Pk3	Pk4	Pk5	Pk6	Pk7
A. AR red water		12	–	30	32	19	5
SR red water		12		31	33	18	5
B. SR/CLP/25-4hr	11		–	26	26	32	5
SR/CLP/25-1wk	9		4	26	28	24	7
C. SR/CLP/25-1wk	9	–	4	26	28	24	7
SR/CLP/39-1wk	10	–	4	31	33	15	5
D. SR-UV	–	12	5	27	32	20	4
SR-UV/CLP/25-1wk	11	–	4	29	33	15	5

[a]Retention times are 0.78, 0.83, 1.19, 1.89, 2.15, and 3.74 min, respectively, for peaks Pk1-Pk5.

[b]Abbreviations: AR, as-received red water; SR, salt-reduced red water; CLP, concentrated ligninase preparation; 25, 39, red water sample treated at 25°C or 39°C; 4 hr, 1 wk, sample aliquots taken at 4 hr or 1 week of red water biotreatment incubation; UV, SR red water subjected to UV pretreatment for 3 days before biotreatment.

treatment, 0% peak height of TNT isomers was found. In general, the percent peak heights of all resolved peaks from the AR red water, the SR red water and the UV-pretreated SR red water were identical. When the SR red water was treated with CLP (at 25° C), Peak 1 appeared with a corresponding decrease in Peak 2 in both the 4-hr and 7-day samples (Table 1A). A decrease in percent peak height was also found in peak PSA-B in those two samples. Similar changes in percent peak height were observed when the UV-treated SR red water was further treated with CLP at 25° C (Table 1B). The 25° C and 39° C incubations were identical when SR red water was treated with CLP for 7 days (Table 1B).

The HPLC elution profile for the Beckman column is in Figure 8. The AR red water was spiked with PSA (19 ug), TNT (0.15 ug), 2,4 DNT (0.22 ug) and 2,6-DNT (0.19 ug). The elution pattern and the retention times for each peak are different from those of the Supelcosil column. Three peaks were resolved for the PSA standard (PSA-A, B and C). The treated sample aliquot was again resolved into five distinctive peaks, and TNT, 2,4-DNT and 2,6-DNT were eluted toward the end of the run.

The changes in metabolite peaks observed in the Beckman column HPLC profile, using isocratic conditions, are summarized in Table 2. Under these conditions, PSA peaks do not overlap with sample peaks. The patterns of percent peak height for the AR and SR red water are not significantly different (Table 2A), as in the Supelcosil column peak distribution. However, even though in both HPLC analyses, organic components in AR and SR red water had the same percent peak heights, the UV spectral analysis and toxicity data suggested that the AR and SR red waters and their biodegradabilities with the fungal system are different. A shift from Peak 2 to Peak 1 and the appearance of Peak 3 (less than 5% of the total peak height) were observed in all CLP-treated SR red water samples (Table 2). Profiles for the 25° C and 39° C treatment are similar (Table 2C). Peak 1 does not appear until the UV-pretreated SR red water is further treated with CLP at 25° C (Table 2D).

The combination of HPLC and nuclear magnetic resonance (NMR) analysis can further demonstrate ring hydrolysis and changes between organic aromatic and aliphatics in the treated samples.

Toxicity Screening

The degree of toxicity, as derived from the Microtox data for various biotreatment protocols, is summarized in Table 3. No

toxicity was found in the control incubation (CLP only). The degree of toxicity is equal to $(1/EC50) \times 100$, where EC50 is the concentration of a compound that causes a 50% reduction in light production in luminescent bacteria exposed to it. The degree of toxicity of the SR red water is set at 100%, and the data obtained for the other samples are expressed as a percentage of the value for SR red water.

The AR red water showed less toxicity than SR red water. After UV treatment, the toxicity of the SR red water was reduced to one third its original value (Table 3A). The ligninase (CLP) treatment reduced toxicity in both AR and SR red water and further reduced the toxicity of the UV-pretreated SR red water (Table 3B). Toxicity decreases with time of biotreatment, i.e., less toxicity is observed in samples treated for 7 days than in samples treated for 4 hr (Table 3C). Direct enzyme treatment seems to be more effective in reducing toxicity of the SR red water than whole fungal culture (PFB) treatment, and the addition of veratryl alcohol (V-OH) resulted in additional detoxification of the PFB-treated red water (Table 3D).

CONCLUSIONS

Preliminary studies suggested that the white rot fungal system is effective in biodegrading the red water waste stream during 7-day laboratory incubation with the whole fungal culture or with

Table 3
Summary of Red Water Biotreatment Toxicity Data

Biotreatment Protocols[*]	Degree of Toxicity %	
	4 hr	1 wk
A. AR Red Water	10	
SR Red Water	100	
SR UV	33	
B. SR Red Water	100	
SR/CLP/25	14	
SR UV	33	
SR-UV/CLP/25	4	
AR Red Water	10	
AR/CLP/25	4	
AR(1:10 dil)/CLP/25	4	
C. SR/CLP/25	14	6
SR(1:20 dil)/CLP/25	8	3
AR/CLP/25	4	1
SR/PFB-V-OH/39	42	4
D. SR/CLP/39		5
SR/PFB/39		11
SR/PFB-V-OH/39		4

[*]Abbreviations: AR, as-received red water; SR, salt-reduced red water; CLP, concentrated ligninase preparation; 25, 39, red water sample treated at 25°C or 39°C; 4 hr, 1 wk, sample aliquots taken at 4 hr or 1 wk of red water biotreatment incubation; UV, SR red water subjected to UV pretreatment for 3 days before biotreatment; PFB, peak fungal broth (whole fungal culture collected for biotreatment incubation when it contains the highest ligninase activity); V-OH, veratryl alcohol (115 namomoles/ml) added to the incubation mixture.

the extracellular ligninase preparation. Certain aromatic components of the red water waste were biotransformed, and the red color intensity and biotoxicity were reduced after the biotreatment. The ligninase activity was stable (at 70 to 80% of its original level) for a minimum of 7 days at 25°C or 39°C. Pretreatment of the red water with UV seems to make the waste more sensitive to biodegradation.

ACKNOWLEDGEMENT

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Biodegradability of Sixteen Chemicals in a Hazardous Waste Site by an Indigenous Microbial Consortium

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ABSTRACT

A laboratory, batch biodegradation study was conducted to evaluate the biodegradation potential of soil from a hazardous waste site containing chemicals associated with polystyrene waste. The study focused on: (1) total waste biodegradability; (2) quantitative losses of certain volatile compounds added, i.e., 1,2-dichloroethane (DCE) and 1,1,2-trichloroethane (TCE); and (3) kinetic removal rates for all chromatographable organic compounds in the waste.

Sixteen nonvolatile chromatographable compounds were monitored in seven bioreactors in a 14-day study. The experimental design consisted of two open bioactive reactors, a sealed bioactive reactor, two sterile open control reactors to measure abiotic degradability and two open reactors not exposed to wastes as background controls for quality control. All bioreactors were spiked with DCE and TCE to quantitate losses due to volatility.

High resolution GC/MS analyses indicated that a major fraction of the organic components was biodegraded with reaction half-lives ranging from 24 hours to 72 hours. All nonvolatile chromatographable compounds were reduced to less than the limit of detection (1.0 ppm). Difference between the volatile and nonvolatile chemicals was successfully measured. Organic chemicals with GC retention times shorter than biphenyl, including DCE and TCE were rapidly volatilized. Enumeration of microorganisms confirmed an active microbial consortium present at all times of the study except in the control reactors. Acute toxicity analysis using Microtox confirmed a decrease in toxicity of extracts from the bioactive reactors over time.

INTRODUCTION

Hazardous wastes produced by industry must be disposed of in a manner which is both environmentally acceptable and cost-effective.[1,3,6,7,15] The waste disposal problem includes past disposal sites that now must be cleaned up. The remediation method chosen for each site is a key factor affecting the cost of any site remediation project.[7] Since the reauthorization of CERCLA, incineration has been the primary technique for waste site remediation of organic contaminants. Incineration may be cost-effective and efficient in specific instances where wastes contain high levels of organic components and high BTU content. However, when the site consists primarily of soil containing less than approximately 5% organic components, microbial treatment is a viable and cost-competitive alternative to incineration. It has been demonstrated that, under favorable environmental conditions, biodegradation of contaminated organics such as hydrocarbons and oily sludges may occur in soils.[6,7,8,13]

Since most hazardous waste sites contain mixtures of many chemicals, a microbial technology must demonstrate the removal of all listed chemicals to acceptable levels. This paper summarizes results from a laboratory-scale biological treatment study which was conducted to demonstrate the feasibility of biologically treating soil contaminated with polystyrene tars. The objectives of this study were: (1) total waste biodegradability; (2) measurement of quantitative vapor losses of certain volatile compounds added, i.e., 1,2-dichloroethane (DCE) and 1,1,2-trichloroethane (TCE) and (3) kinetic removal rates for all chromatographable organic compounds in the waste.

MATERIALS AND METHODS

Experimental Design

Seven glass bioreactors (2-L beakers) were used to conduct the study. Each bioreactor, except reactor D, contained 1450 mL of soil-water slurry. Reactors A and B were duplicate vessels to which 300 mg of $HgCl_2$ (Granular, Mallinckrodt Chemical Works, St. Louis, Missouri) were added on Day 0 and again on Day 10. The absence of microbial activity in these reactors should provide information about abiotic degradation processes. Reactor C contained all components except the waste to provide quality control. Reactor D was sealed with no headspace to eliminate volatility and demonstrate quantitative recovery of the chemicals at the end of the experiment. It consisted of a 1-L glass bottle filled up to the neck in order to eliminate all headspace and sealed with a foil-lined cap. Reactors E and F were bioactive duplicates of A and B and were the key reactors for monitoring biodegradation of the waste chemicals. Reactor G served as secondary control for analytical purposes and contained only well water, DCE and TCE. All reactors except C and G were amended with nutrients and a surfactant. Previous research has shown that nutrient supplementation may enhance biodegradation of organics[4,9] and that soils contaminated with hydrophobic or slightly hydrophilic organics have been previously treated with surfactants.[7]

Procedures

All waste and surface soils were collected from the waste site and characterized as containing polystyrene tar polymers and chlorinated organics.[18] Two duplicate composite soil mixtures containing 20% total solids (wet wt/vol) were used to prepare the test soil water slurry. The mixtures were homogenized in small increments with a blender. The first mixture was then transferred into a 4-L Erlenmeyer flask and further stirred with a spatula. The second mixture was further handmixed in a 6-L Erlenmeyer flask. Equal volumes of each mixture were transferred into 2-L beakers and allowed to stir on heavy duty magnetic stirrers for 18 hr in a closed environmental chamber (Vollrath, River Falls, Wisconsin) at 22 °C. During this mixing period, a portion of the styrene polymers contained in the waste was visibly adsorbed to the stir bars. The stir bars coated with styrene tars were removed and a new stir bar was added to each reactor prior to test initiation. After

stirring, the mixtures were transferred back into the large Erlenmeyer flask and rehomogenized with a Talboys Model 101 homogenizer (Cole Parmer Instr., Chicago, Illinois). Aliquots of 1450 mL were then transferred into 2-L open glass vessels. The first batch provided the slurry for reactors A and E, and the second for B, D and F.

Assuming a total organic carbon content of 1% of the soil slurry, nutrients (K_2HPO_4 and NH_4NO_3) were added at a C:N:P ratio of 100:10:1. Surfactant, Triton x 100 was added at a concentration of 200 ug/mL, and DCE and TCE were both added at 61.1 ug/mL to all reactors but D to which 86.8 ug/mL were added. The pH was adjusted to pH 7.8 for all reactors. All reactors were incubated on heavy duty stirrers in a closed environmental chamber at 22 °C. A light source consisting of 50% Gro-Lux and 50% Cool White fluorescent bulbs provided a light intensity of 175 ftc ±5% at reactor liquid level. A 16 hour light period was alternated with an 8 hour dark period. The lack of humidity control in the environmental chamber necessitated daily adjustment of the liquid level in all reactors but D, which was sealed.

Samples for analytical work were withdrawn for Volatile Organics, Gas Chromatography/Mass Spectrometry (GC/MS) Extractables, acute toxicity as measured with Microtox and enumeration of microorganisms.

Enumeration of Test Organisms

Microorganisms were collected from contaminated surface soil from the site (0 to 6 in. depth). This soil was used to prepare a soil slurry of 20% waste (wet weight/vol) with well water. The soil slurry was placed in an open glass container and continuously stirred on a heavy duty magnetic stirrer and periodically amended with nutrients and waste for a period of 2 months. This slurry was used as inoculum for the present study. Thirty mL of the slurry was used as an inoculum for each flask. Enumeration of microorganisms was performed using disposable presterilized Millipore Total-Count™ Water Testers.[17] Each sample was plated in duplicate using serial dilutions of the waste. Two sterile controls with autoclaved distilled deionized dilution water were also plated to test for contamination in plates, pipettes and dilution water. The Total-Count™ samplers were incubated at 35 °C for 24 hours. Growth of heterotrophic bacteria was determined by visual detection of colonies or turbidity. Results were reported in colony forming units per mL (CFU/mL).

Isolation of Microorganisms

Microorganisms were isolated from reactors using an enrichment medium consisting of minimal inorganic salts[14] supplemented with wastes containing the mixture of organics (0.02% total organic carbon) as the sole source of carbon. A series of 500-mL Erlenmeyer flasks containing 200 mL of this medium was prepared, autoclaved, inoculated with 1 mL of slurry from reactors E and F and incubated at 22 °C. Control flasks lacking wastes were also inoculated. Bacterial populations in the flasks were measured by plating onto minimal inorganic salts solidified with purified agar and on nutrient agar (Bacto, Difco Laboratories, Detroit, Michigan). Nineteen microbial isolates were obtained from the plating studies. Pure cultures of each microbial isolate were examined with a Zeiss Axioskop light microscope (Zeiss, West Germany) for cellular morphology and gram stain reactions. The isolates were further characterized and identified with a Vitek AMS microbial identification system (McDonnell Douglas Health Systems Co., St. Louis, Missouri) using the gram-negative GNI identification card (Vitek No. 51-1306).

Acute Toxicity

One method of defining the potential toxicity of chemical residues is the use of bioassays such as the Microtox™ test. A major advantage of microbial toxicity testing over chemical analysis is the direct assessment of potential biotic impact without extrapolation from chemical analysis of uncertain completeness.[12] A Beckman Model 2055 Toxicity Analyzer (Beckman Instruments, Inc., Microbics Operations, Carlsbad, California) was used to measure the toxicity of the liquid fraction of the wastes to the marine bioluminescent bacterium Photobacterium phosphoreum in a temperature-controlled photometer (15 °C). The procedure for the assay is detailed in the Microtox™ System Operating

Manual. Bioreactor sample aliquots (7 mL) were placed in 20-mL scintillation vials on Days 0, 7 and 14 and stored in the refrigerator at 4 °C until analysis. A statistical analysis method was used to determine the percent normalized light decrease for all dilutions.[10] The decrease in toxicity is reported as normalized percent light decrease.

Method of Analysis

Instrumental analysis methods (GC/MS) were developed to quantify the major volatile and nonvolatile extractable chromatographable compounds in the waste from each bioreactor. Since some of the wastes at the site contained large amounts of DCE and TCE, which were absent in the present samples, 70 uL of these two compounds were added at day 0 to all bioreactors. This addition resulted in a beginning concentration of 61.1 ug/mL of DCE for all reactors but D, which contained 86.8 ug/mL. The beginning concentration for TCE was 70 ug/mL for all reactors but D, which contained 99.5 ug/mL. Reactor D was the only vessel that was sealed immediately after spiking; therefore no loss of chemical occurred before the time zero samples could be collected.

Volatile Organics Analysis

Duplicate samples were collected and analyzed at each sampling period. A 10-mL aliquot of bioreactor sample was pipetted into a 14-mL Pierce vial, and 1 mL of n-dodecane was added to each vial. The vials were sealed with Teflon-lined caps. The samples were vortexed for approximately 2 min and the phases were allowed to separate. The vials were then stored at 4 °C until further extraction. The extraction was completed after bringing the vials to room temperature, shaking them and withdrawing 0.5-mL samples, which were placed in 1.6-mL autosampler vials. An aliquot of this extract was placed with an equal volume of n-dodecane which contained 100 ug/L benzene-d6 internal standard. The samples were analyzed by split injection on an HP 5985 Capillary GC/MS. The chromatographic column used was a 30-meter fused silica J&W DB-5 (250 u) with a wide bore (0.32-mm I.D.). Column temperature program was held at 10 °C for 4 min and then increased at 8 °C/min to the final temperature of 300 °C. Typically, data were acquired for 40 min. Masses were monitored from 10 to 250 Atomic Mass Units. The concentrations of DCE and TCE were determined by using an internal standard quantitation method. Relative response factors for these compounds were determined by analyzing a standard solution containing these two compounds. Samples for volatiles were not collected after day 3 because analysis showed 100% removal by day 1.

Extractables Analysis

Ten mL of bioreactor sample were pipetted into a 40 mL Pierce vial and serially extracted with 20 mL of methylene chloride three times. After each 20 mL addition, the vial was agitated and the methylene chloride was removed. The three methylene chloride extracts were combined and concentrated to a final volume of 10 mL. An aliquot of this extract was added to an equal volume of methylene chloride which contained 100 ug/mL anthracene-d10 internal standard. The samples were analyzed by splitless injection using an HP 5985 Capillary GC/MS as previously described. Column temperature program was held at 50 °C for 4 min and then increased at 8 °C/min to the final temperature of 300 °C. Typically, data were acquired for 40 min. Masses were monitored from 10 to 500 Atomic Mass Units. The concentrations of the major extractable compounds were calculated by dividing the total ion areas of the organic compounds by the total ion area of the anthracene-d10 internal standard and by performing the same calculation using the selected ion areas. All values are reported on a wet weight basis and are not corrected for extraction efficiency.

The experimental design required that 16 compounds, in seven biodegradation reactors, at 10 different days, be analyzed in duplicate. This requirement resulted in the analysis of 16 compounds in approximately 100 reactor samples. Approximately two-thirds of these samples contained the 16 compounds of interest, with the remaining one-third being method blanks, reactor blanks and QA/QC samples which did not contain the total array of analytes. This procedure resulted in the generation of 3,200 concentration values and 4,800 additional values

which required summing, averaging and displaying in an efficient manner. Thus the GC/MS study was divided into a data acquisition part collecting data in the MS system, and a data analysis part transferring the data to Lotus 1-2-3 and performing calculations. Both parts of the process were designed to be interrelated and to produce high quality data in a cost-effective manner.

Analyte concentrations were calculated by using the total ion (or selected ion) areas of the analytes, the total ion (or selected ion) area of the internal standard and the concentration of the internal standard to calculate the "Total Ion Concentrations" or "Selected Ion Concentrations." Detailed compound identification can be accomplished best only after all possible isomers of identified compounds are obtained and retention times of authentic standards are compared to the retention times of the components in the waste. However, this detailed identification was not considered critical to the present study since degradation profiles of compounds and relative changes in concentration, were of primary concern. Therefore, compounds which were not uniquely identified by standard library search algorithms were identified by molecular formula and/or molecular weight, when possible.

GC/MS Quality Control

False Positives

Bioreactors C and G served as Quality Control reactors to which no wastes had been added. Therefore, analysis of these bioreactor samples would indicate whether contamination was occurring which would have resulted in the reporting of false positive values. In addition, extraction method blanks were prepared and analyzed in order to detect any source of contamination in the extraction of samples. No method blanks contained any of the analytes. Finally, either methylene chloride or n-dodecane was analyzed using capillary GC/MS to identify whether instrument contamination could be causing the measurement of false positives. Again, no analytes were detected in any of the instrument blanks analyzed.

False Negatives

An instrumental analysis protocol was developed which assured that adequate levels of detection and system performance were maintained so that the incorrect reporting of analytes did not occur. This analysis protocol included the analysis of a system performance standard which contained compounds of wide volatility to evaluate chromatographic performance, and decafluorotriphenylphosphine which evaluated mass spectrometer performance. In addition, all bioreactor extracts were analyzed at random times so that there could be no systematic bias produced in one set of bioreactor samples. Therefore, in a given set of analyses, there would be Day 7 extracts from Reactors A and B which showed the presence of a large number of components which were present on Day 0, and also Day 7 extracts from Reactors E and F which showed the absence of almost all of these components. These data were analyzed in a blind manner so that no bias would result in human interpretation where preconceived biasses may exist.

RESULTS

Biodegradation of Chromatographable Chemicals

Analytical measurements indicated rapid removal of all chromatographable compounds in the bioactive reactors (Table 1). The data for the average total ion (TI) concentrations for duplicate samples for Bioreactors A, B, D, E and F are shown in Figure 1. Reactors C and G are not included in this Figure, since they served as quality control reactors and did not contain any of the analytes of interest. Three disappearance patterns are evident. Reactors A and B, sterile duplicates, showed some degradation within the first 7 days of the experiment. This degradation may be due to unidentified abiotic loss, but is thought to be partially due to microbial activity, as evidenced by an increase in microbial cell counts (Table 2). It is believed that these microorganisms contributed to the overall TI removal of 49.5% for Reactor A and 48.8% for Reactor B. The second addition of HgCl$_2$ eliminated further degradation in both reactors.
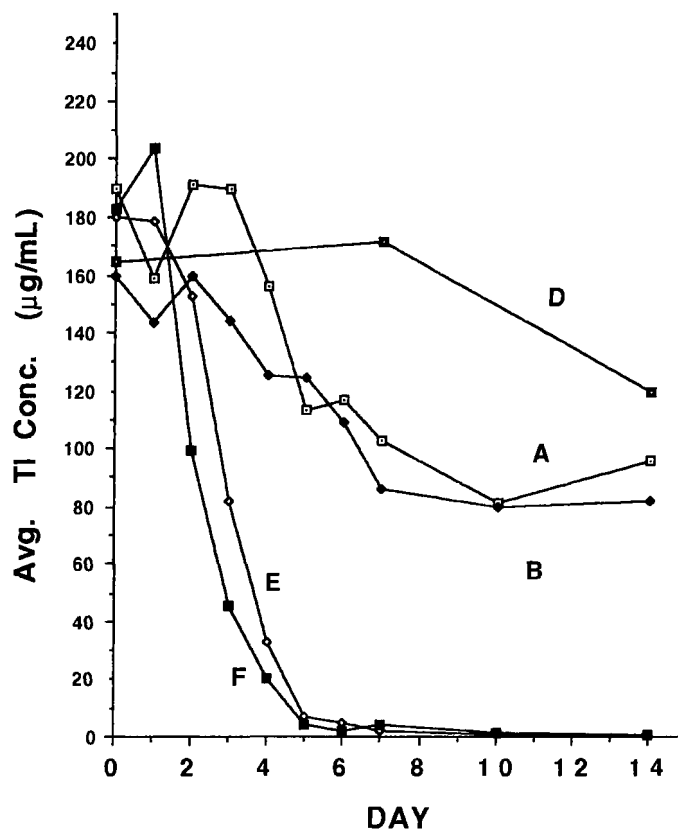
Figure 1
Average Total Ion (TI) Concentrations for all Bioreactors

Table 1
Biodegradation (% removal) of Nonvolatile Chromatographic Chemicals at the End of the Study (Day 14)

Compound* Identification	Percent Removal in Bioreactors				
	A	B	D	E	F
#01 = anthracene-d10	0	0	0	0	0
#02 = biphenyl	≥99.0	≥99.0	63.9	≥99.0	≥99.0
#03 = ethylbiphenyl isomer #1	93.4	93.2	30.2	≥99.0	≥99.0
#04 = ethylbiphenyl isomer #2	70.2	68.9	23.4	≥99.0	≥99.0
#05 = bibenzyl	90.2	88.6	32.8	≥99.0	≥99.0
#06 = methyldiphenyl isomer	80.0	78.4	27.1	≥99.0	≥99.0
#07 = diphenylpropane isomer #1	51.1	42.3	21.4	≥99.0	≥99.0
#08 = diphenylbutane isomer #2	40.9	9.7	21.7	≥99.0	≥99.0
#09 = diethylbiphenyl isomer #1	42.8	35.8	18.3	≥99.0	≥99.0
#10 = diethylbiphenyl isomer #2	34.2	23.5	14.4	≥99.0	≥99.0
#11 = ethylenebiphenyl isomer	30.8	12.9	16.6	≥99.0	≥99.0
#12 = phenanthrene	24.7	≥99.0	85.4	≥99.0	≥99.0
#13 = 1-phenylnaphthalene	15.3	-9.8	7.1	95.2	91.8
#14 = 2-phenylnaphthalene	13.2	-9.6	8.7	98.9	≥99.0
#15 = elemental sulfur	-37.5	-206.3	≥99.0	≥99.0	≥99.0
#16 = diphenylthiophene isomer #1	29.7	11.8	19.5	96.0	94.2
#17 = diphenylthiophene isomer #2	27.0	19.8	17.9	93.9	92.8
Total Conc. of all SI Compounds	56.6	58.1	29.5	98.9	99.1
Total Conc. of all TI Compounds	49.5	48.8	27.3	99.5	99.5

* compound identification was done with selected mass.

SI   Estimated level of detection is 0.1 µg/mL for most compounds.

TI   Estimated level of detection is 1µg/mL for most compounds.

Table 2
Enumerations of Microorganisms (CFU/mL)

Bioreactor	Day 1 (CFU/mL)	Day 7 (CFU/mL)	Day 14 (CFU/mL)
A	<1	5.5×10^2	<1
B	<1	$>3 \times 10^4$	<1
C	<1	$>3.0 \times 10^2$	1.4×10^5
D	3.0×10^5	4.7×10^5	6.3×10^5
E	$>3.0 \times 10^5$	2.3×10^7	2.0×10^7
F	$>3.0 \times 10^5$	1.0×10^7	2.8×10^7
G	2.0×10^3	$>3.0 \times 10^2$	5.5×10^4
Control*	<1	<1	<1

Samples too numerous too count are reported as > the highest tested dilution.

Values are averages of duplicate measurements.

* A control was plated using sterile dilution water.

Reactor D showed 27.3% TI removal. Since it was sealed, volatile components were prevented from escaping and reoxygenation was eliminated. The minor degradation which did occur could be attributed to microorganisms utilizing the dissolved oxygen in the aqueous fraction as an electron acceptor for the metabolism of some of the organics.

Reactors E and F showed TI removal rates of 99.5%. A lag phase required by the microbiota to adapt to the system explained the low degradation rates during the first day. Almost linear degradation rates were observed from Days 2 to 5. Since neither the sealed nor the sterilized reactors exhibited similar removal rates under equal conditions, the degradation was interpreted as being microbial.

Reasonably good agreement was obtained between the TI and SI chromatographable measurements. The response factors for the SI concentrations are slightly lower than for the TI concentrations (Fig. 2). The detection limits were 1 ug/mL for TI and 0.1 ug/mL for SI concentrations. Seventeen compounds were identified with Selected Ion Mass (Table 1). The first compound, anthracene-d10, was used as an internal standard in all cases. Biphenyl (Compound #02) was completely removed in Reactors A, B, E and F, however at different rates. While 6 and 5 days were needed in Reactors A and B, respectively, to remove biphenyl >99%, it degraded in 3 and 2 days, respectively, in the Bioactive Reactors E and F to below the detection limit. The total TI removal of biphenyl in Reactor D was 61.0%. Since volatilization was excluded in this system, it is assumed that biphenyl was microbially degraded in Reactor D. However, biphenyl may have partially degraded and/or partially volatilized in Systems A, B, E and F. Compounds #2-12 and compound #15 (elemental sulfur) were removed 100% in Reactors E and F, while they partially persisted in Bioreactors A, B and D.

Plots of the chemical concentrations over time are presented for 2-phenylnaphthalene and phenanthrene as typical examples demonstrating the biodegradation of all 16 chromatographable compounds (Figures 3 and 4). 2-Phenylnaphthalene and phenanthrene degraded rapidly below the detection limit. Previous literature reports indicate the ability of bacteria and fungi to utilize naphthalene and phenanthrene as a source of carbon.[2,3,13] It was expected, therefore, that these compounds or isomers would be biologically oxidized. The two compounds typically were not removed in the sterile and sealed bioreactors with the exception of phenanthrene in sterile reactor B which exhibited significant microbial activity by Day 7. This result clearly indicated that the compound was biodegraded and not volatilized. The estimated half-life under the given environmental conditions was less than 36 hours. If one takes into consideration the fact that the experiment consisted of a batch microbial system with a small amount of inoculum, the initial lag phase where no degradation occurred is not unex-

pected. Therefore it appears possible to design a system that would reduce the lag phase and the amount of time required to degrade the chemicals.
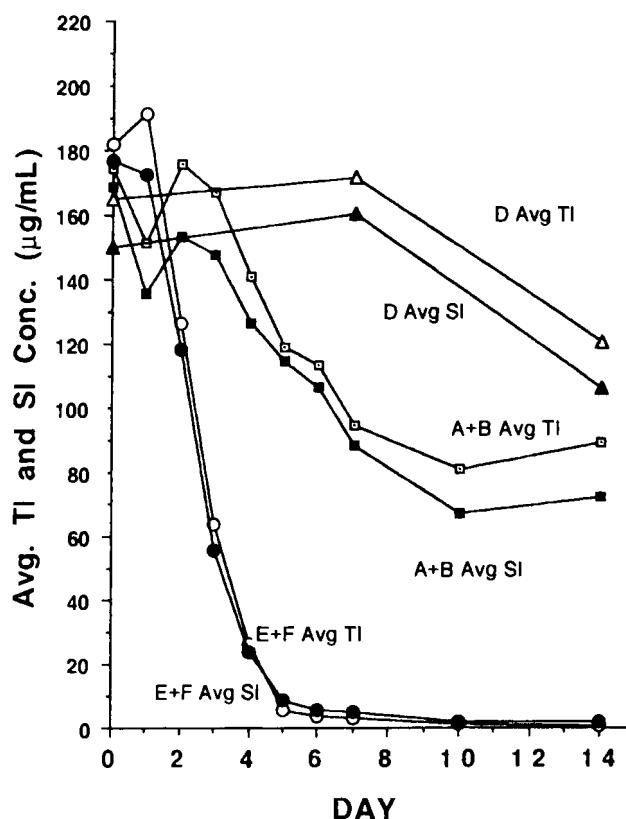
Figure 2
Average Total Ion and Selected Ion (TI and SI)
Concentrations for All Bioreactors

The presence of elemental sulfur was monitored by GC/MS (Fig. 5). It was observed to rapidly disappear from the bioreactors containing bacteria. Sulfur is required as an essential constituent for bacterial cell growth and used in the synthesis of amino acids. Most bacteria assimilate sulfur in the form of soluble sulfates or reduced organic sulfur compounds, but elemental sulfur can be utilized.[5,16] The process of the oxidation of elemental sulfur has been studied in detail.[5] In all the reactors containing bacteria (D, E and F), elemental sulfur was completely removed, while it persisted in the Sterile Controls A and B (Fig. 5). Some sample variability for Reactors A and B may be due to the fact that elemental sulfur is insoluble, but it was consistently observed in all studies that it was removed in active bioreactors. It is thought that the sulfur was microbially converted to a form which was not chromatographable.

The data obtained on the removal of volatile compounds (DCE and TCE) indicate that these chemicals are in fact removed by volatilization and not biodegradation under the conditions of this test (Fig. 6). Concentrations of both chemicals in Bioreactors A, B, E and F dropped to less than 10 ug/mL (initial concentration was 70 ug/mL) after 1 hour. However, the concentrations of both DCE and TCE in Bioreactor D were only slightly below the initial concentration of 99.5 ug/mL. This result was interpreted as evidence that these two compounds were volatilized and not biodegraded. No data are shown for DCE, Reactors B and F, in Fig. 6, because the values were less than the method limit of detection (1 ug/mL).

Enumeration of Microorganisms

The enumeration of microorganisms in Bioreactors E and F increased approximately two orders of magnitude from Day 1 to Day 7 and

remained in the order of 10^7 CFU/mL over the last 7 days (Table 2). The highest enumeration of heterotrophic bacteria occurred in Reactors E and F and correlated with the highest compound removal in these reactors. All other reactors that had received the same initial nutrient amendment as E and F did not exhibit such high cell counts. These data indicated that the bacteria in Reactors E and F used the organics present in the waste as a carbon source for cell growth. Reactor D exhibited a steady increase in enumerations of microorganisms over the time of the experiment. The biomass in this reactor doubled from the first to the last day of the experiment, suggesting that nutrient sources were available to support growth. The microbial population in Reactor G also increased over time but remained below the reactors containing waste.

Acute Toxicity

The Microtox™ test measures the toxicity of chemicals to a phosphorescing bacterium by measuring a loss in its ability to produce light. The Bioactive Reactors E and F exhibited 82.2% and 78.2% light loss, respectively, on Day 0, while on Day 14, the percent light loss was only 13.9% and 18.1%, respectively. Thus, these reactors showed the highest reduction in toxicity over time. These data correlated well with results obtained using GC/MS which showed the largest reduction in chemicals for these two reactors. Reactor G, like Reactor C, served as a quality control. The only difference between Reactors C and G consisted in the amount of surfactant added. Reactor C received the same amount of surfactant as all other bioreactors; Reactor G did not receive surfactant. This difference explains the lack of toxicity and light loss over time in Reactor G while Reactor C exhibited some toxicity at Day 0 as evidenced by a 57.4% light loss. However, this light loss dropped to 23.2% on Day 14, suggesting metabolism of the surfactant by bacteria in the reactor.
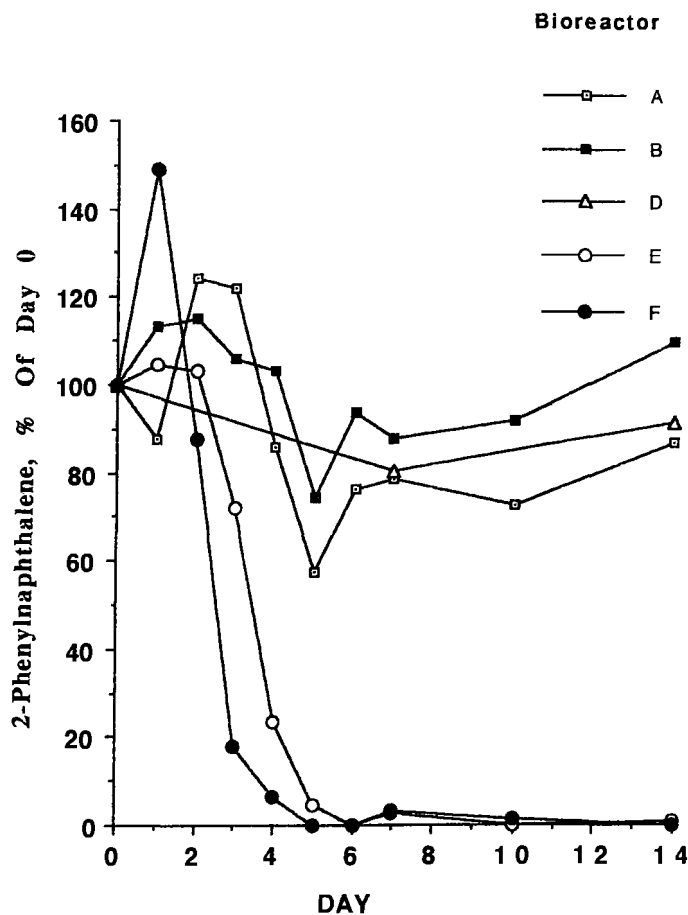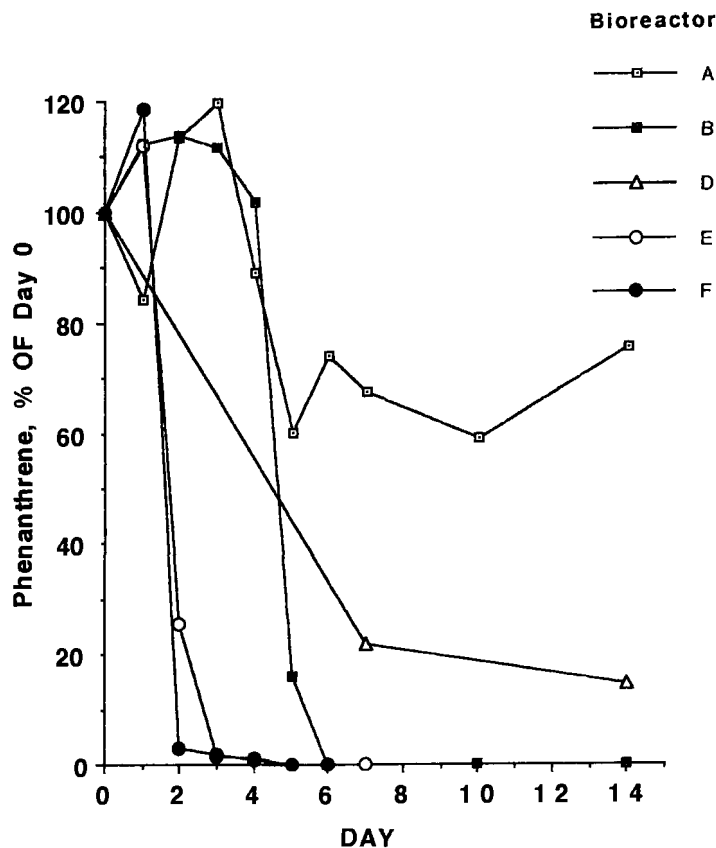
Figure 4
Phenanthrene Removal Expressed as a Percentage of
Day 0 Using Average Selected Ion Concentrations

Figure 3
2-phenylnaphthalene Removal Expressed as a Percentage
of Day 0 Using Average Selected Ion Concentrations
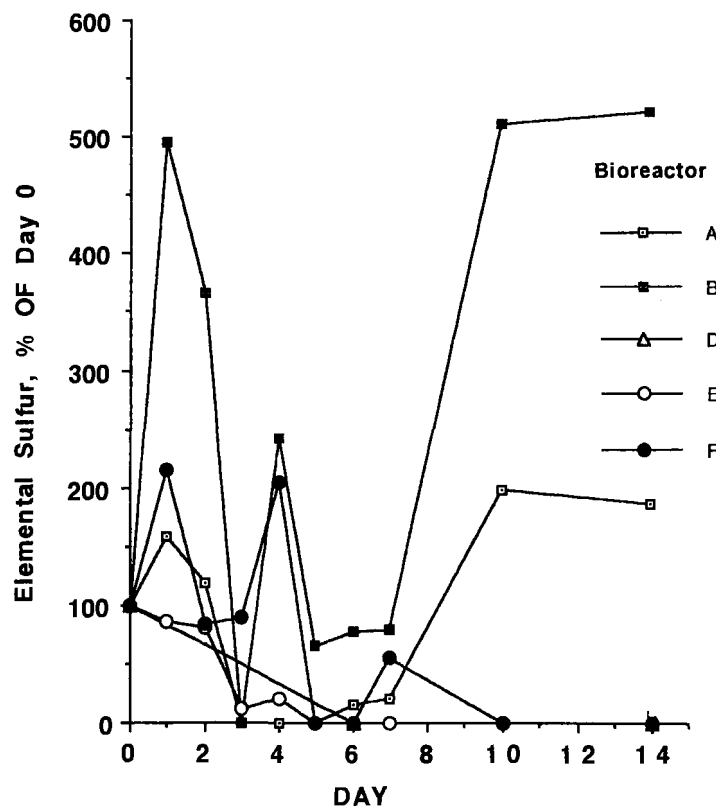
Figure 5
Disappearance of Elemental Sulfur Expressed as a
Percentage of Day 0 Using Average Selected Ion Concentrations

Table 3
Microtox Normalized % Light
Decrease Over Time

Bioreactor	Day 0	Day 7	Day 14
A	100	75.3	ND[*]
B	100	80.6	ND[*]
C	57.4	14.6	23.2
D	77.66	74.1	64.4
E	77.9	25.1	13.9
F	83.0	23.9	18.1
G	1.7	0	1.1

Data are presented for the highest tested dilution mixed with Microtox diluent in a

1:1 ratio

(*)   ND= Not Determined
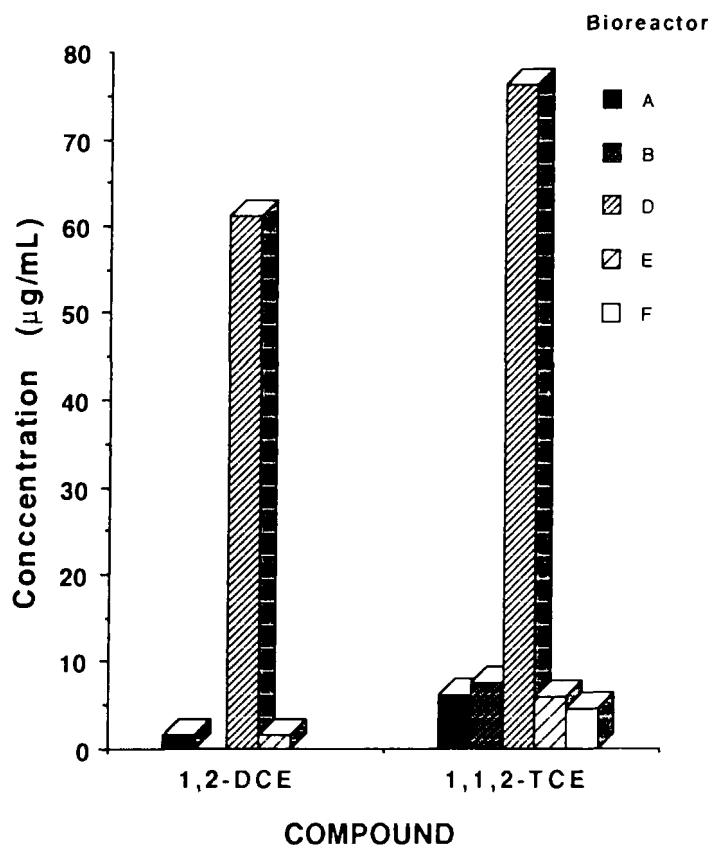
Figure 6
Concentrations of Volatile Compounds One Hour
After the Study Started

The normalized percent light decrease for Days 0, 7 and 14 is presented in Table 3. Both sterile controls, Reactors A and B, exhibited a 100% light decrease on Day 0 due to the presence of HgCl₂. The toxicity of these samples decreased 20% to 25% by Day 7, which indicates a lack of complete sterility and correlates well with the microbial growth in these bioreactors and the degradation shown in Fig. 1. A second addition of HgCl₂ on Day 7 was necessary to insure sterility during the remaining 7 days. Reactor D showed a minor decrease in toxicity correlating with a small amount of degradation occurring in this reactor.

Characterization of Microorganisms

After approximately 3 to 5 weeks of enrichment, a clear difference in growth and number of colonies between the plates from the test flasks (with waste) and plates from the control plates (no waste) was evident. Nineteen microbial isolates were initially obtained and studied by light microscopy. Colonial morphologies ranged from yellow to white and from oval to circular with a predominance of round white and bright yellow colonies. All isolates were nonfermenting obligate aerobes and gram negative short rods with the exception of one strain which was a gram positive rod. This gram positive strain, however, was always found in combination with a gram negative culture and could not be isolated into a pure culture.

Four of the isolates were tentatively identified as Acinetobacter calcoaceticus (98%, 98%, 91% and 99% probability), two strains as Pseudomonas vesicularis (96% and 99% probability) and one strain as Pseudomonas paucimobilis (99% probability). Tentative identification of the other strains showed 49% probability for Flavobacterium sp. and 23% probability for Pseudomonas stutzeri. Eight isolates could not be identified by the Vitek system.

DISCUSSION

The concept of using biological treatment as a remediation technology for contaminated waste is an attractive idea because of the potential cost savings. Additionally, bioremediation offers the advantages that the chemicals of interest are destroyed, future liability is eliminated and the remediation can be done on-site. The present study has demonstrated that 16 chemical constituents associated with styrene tar polymers can be removed in a biological treatment system to acceptable levels. Acceptability of this process is based on: (1) reduction of key chemical constituents to acceptable levels; less than 1.0 mg/kg was achieved for 16 chromatographable compounds, (2) significant reduction in the toxicity of the soil slurry to Photobacterium phosphoreum as measured in the Microtox test; (3) demonstration that biodegradation is the primary route of degradation, not volatilization for most of the 16 chromatographable chemicals; (4) rapid growth of microorganisms in the active treatment reactors; and (5) demonstration of removal rates that are rapid enough to allow for this bioprocess to be scaled up and used on a field scale.

It is recognized under the test conditions used that chlorinated solvents were most likely air stripped and the lower molecular weight organics such as biphenyl were at least partially air stripped. Full-scale use of this technology would most likely require carbon adsorption of the bioreactor gasses.

It was demonstrated in this study that the indigenous microflora was adapted to the system and capable of rapidly metabolizing the major chromatographable compounds present. The persistence of most of the compounds in the sterile control reactors and the sealed reactor was interpreted as proof that losses of these compounds in the reactors containing the bacteria can best be explained by biodegradation and not volatilization. No new chromatographable components were detected during the study, indicating that no new chromatographable degradation products were produced during biodegradation. It is not clear, however, if one or several dominant species were responsible for the metabolism or if cometabolism played a major role. It is not known what role the individual isolates played in the overall degradation processes, but it does warrant further investigation. Since cometabolism may play a significant role, chemical degradation may be dependent on the presence of all or a mixture of some members of the consortium.

The data presented in this paper have been used to justify a field pilot study for a biodemonstration of this method. The data suggest that adequate treatment could be achieved on a full-scale level using a 4-day batch treatment of a 20% soil/water slurry.

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In Situ Bioremediation of TCE and Other Solvents

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ABSTRACT

In situ bioremediation of industrial solvents, hydrocarbons, and pesticides has been demonstrated as an effective alternative to aboveground treatment using physical processes such as air stripping and carbon adsorption. These competing physical cleanup methods do not destroy the compounds of concern but merely transfer them from one medium to another. Biological treatment is an alternative treatment process that could result in complete destruction of TCE, hydrocarbons and related compounds. As an overview, in situ biological treatment techniques will be presented followed by a discussion of several field case histories.

Chlorinated solvents such as TCE are ubiquitous and persistent groundwater contaminants. Currently, physical processes such as air stripping and carbon adsorption are used to remove these compounds.

Biological degradation was demonstrated by ECOVA in a continuous-flow bioreactor with influent TCE concentrations of 1 to 5 mg/L being degraded to below detectable levels. The results indicate the utility of the system for field applications using surface bioreactors in pump-and-treat processes. Subsequent laboratory studies identified conditions that would maintain TCE and thus be suitable to use in situ. Utilizing these conditions, ECOVA tested a pilot system in the field for developing and maintaining TCE-degradative activity within an aquifer. Initial concentrations ranged from 2500 to 3500 ug/L TCE. After 24 hr of treatment, a downgradient monitor well had less than 500 ug/L TCE; the concentration decreased less than 100 ug/L TCE after 7 days of operation. The test results indicate that in situ biological removal of TCE can be achieved in subsurface aquifers.

ECOVA has designed and installed an in situ bioremediation system for groundwater contaminated with 4-chloro-2-methyl-phenol (4C2MP). Prior to the design and installation of the bioremediation system, hydrogeological and microbiological evaluations were conducted to determine if in situ bioremediation was a viable treatment technology for the contaminated groundwater. The microbiological evaluation demonstrated that the groundwater contained a high existing 4C2MP biodegradation potential. Under laboratory conditions, the existing microorganisms in groundwater samples removed from the site generally reduced the 4C2MP concentration by more than 90% after 7 days of incubation. The hydrogeological evaluation demonstrated that aquifer permeabilities and subsurface mass transport parameters were amenable to in situ bioremediation. A groundwater model for the site was developed to determine optimum spacing of the groundwater recovery and reinjection wells. The in situ bioremediation system consists of aeration and recycling of recovered groundwater to stimulate the existing microorganisms to degrade the 4C2MP. In the initial 3 mo of operation, the total contaminated plume exhibited a 25% to 35% reduction in size; after 6 mo, a 50% reduction was observed.

In situ biotreatment is being implemented in a multicomponent

cleanup program currently underway at a former marketing fuel terminal in the Western United States. Two separate zones of contamination are being treated in situ via series of trenches and wells for recovery and recharge of groundwater contaminated with petroleum hydrocarbons at a mean concentration of 2,660 mg/L. The primary contaminants are weathered gasoline and diesel. Recovered water is pumped to the surface bioreactor where free product is reclaimed, contaminant concentrations are reduced and the treated water is amended with oxygen and specific nutrients and recharged into the subsurface. Soil oxygenation is also being used to provide oxygen to the zones where in situ treatment is underway and remove limited amounts of volatile compounds from the shallow unsaturated soil above the in situ biotreatment zone. This remedial program will reduce total petroleum hydrocarbon contamination from the mean concentration of 2,660 ppm to less than 15 ppm cleanup criteria for groundwater. To date, the in situ system operation is effectively producing biodegradation in the subsurface.

INTRODUCTION

Groundwater beneath industrial sites is commonly contaminated with a variety of organic chemicals.[1] The contaminants originate from surface lagoons, tanks and pipelines and percolate into aquifers where they migrate in both the free and dissolved phase. The standard approach for solving this problem is to install a series of recovery wells which pump the contaminated groundwater to above ground treatment systems. The most commonly used treatment systems are air strippers and/or activated carbon filters.

Both of these treatment methods are really transfer technologies; that is, they transfer the contaminants from the water into either the atmosphere or onto the carbon. Alternatives to this standard approach are required for two reasons: (1) transferring the contaminants merely results in contamination of another medium, and (2) pump-and-treat technology fails to achieve site cleanup goals. The U.S. EPA has recognized that while pump-and-treat systems are generally effective in containing contaminant plumes, full system optimization (pumping rates, screened intervals and well locations) and cleanup goals have not been attained.[2] The in situ biological removal of organic groundwater contaminants addresses both concerns. The contaminants are degraded (not transferred to another medium) and, thus, more efficiently removed from the subsurface.

The successful implementation of in situ degradation systems requires an in-depth understanding of the subsurface environment generally followed by a three-phased development program: (1) laboratory treatability evaluation, (2) pilot-scale demonstration and (3) full-scale system implementation. This approach ensures that only the most effective treatment program is implemented for full-scale remediation.

THE SUBSURFACE ENVIRONMENT

The subsurface groundwater environment consists of three components; physical, chemical and biological. Each component plays an integral part in the evaluation, design and implementation of in situ treatment systems. The physical system governs the rate at which groundwater contaminants move through the subsurface and the ease with which they will be removed. Contaminant chemistry defines the geometry and behavior of the contaminant plume while an assessment of subsurface microbiological activity determines the presence of contaminant degrading microorganisms and the subsurface oxygen conditions. To engineer an effective in situ biotreatment system, each of these components must be defined and understood.

Hydrostratigraphy

Subsurface geological strata are defined by drilling soil borings and collecting soil/rock samples. Stratigraphic profiles are developed that delineate various hydrostratigraphic units: water bearing aquifers and low permeability aquitards. Measurements of hydraulic gradients and conductivity are used to determine groundwater flow velocities and the rate of contaminant plume migration.

Hydrochemistry

The chemical compositions of the aquifer matrix and the groundwater are defined through the analysis of soil and groundwater samples. The ability of the contaminants to dissolve and migrate through the aquifer is determined together their ability to absorb on the solid matrix.

Hydrobiology

Microorganisms represent the biological component of the subsurface environment. To survive, they must obtain a variety of inorganic substances, carbon and a source of energy. When these conditions are met, the microbial population flourishes and in so doing transforms the chemical contaminants to harmless byproducts.

IN SITU BIOTREATMENT

In situ bioremediation is the controlled management of microbial subsurface processes. In situ systems generally utilize aerobic processes and involve the introduction of oxygen, nutrients and sometimes specific microorganisms, to the subsurface. Two key criteria for in situ treatment are: (1) a permeable matrix to allow rapid oxygen and nutrient transport and (2) contaminant-degrading microorganisms.

In situ treatment systems involve either: (1) pumping the contaminated groundwater to the surface from a downgradient recovery well, passing it through a surface treatment unit, amending it with nutrients and oxygen and reinjecting it into the subsurface via an upgradient injection well; or (2) directly stimulating microbial activity in the aquifer via direct injection.

PROGRAM DEVELOPMENT

The key to successful in situ biotreatment of contaminated groundwater is to understand the complete hydrobiological system. For example, some hydrogeologic environments may contain sufficient nutrients, others may not require the addition of oxygen (if anaerobic conditions are preferred), or low permeability may cause accumulation of biomass in the treatment zone. An in situ program generally involves three steps: (1) laboratory treatability study, (2) pilot program and (3) full-scale implementation.

Treatability Studies

The purpose of a treatability study is to determine the:

* Biodegradability of the groundwater contaminants
* The rate at which they degrade
* The amounts of oxygen and nutrients required to sustain the reaction
* The interaction between the degrading compounds and the aquifer media (plugging potential).

There are two basic types of treatability studies: (1) the flask study and (2) the column study.

For flask studies, the contaminated groundwater is analyzed for organic, inorganic and metallic compounds. A minimum of three test conditions are generally performed over a period of 6 to 8 wk. During this time, the tests are periodically analyzed to determine the rate of biological degradation. The basic test conditions are: sterile, unamended and nutrient-amended. Typical data are shown in Figure 1. At the completion of the study, a preliminary treatment design is prepared that specifies the anticipated rate of contaminant reduction (cleanup time) and the amounts of oxygen and nutrients required.

Column studies employ the same approach as flask studies with the added benefit of measuring the effect of the aquifer media on the biological reactions. Glass columns are filled with soil samples, and contaminated groundwater is percolated through the columns; sterile and nutrient-amended columns also are evaluated. While the columns do not accurately recreate actual in situ conditions, they do provide an indication of the likely effects of compound adsorption and precipitation.

System Design

Thought must be given to the design of the in situ system such that several key questions are addressed. The treatability study determines if the site contaminants are biodegradable and the rates at which they degrade under laboratory conditions. The next step is to run a field pilot test to confirm these experimental results under "real" conditions, quantify the effects of dilution on contaminant concentrations and evaluate hardware components that will be used in the full-scale system.

Pilot Program

The pilot test must be capable of simulating full-scale operations and yet be brief enough to obtain data that can be fed into the system design. The ideal setup for the in situ program is to monitor groundwater flow and quality up and downgradient of the injection location. The monitoring wells should be located within several days' hydraulic travel
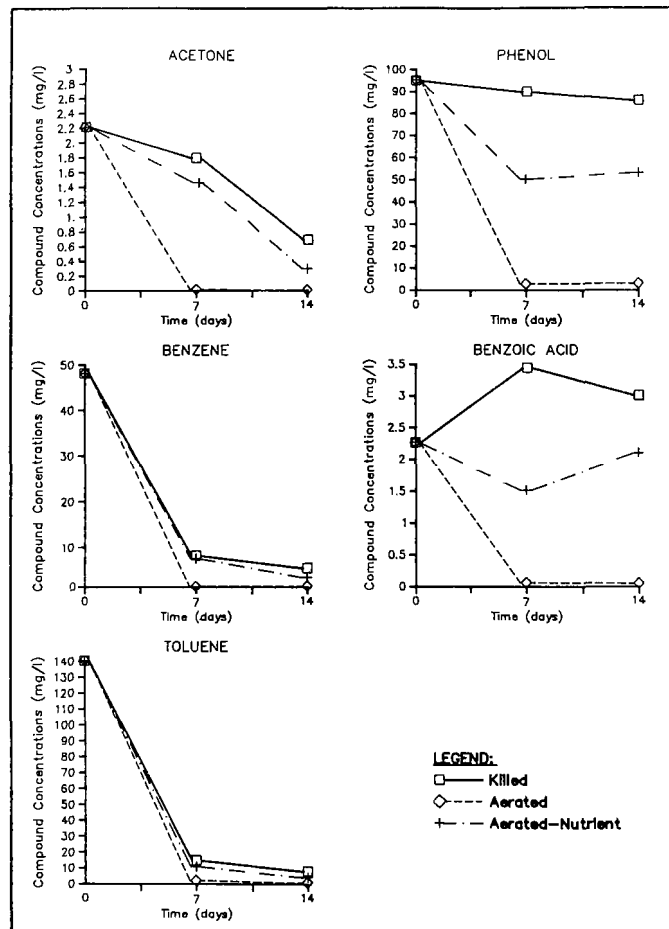
Figure 1
Compound Concentrations in Aerobic Culture Flasks

time of the injection well so that the biological process can be monitored rapidly following injection.

Before performing the biological pilot test, a preliminary test using clean, unchlorinated water should be run without oxygen and nutrients. This test determines the potential effects of water injection (dilution) on contaminant concentrations and is used as a base line against which the effects of biological test are compared. A conservative tracer can be used at this stage to help define groundwater velocities and flowpaths in the vicinity of the injection well and identify potential zones of anisotropy within the aquifer and hence the ability of the feed stock to reach the contaminants.

Full-Scale System

The full-scale system must be capable of degrading the entire plume without causing the spread of contaminants through pumping and injection. For complex sites, this information can be obtained by simulating a variety of scenarios using computer models. The model aids in locating injection and recovery wells and estimating cleanup time.

A series of case histories is presented to illustrate the details of the three steps of an in situ program. Separate projects were selected to illustrate the application to different organic contaminants.

CASE HISTORY: PILOT-SCALE DEMONSTRATION

The aerobic biodegradation of trichloroethylene (TCE) has been demonstrated in laboratory treatability tests.[4] A pilot program was designed to demonstrate the viability of using this process in situ.[5]

The test site is underlain by a thick and extensive sand aquifer (Upper Aquifer) that contains two zones (shallow and deep) contaminated with TCE. The pilot program was performed upgradient of the plant production well N-1. This well pumps 200 gpm from the deep zone of the Upper Aquifer and runs the effluent through a carbon filter before delivering it to the plant water system. An injection well (EI-1) and up (EU-1) and downgradient (ED-1, M-1A) monitoring wells were installed for the test program. Figure 2 shows the locations and layout of the test wells.

A tapline, installed downstream of the N-1 carbon unit, conveyed clean, unchlorinated water to an aeration column, nutrient/bacteria feed system and into the Upper Aquifer via injection well EI-1. To ensure a maximum feed rate, the delivery zone was vertically restricted by means of an inflatable packer. Dedicated, submersible, air-driven sampling pumps were installed in monitoring wells ED-1 and M-1A.

A two-phased pilot program was implemented. Phase 1 involved the injection of TCE-free water containing a sodium chloride tracer into the aquifer to quantify the effects of dilution on groundwater TCE concentrations. Phase 2 involved the injection of oxygen, nutrients and a

strain of TCE-degrading bacteria (G-4) into the aquifer to quantify the effect of in situ microbial degradation of TCE.

Phase 1 - Tracer Test

Sodium chloride was selected as the tracer; an increase in specific conductance in the monitoring wells would indicate the migration of the tracer. The saline solution was fed to the water stream which was injected into the well (EI-1) at a rate of 5 gpm. Before starting the test, base line conductivity measurements were taken in the three monitoring wells; injected water was detected in both the up and downgradient monitoring wells. Groundwater velocity in the lower permeable unit was calculated to range between 2 and 5 ft/hr. This figure was determined by dividing the time taken for the first occurrence of tracer at the two downgradient wells by their respective distances from the injection well.

The issue of dilution is a key point in verifying the validity of the in situ biotreatment process. TCE values were plotted versus conductivity to determine if there was a correlation between TCE and salt concentration. An increase in conductivity would parallel the ingress of the injected water. If the freshwater injection was diluting the contaminated groundwater, then a decrease in TCE levels could be expected to correspond with an increase in conductivity.

By calculating the daily flow of groundwater in injection zone and comparing it with the amount of water injected, it is possible to calculate the expected dilution effect. The receiving zone had a saturated thickness of 14 ft and a width of 20 ft (minimum, based on the appearance of tracer at all monitoring wells), an effective porosity of 25% and a flow velocity of 48 ft/day. Based on these data, approximately 25,000 gal/day (gpd) were flowing through the receiving zone. By comparison, the injection stream was run at a steady rate of 5 gpm (7,200 gpd) representing 29% of the flow into which it was placed. Based on this calculation, a 30% decline in TCE levels could be ascribed to dilution in ED-1, the directly downgradient well. No evidence of dilution was seen in wells EU-1 or M1-A. By contrast, the overall reduction (95%) in TCE values achieved during the subsequent biological test far exceeded the effects of dilution.

Direct measurements of the injected salt concentrations were not made in Salt Test 1 and therefore dilution estimates could only be approximated. In Salt Test 2 influent salt concentration was measured, allowing the calculation of dilution at the monitor wells. The results of the test are presented graphically in Figure 3. The time-weighted average concentration of the saline feed was determined by weighing the data points using the length of time between the readings. Using the time-weighted average smoothed the injection concentration data that would improperly skew the test results.

In Salt Test 2, Wells ED-1 and EU-1 recorded the greatest breakthrough of salt solution from the injection well EI-1. Well M1-A showed
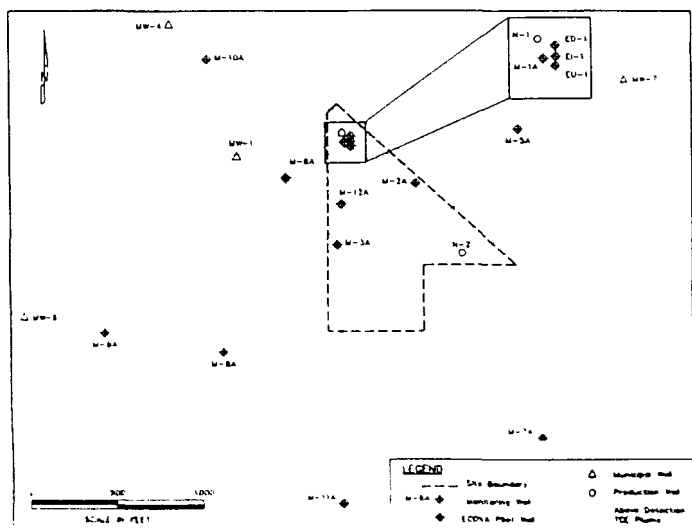
Figure 2
Upper Aquifer, Deep Hydrochemistry
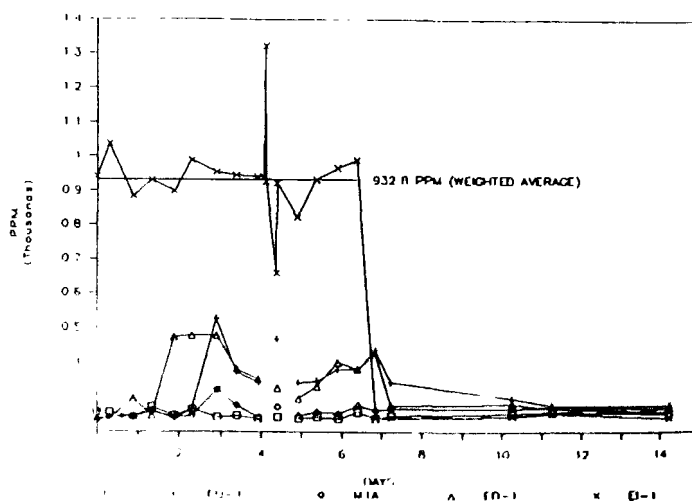
Figure 3
Salt Injection Test

very little breakthrough (one peak at 500 mg/L over background). Dilution (of groundwater) was calculated from the following formula:

DILUTION = (SAMPLE CONC.-BACKGROUND CONC./
(INJECTION CONC. BACKGROUND CONC.)   (1)

Figure 4 represents the calculated percent dilution during the test for all the wells. Dilution in the upgradient and downgradient wells (EU-1, ED-1) was the most significant; the greatest calculated dilution was 40% and only then for one sampling. Well M1-A showed only minimal dilution effects of the injected water, less than 13%. These data suggest that dilution is a very localized process and would become insignificant during full-scale operations. The large fluctuations are due to fluctuating water demands by production well N1. Time weighted averages of dilution calculated for wells ED-1 and EU-1 (not including the lag phase) were 23% and 20%, respectively.

From the Salt Test 1 data we calculated that dilution by the injection stream would account for a 29% decrease in TCE plume concentrations. This number was calculated using flowrate ratios between the injection stream and groundwater flow in the aquifer. However, no data were taken during the first test on the exact salt concentrations being injected; therefore, the exact dilution could not be calculated. In the second test, we monitored the salt concentrations being injected throughout the test, this allowing exact concentrations to be calculated.

Phase 2 - Biotreatment Test

The in situ biotreatment system utilized the same injection and monitoring wells and the same injection rate (5 gpm) as the tracer test. Clean unchlorinated water was injected for 1 day; nutrient feeds were initiated the following day. Various additions were made to the recharge water to stimulate degradation of TCE. The water was oxygenated and both inorganic and organic nutrients were introduced into the feed. In addition, a culture of strain G4 was added during the initial phase of the test. Nutrients and oxygen were added continuously for 6 days.

Oxygen Concentrations:

The addition of oxygen to the feed maintained high levels of oxygen downgradient during the test period, ensuring the necessary aerobic conditions for treatment. The range of oxygen concentrations from initiation of the test to termination of feed is summarized in Table 1 for the three monitoring wells. As expected, as treatment continued and microbial activity was expected to increase, the oxygen levels decreased. However, at no time did oxygen concentrations decrease to levels approaching anaerobic conditions.

Table 1
Range of Oxygen Concentrations During the Pilot Treatment Test

Well	Oxygen Concentration (mg/L)	
	Min	Max
ED-1	4.0	14.6
M1-A	4.0	12.3
EU-1	2.8	12.5

Microorganisms:

The monitoring wells were periodically tested for the presence of strain G4 suing a semi-selective plate count method. These results indicate that very low levels of strain-G4-like microorganisms were already present in the aquifer. The results for the following 5 days showed less than 10^3 cfu/mL of organisms in all three monitoring wells.

Detectable increases in G4-like microorganisms were first detected at T=6.2 days, and they were 7.6 x 10^4 and 1.6 x 10^4 cfu/mL in wells M1-A and EU-1, respectively. Similar results were obtained at T=6.9 days, which was the final test for microorganisms. In this instance, all three wells showed significant levels of microorganisms.

TCE Disappearance:

After 24 hr of feed (T=2 days), TCE concentration in the downgradient well (ED-1) had decreased from 2500 ug/L to 466 ug/L. By Day 3 of the test, the concentrations had fallen below 200 ug/L. With the exception of one data point (T=5.8 days), all subsequent concentra-
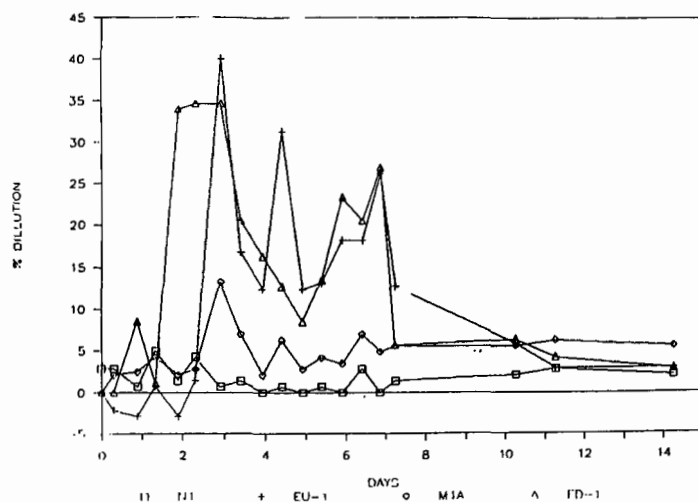
Figure 4
Salt Injection Test, Percent Dilution

tions were below 300 ug/L. Decreases in the concentration of TCE also occurred in wells M1-A and EU-a. The time of response was longer and the magnitude of the decrease was less than observed for ED-1. These results were consistent with the results of the tracer studies, which showed the most rapid communication between the injection well (EI-1) and well ED-1, followed by well M1-A and finally the upgradient well (EU-1).

Results:

Figure 5 summarizes before (T=0 days) and after (T=10 days) test plume configurations. The effect of treatment continued after termination of the feeds. The pilot test allowed the following important conclusions to be made regarding the in situ treatment of TCE:

• The tracer test confirmed that the injection water spread up and downgradient of the injection well and that groundwater flow velocities within the receiving zone were on the order of 2 to 5 ft/hr. A theoretical dilution of TCE concentrations was calculated based on the ratios between the rate of injection and the flowrate of the receiving zone. Measurable dilution effects were only observed in the downgradient monitoring well ED-1.

• The tracer test was followed by the introduction of TCE-degrading bacteria, organic and inorganic nutrients and oxygen into the lower permeable unit of the Upper Aquifer over a 6-day period. Within 8 hr of initiation, a measurable decline in TCE concentrations was observed. A corresponding decline in oxygen levels was observed, suggesting that microbial degradation had been activated.

• The in situ test demonstrated biological degradation of TCE-contaminated groundwater from a high value of 3,000 ug/L to a mean concentration of 135 ug/L, which was maintained form Day 3 to Day 8. A further decline to a mean value of 78 ug/L was observed over the next 10 days.

The pilot test proved that TCE can be removed from groundwater by in situ aerobic biodegradation. The rapid rates are very encouraging as they indicate that under the right conditions, this contaminant can be significantly reduced within a short time frame.

CASE HISTORY: IN SITU BIODEGRADATION OF HERBICIDES

Shallow groundwater contamination was detected beneath a herbicide formulation facility in 1981. The major contaminants were identified as chlorinated phenols, primarily 4-chloro-2-methylphenol (4C2MP), and were present in a shallow (35ft. thick) glacial aquifer overlying bedrock. A pump-and-treat system (consisting of 11 extraction wells feeding two activated carbon units) was installed in 1983. Effluent from the system was returned to the aquifer via eight injection wells. To achieve a more rapid reduction in contaminant levels, an in situ program was evaluated in 1987.
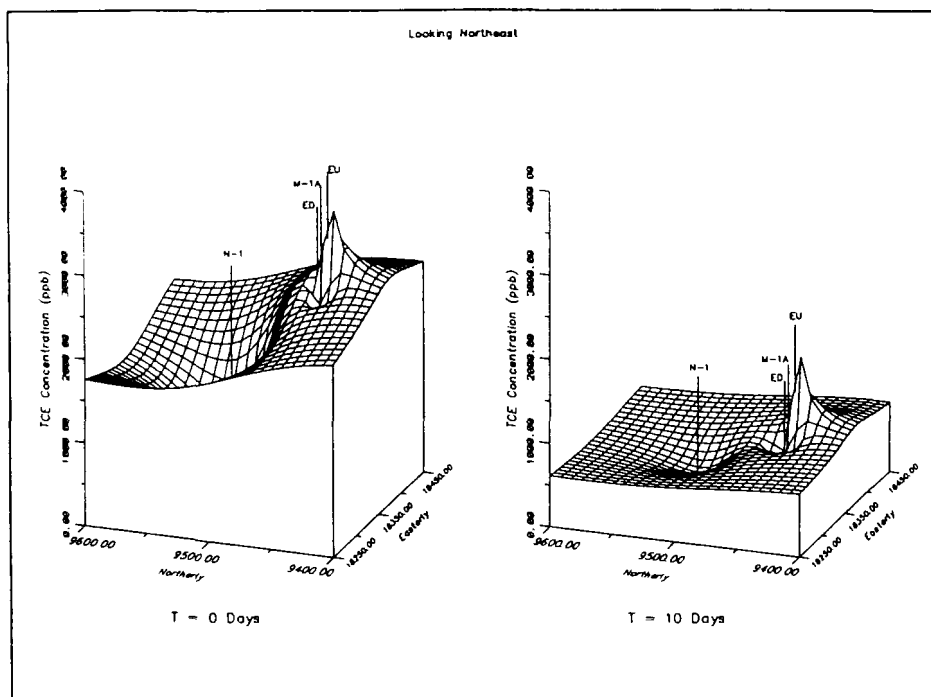
Figure 5
Pre and Post Test TCE Concentrations

Aerobic laboratory culture techniques were used to assess 4C2MP biodegradation in the site groundwater. High 4C3MP biodegradation potentials were observed in groundwater samples obtained from three site wells (Table 2):

Table 2
4C2MP Concentrations in Aerobic Cultures

Well	C_0 (mg/L)	C_{fc} (mg/L)	C_{ft} (mg/L)
I-4	X = 1133	X = 1133	X = <41
P-4	X = 3400	X = 3800	X = 1380
P-8	X = 710	X = 710	X = <41

X = Average 4C2MP concentration (3 replicates).
C_0 = Initial Concentration.
C_{fc} = Final Control Concentration (7 days).
C_{ft} = Final Test Concentration (7 days).

High 4C2MP biodegradation potentials were observed with no nutrient adjustment. This study showed that only aeration was needed to reduce 4C2MP concentrations in the groundwater. In 1988, the number of recovery wells was increased to 19 and two additional injection wells were installed. Airlift pumps were placed in the recovery wells, thereby increasing the oxygen concentration in the injected effluent.

Results

Within the first year of system operation, the following results were obtained:

• Reduction in off-site contaminant plume size was effected by gradient control of the recovery system.
• Decreased dissolved oxygen concentrations were initially measured in the injection wells; this suggested that phenolic degrading microbial populations had been established adjacent to the injection wells.
• In the initial 3 mo of operation, the total phenol plume exhibited a 25 to 35% reduction in area; after 6 mo, a 50% reduction was observed.

The system has continued to operate successfully and is expected to result in total site remediation within five years of initiation.

CASE HISTORY-IN SITU BIODEGRADATION OF PETROLEUM

A former marketing terminal in the Western United States had been contaminated by losses incurred during the handling of petroleum products during 65 yr of operation. More than 60,000 yd^3 of soil are contaminated with petroleum hydrocarbons at a mean concentration of 2,660 ppm. Groundwater analyses identified benzene as the compound of concern. Ethylbenzene, toluene and xylenes are present at low levels.

A laboratory treatability study evaluated treatment options and cleanup levels achievable through bioremediation. Options studied included excavation and off-site disposal, off-site treatment and on-site treatment focusing on bioremediation. Activities managed in support of the Remedial Action Plan (RAP) included preliminary design of cleanup systems and regulatory liaison and public involvement activities.

Two recommended treatment alternatives, on-site solid-phase biotreatment and in situ biotreatment, were selected because of the destruction of the contaminants and significant cost savings compared to off-site disposal. Bioremediation of the contaminated soil reduces the hydrocarbon contaminant level to below the agreed to cleanup level of 200 ppm. Water cleanup criteria for the contaminants are as follows: total hydrocarbons-15 mg/L, benzene-40 ug/L and ethylbenzene-3.5 mg/L. Once these levels are achieved, the site will be rendered clean and suitable for development.

The site is divided into four areas (Fig. 6). The in situ system plan called for installation of trenches on either side of Area C and either side of Area D. Figure 7 shows the general installation and operation of the two situ systems.

The in situ systems are comprised of extraction and reintroduction trenches/wells and surface bioreactors. Contaminated groundwater is pumped from the extraction trench/well to the surface bioreactor. Baffles on the influent end of the bioreactor separate free product which is pumped to an oil/water separator for further separation and eventual reclamation. The contaminated water flows over a weir into the active zone of the bioreactor. In this zone, oxygen (via diffused air bubblers) and nutrients are added to promote optimal degradation. The residence time of the water in the reactors is controlled to ensure degradation of the contaminants.

Once the contaminants are degraded, the treated water is pumped from the surface bioreactors through nutrient amendment and oxygenation contactors and reintroduced to the subsurface via the reintroduction trenches. The nutrient additions are monitored to maintain optimal
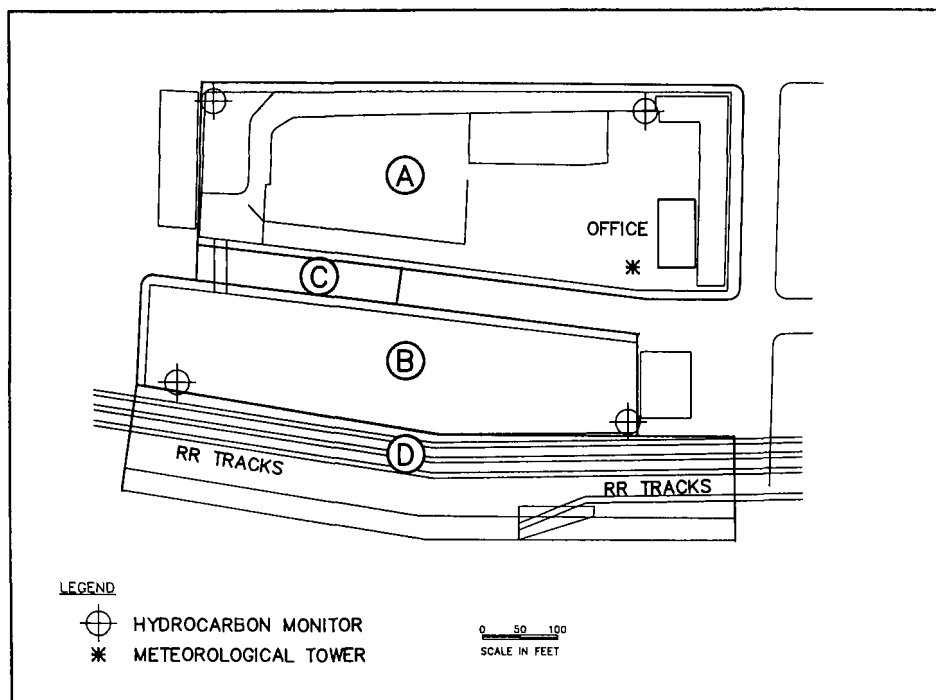
Figure 6
Site Map

levels. The oxygenation is accomplished with both diffused air bubblers and pure oxygen contactors. The oxygen is supplied by an on-site oxygen generator, thereby avoiding the dangers associated with compressed oxygen storage. The oxygen generator uses a molecular sieve bed that selectively excludes nitrogen from an ambient air stream and allows only oxygen to pass. As a result, a 98% pure oxygen stream can be produced. The molecular sieve uses size exclusion to prohibit the nitrogen flow and is regenerated each cycle.

The in situ system cleans contaminated zones by increasing the flow above normal groundwater flowrates, promotes in situ degradation, promotes mobilization of contaminants and treats unsaturated zones more effectively. The higher flowrate through the zone of contamination promotes soil washing. Any contaminants that are mobilized by the system are captured by the extraction trench and treated in the surface bioreactor. By supplying oxygen and nutrients to the subsurface, organisms present in the soil reach optimal degradation rates and reduce the contaminants

at the source. The enhanced biodegradation also assists in promoting mobilization of contaminants for capture and treatment by the extraction trench and surface bioreactor.

The development of active biodegradation in the subsurface enhances mobilization of contaminants through the action of biosurfactants. The microorganisms produce extracellular proteins (biosurfactants) which liberate contaminant molecules from soil particle surfaces into solution. Once in solution, the microbes can absorb and utilize the contaminant molecule as direct or co-metabolic carbon sources. The active microbial culture is very efficient at producing biosurfactants but not as efficient at capturing and utilizing all of the mobilized contaminant. As a result, with the increased groundwater flowrates and the action of the biosurfactants, soil washing is enhanced and the extraction trench recovers the mobilized contaminants for treatment in the surface bioreactors.

Finally, the reintroduction trench supplies treated and oxygen/nutrient-amended groundwater at a faster rate than the subsurface strata can accept. As a result, the groundwater surface in the area of the reintroduction trench is mounded. This mounding of the groundwater surface saturates previously unsaturated soils and provides a more optimal condition for in situ biodegradation.

The Area C system is comprised of a 300-ft long extraction trench coupled to a 250-ft long reintroduction trench. The pipe invert for the extraction/reintroduction piping is 2 ft below static water surface, or approximately 13 ft below ground surface. The design flow rate for the Area C system is approximately 20 gpm.

The Area D system is comprised of a series of 15 extraction wells on 50-ft centers. The wells were required because of lower permeabilities and restricted access problems. The extraction wells are coupled to a 650-ft long reintroduction trench. The invert elevation for the extraction wells is between 5 to 10 ft below static water levels and the pipe invert for the reintroduction trench is 2 ft below static groundwater levels. The design flow rate for the Area D system is approximately 100 gpm.

Included in the Area C and D in situ system trenches are vacuum lines that induce soil oxygenation in the contaminated zones. Ambient air is drawn into the subsurface from exposed surfaces within the zone of influence of the trench by a vacuum applied to the subsurface piping. The soil oxygenation pipe invert is 6 ft above the groundwater surface and 4 ft below ground surface.
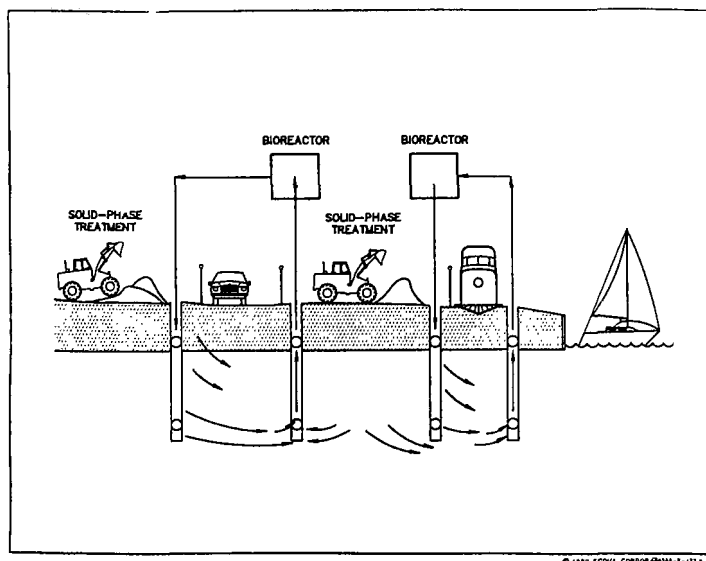
Figure 7
In Situ System

Figure 8 presents some process monitoring data collected during the initial 8 mo of operation. As can be seen from this figure, the in situ system has clearly affected the subsurface. The concentration of ammonia nitrogen has increased consistently since operation of the system began in early 1990. The other parameters, nitrate nitrogen, phosphate and dissolved oxygen also show potential increasing trends but are not as clear as the trend for the ammonia nitrogen. Based on the data collected to date, we project that the cleanup goals will be achieved within 7 yr of initiation of treatment.

CONCLUSIONS

In situ biotreatment of groundwater contaminated with organic compounds is a proven remedial method that may provide an alternative or adjunct to conventional solutions. The method uses naturally occurring microorganisms that are adapted to site conditions to remove groundwater contaminants. Laboratory treatability studies provide an evaluation of the biodegradability of the contaminants. Pilot testing gathers information on the performance of the injection/recovery system and determines the degree of dilution. Full-scale implementation results in terminal destruction of the contaminants and rapid site cleanup.

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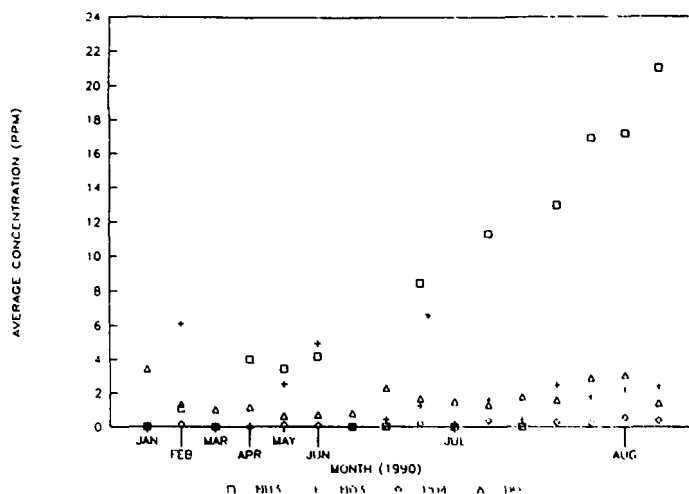
Figure 8
Average Nutrients and Dissolved Oxygen vs. Time

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Selection, Testing and Design of an Integrated Biotreatment System for Remediation of a Former Oil Refinery Site

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INTRODUCTION

OHM Remediation Services Corp. (OHM) was hired in 1985 by a major Midwestern refiner to provide environmental services for a petroleum refining site. The refinery operations had been previously dismantled, but the site needed further assessment and remedial efforts to address the residual contamination that had originated from the facility. During the last 5 years, OHM has completed the site characterization, provided interim site mitigation measures to prevent further groundwater contamination, performed biotreatability tests, conducted bench-scale tests and completed a detailed design for an integrated treatment system. This system includes a variety of processes, but biological treatment is the cornerstone of the process with carbon adsorption used for polishing effluents.

This paper discusses the tasks related to the development and design of a treatment system to recover and treat benzene, toluene, ethylbenzene and xylene (BTEX) contaminants in groundwater. Over a long period of time these soluble petroleum hydrocarbon components (PHC) had dissolved into the shallow groundwater aquifer. The primary objectives of this project were to:

- Provide a site perimeter groundwater containment system consisting of fully penetrating recovery wells designed to halt the off-site migration of groundwater containing dissolved PHCs.
- Identify the optimal method to treat groundwater containing BTEX and dissolved PHCs to levels suitable for discharge into a surface drain under a NPDES permit.
- Design a full-scale treatment system for the selected remedial process.

The information gained during the prior 4 years of hydrogeological and biodegradation studies was used as a basis for this design.

The significance of this project is that it provides an excellent example of how, by combining technologies, project costs can be reduced while meeting the established cleanup criteria. Although this groundwater cleanup could have been achieved by using either carbon adsorption or biological treatment alone, combining these technologies optimized both the technical results and the cost-effectiveness.

BACKGROUND

The site geology consists of a 75- to 80-foot thick interval of coarse- to medium-grained sands that fine downward and overlay a blue silty clay. The depth to groundwater ranges from 2 to 5 feet below grade. The upper 20 feet of the water table aquifer possesses a hydraulic conductivity of 1,000 gal/day/ft.^{2}

The contamination originated from the oil products that were produced by the refinery. Over the years of refinery operation, these products spilled and were also discharged into ponds which most likely leaked. The result was that the underlying soil and groundwater were contaminated with PHCs.

Table 1 lists the influent parameters and contaminant concentrations for the design basis. Table 2 lists the discharge limitations as outlined in the NPDES permit. The primary hydrocarbon constituents for which regulatory agencies established cleanup criteria are BTEX. Other hydrocarbon constituents are present in the water, but they have not been regulated. The total influent BTEX concentration is 2 mg/L. The treatment criteria establish that the total concentration of BTEX compounds must be reduced to less than 20 parts per billion μg/L (24-hour sample) with a benzene limit of 5 μg/L.

Available on- and off-site hydrogeological, hydrochemical and biological data were used to design a groundwater recovery treatment system. Additional data generated from initial laboratory treatment studies were also utilized to prepare the preliminary design and to estimate operational costs.

Table 1
Design Basis

Parameter	Value
Hydraulic Conductivity	1,000 gallons/day/ft^2
Porosity	0.3
Ground-Water Gradient	0.0026
Saturated Thickness	78 ft
Maximum Influent Flowrate	400 gallons per minute
Normal Influent Flowrate	360 gallons per minute
Ground-Water Chemistry	
Lead	<0.05 ppm
Chromium	<0.05 ppm
BTEX (total)	2 ppm
BOD$_5$	<10 ppm
Total Organic Carbon (TOC)	40 ppm
Total Suspended Solids (TSS)	5 ppm
Dissolved Oxygen (DO)	2 ppm
pH	6.7 SU
Oil and Grease	<10 ppm
Water Temperature	55°F
Nitrogen	3 ppm
Phosphorous	0 ppm

Table 2
Effluent Limitations and Monitoring Requirements

Effluent Characteristics	Discharge Limitations		Monitoring Requirements	
	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type
Flow (MGD)	(report)	(report)	Daily	Report Total Daily Flow
5-day Biochemical Oxygen Demand	4 mg/l	10 mg/l	Weekly	Grab
Total Phosphorus as P	5 mg/l	20 mg/l	Weekly	Grab
Ammonia Nitrogen, as N	0.2 mg/l	---	Weekly	Grab
Total Suspended Solids	0.8 mg/l	1.0 mg/l	Weekly	Grab
Benzene	---	5.0 ug/l	1/monthly	Grab
BTEX (total)	---	10 ug/l	2/monthly	Grab
Temperature, °F	(report)	(report)	5/monthly	Reading
Outfall Observation	(report)	(report)	5/Weekly	Visual
	Daily Minimum	Daily Maximum	Measurement Frequency	Sample Type
pH (Standard Units)	6.5	8.0	Weekly	Grab
Dissolved Oxygen, mg/L	6.0	---	Weekly	Grab

The groundwater extraction wells have already been designed and installed to halt the off-site migration of PHC contamination. The groundwater treatment system design was based upon the flowrate of these wells, which produce a maximum flowrate of 400 gpm.

The following studies and work phases are described in this paper:

- Review of viable treatment processes for groundwater treatment
- Selection of an appropriate biotreatment process
- Bench-scale biotower treatability study
- Detailed design of integrated treatment system

TECHNOLOGIES SELECTION

Several technologies were evaluated as potential treatment methods for destroying or removing the dissolved PHC contaminants from the site groundwater. The following treatment processes were considered:

- Biological treatment
- Ultraviolet (UV) oxidation
- Carbon adsorption
- Air stripping

The advantages of first two processes are that they both would destroy the contaminants, rather than transfer them to another medium. However, at the time this evaluation was performed, UV oxidation was not considered cost-effective for the low level contaminant concentrations present at this site. Also, the water would need pretreatment to remove any turbidity that would interfere with UV light absorption.

Air Stripping/Activated Carbon

Air stripping and carbon adsorption are both effective methods for removing BTEX compounds, but these compounds still must be transferred to another medium. Air stripping would have to be used in combination with vapor phase carbon adsorption.

Carbon adsorption (for the liquid phase) presents definite advantages in that it is tolerant of concentration and flowrate variations and can adsorb a broad spectrum of compounds. However, oil and grease can plug a carbon bed if the concentration is greater than 10 mg/L. Carbon preferentially adsorbs certain organics. Of the BTEX compounds, carbon adsorbs less benzene than the other BTEX components. The primary disadvantages of carbon are the relatively high cost of operation and the need to further treat and/or dispose of the carbon.

A carbon isotherm study was conducted in the laboratory to measure the adsorption of BTEX components onto granular activated carbon (GAC) to assure that contaminant concentrations could be reduced to μg/L levels. The carbon adsorption isotherms demonstrated that for the major contaminant, benzene, the carbon capacity was 0.175 mg/g. The study also addressed total organic carbon (TOC) removal, showing that 1,000 pounds/day of carbon would be required to treat a representative flow of 150 gpm down to low μg/L levels of TOC.

Bioremediation

Bioremediation is a cost-effective treatment process that uses microorganisms to degrade organic materials. This process is enhanced by providing the organisms with the appropriate nutrients (nitrogen, phosphorus and trace minerals) and environmental conditions (Ph, temperature, moisture, etc.) to optimize the reaction rates. Bioremedia-

tion of PHC compounds results in the organics being degraded to carbon dioxide and water; therefore, little or no residual hazardous chemicals result from the treatment process.

The PHC and BTEX compounds present in the groundwater and soil at the site are known to be readily biodegradable. Biological treatment of PHCs is well-documented in the published literature.[1-6] Priority Pollutant phthalates, benzenes and PAHs are included on the Appendix VIII list of hazardous organics under 40 CFR Part 251 and, therefore, are subject to the regulations specified under the RCRA. A report prepared by ERT for the American Petroleum Institute stated that the all Appendix VIII organic compounds that may be present in land-treated petroleum wastes can be degraded in soil under proper environmental conditions.[7] Tabak et al.[8] demonstrated biodegradation of benzene, ethylbenzene and toluene in basal salts-yeast extract enrichment flasks using 5 and 10 mg/L concentrations of each compound as sole carbon and energy sources for microbial growth. A wastewater inoculum was used and adaptation was rapid. Biodegradation of o-, m- and p-xylene is well-documented.[9]

For the above reasons, bioremediation was selected as the primary remedial technology to treat groundwater at the site. A laboratory treatability study had demonstrated the effectiveness of indigenous microorganisms to degrade BTEX to concentrations less than 1 μg/L in groundwater. These studies also provided information on treatment kinetics to allow an order of magnitude estimate of the reactor volume required to treat a given quantity of water.[10]

BIOLOGICAL TREATMENT SELECTION

The aerobic, static (packed) bed, fixed-film process configuration was selected for biological treatment of the contaminated groundwater after considering a number of process configurations including the rotating biological contactor process; the fluidized-bed, fixed-film process; and the powdered activated carbon-activated sludge process. In the aerobic, static-bed process configuration, wastewater flows upward or downward through a bed of media, fixed within the reactor shell. Oxygen, normally in the form of air, is introduced through diffusers located in the bottom of the reactor.

The full-scale process flowsheet would involve a biological treatment system followed by solid-liquid separation and conventional GAC adsorption. Some components of the groundwater, especially benzene, would quickly exhaust the GAC in the treatment system if not degraded in the biological treatment process. A high removal efficiency of benzene and other aromatic components by biological treatment will assure a longer effective lifetime for the carbon. This design will translate into a savings in activated carbon costs over the system's lifetime. The GAC adsorption step is anticipated to play a significant role in assuring effluent quality requirements are met during startup and upsets of the biological treatment system. Once the biological system reaches its design treatment capacity, the GAC adsorption step will polish the water to assure treatment to discharge criteria.

BENCH-SCALE BIOTOWER TREATABILITY STUDIES

A bench-scale study was performed to develop process operation information for full-scale design of a biological system to treat contaminated groundwater. The goals were to determine the treatment removal efficiency achievable for the BTEX components in the groundwater and to establish the minimum temperature and nutrients needed to operate the upflow bioreactor to achieve design effluent concentrations at an influent flow of 200 gpm (1-hour Hydraulic Residence Time [HRT]) to each biotower. In addition, other important treatment system design and operating parameters (e.g., biological reactor oxygen requirements, chemical requirements for pH control, degree of VOC stripping in the reactor, etc.) were established.

The required size or number of biotowers would be dictated by the treatment kinetics associated with the wastewater in question and the mass of active microorganisms which could be developed and maintained in the reactor. Based on a design Biological Oxygen Demand (BOD) loading of approximately 20 pounds BOD_5/1,000 ft^3/day, one reactor would treat 200 gpm of groundwater.

Materials and Methods

The laboratory study involved operation of an upflow, attached film, 5-L, static bed reactor. The upflow operation assured maximum groundwater/biomass contact and a minimum of short circuiting through the bed. The reactor was filled with random packed, plastic pall rings and enclosed to allow complete material balances to be performed. Air was used as an oxygen source during the study to assess the effect of aeration on VOC stripping. If necessary, high purity oxygen could be used to minimize volatilization/stripping of the organics. The reactor was operated on the site water supplemented with appropriate nutrients to support the growth of biomass. The pH of the reactor was maintained in the neutral range. In order to establish the minimum temperature and nutrients needed to achieve design effluent concentrations, two small biotowers were constructed. Biotower I was operated at 70 °F to simulate heated groundwater, while Biotower II was operated at 55 °F to simulate the ambient groundwater temperature.

The biotowers were constructed as 4-inch diameter Plexiglas columns with flanged top and bottom plates. The influent port was located on the column bottom while the effluent was side discharged near the top of the biotower. A port on the biotower top allowed off-gas to escape.

The packed volume of the reactor was 4 liters. Each column was packed to a height of 29 inches, with 5/8-inch nominal Nor-Pac polypropylene media to provide a support medium for biomass growth. One-half inch glass beads were placed below the packing for air dispersion from the influent throughout the column diameter (Fig. 1).

Each reactor was inoculated with activated sludge from the Findlay, Ohio, wastewater treatment plant. A full recycle flow scheme was initiated with an influent feed consisting of BTEX-spiked site water supplemented with acetate. The acetate was the primary carbon source for the developing biomass since TOC and BOD concentrations in the site water were relatively low. Full recycle operation was continued until sufficient biomass had developed on the column media.

For continuous flow operation, site water was pumped from barrels into a header leading to the bioreactor influent port. Also connected to the header was a line to the carbon/nutrient/BTEX source carboy. This mixture contained measured amounts of ammonia-nitrogen and phosphate-phosphorous nutrients for biomass support, a BTEX addition to increase influent concentrations and acetate to be added as a primary carbon source when necessary. The BTEX addition was necessary due to volatilization of these contaminants from the site water
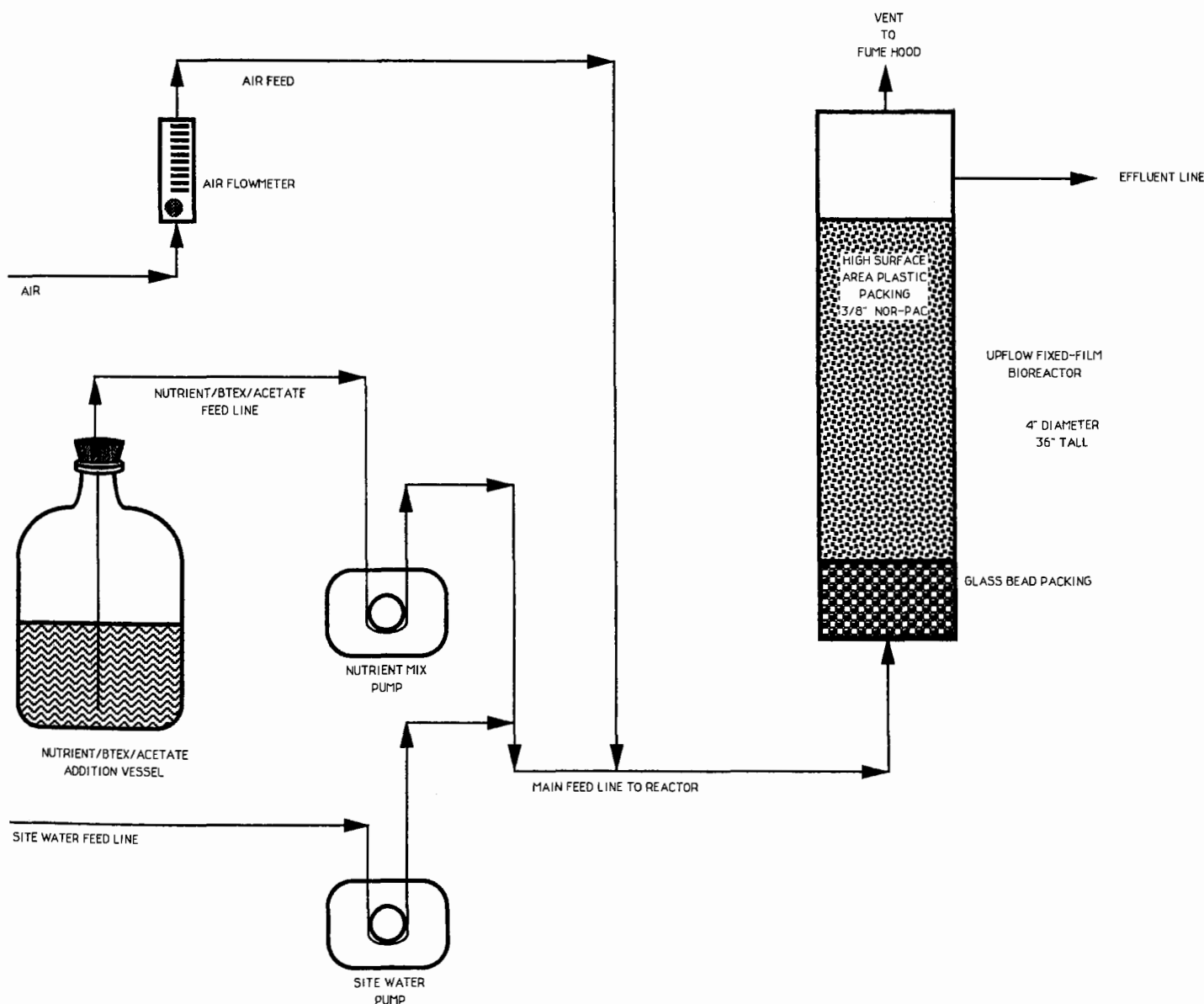
Figure 1
Bench-scale Biowater System

during collection and/or storage. On Biotower I, operated at room temperature to simulate 70 °F (heated) groundwater, a compressed air line was connected to the combined feed header before reaching the column influent port. Biotower II was operated at 55 °F to simulate ambient groundwater temperature. The combined feed was passed through a copper tubing coil immersed in a temperature controlled water reservoir to assure an influent temperature of 55 °F. An aeration line was also connected into the chilled feed line to provide oxygen to the biotower.

Several operating conditions were tested on each biotower from flow initiation to the design 1-hour HRT (Tables 3 and 4). This operating parameter required the adjustment of liquid feed rates and influent concentrations. A period of at least 2 to 3 weeks was allowed for biomass acclimation after operating conditions were changed. Once the performance had stabilized, analytical data were collected over 3 days as representative of steady-state performance (Table 5).

Results and Discussion

Biological removal of BTEX was the primary goal of this study. Greater than 99% treatment removal efficiency was achieved for BTEX during operation of Biotower I at design steady-state conditions during 8 months of operation. An average influent BTEX concentration of 2 mg/L was treated to nondetectable levels in the effluent stream (Limit of Detection [LOD] = 2 μg/L for each BTEX component) (Table 6). A similar treatment efficiency (greater than 99%) has been achieved for BTEX in Biotower II during 5 months operation at design conditions (Table 7). To confirm that microbial degradation was the mechanism responsible for BTEX removal, analyses of the vent gas and biomass solids were performed on both biotowers. The data indicate

that the BTEX components were not detectable in the air or solids process streams (Tables 8 and 9). These data clearly prove the effectiveness of the upflow biotower design for treating BTEX in groundwater.

The total unidentified semivolatiles (total influent concentration = 0.999 mg/L) were not fully degraded by the biotower treatment systems. Biotower I removed an estimated 67% of the semivolatile contaminants while Biotower II removes approximately 31% of these compounds. Volatile or semivolatile compounds were not detected in the biomass

Table 3
Steady State Operating Conditions for Biotower I

(70 Degrees Fahrenheit)

Condition	Hydraulic Residence Time	Influent Total Organic Carbon
1	2 hour	35 ppm site water plus 35 ppm acetate
2	1 hour	35 ppm site water plus 35 ppm acetate
3	1 hour	35 ppm site water plus 17.5 ppm acetate
4	1 hour	35 ppm site water

NOTE: Condition 4 is Design Operating Conditions

Table 4
Steady State Operating Conditions for Biotower II

(55 Degrees Fahrenheit)

Condition	Hydraulic Residence Time	Influent Total Organic Carbon
1	2 hour	35 ppm site water plus 35 ppm acetate
2	1 hour	35 ppm site water plus 35 ppm acetate
3	1.5 hour	35 ppm site water plus 17.5 ppm acetate
4	1.5 hour	35 ppm site water
5	1 hour	35 ppm site water

NOTE: Condition 5 is Design Operating Conditions

Table 5
Samples Collected and Analyses Performed During Steady State Operation of Bench-scale Biotowers

Sample Point	Analysis	Method
Influent, Effluent	Volatiles	SW-846, Method 8240
	Total Organic Carbon	SW-846, Method 9060
	Oil and Grease	600/4-79-020, Method 413.1
	Base/Neutral and Acid Extractables, Semi-Volatiles	SW-846, Method 8270
	NH_3-N	Standard Method 417B
	PO_4-P	Standard Methods 424P
	Total Suspended Solids	Standard Methods 209D
	Chemical Oxygen Demand	Standard Methods 508C
	Biological Oxygen Demand	Standard Methods 507
Vent Gas	Volatiles	SW-846, Method 8240
Biotower Biomass[1]	Volatiles	SW-846, Method 8240
	Base/Neutral and Acid Extractables Semi-Volatiles	SW-846, Method 8270
	ICP Metals	SW-846, Method 6010
	Total Solids	Standard Methods 209F

[1] Composite suspended solid samples were collected from the effluent over a 3-week period

SW-846: USEPA Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, 600/4-79-020, July 1982.

Standard Methods: Greenberg, A., R. Trussell, and L. Clesceri, Standard Methods for the Examination of Water and Wastewater, 16th Edition, American Public Health Association, 1985.

Table 6
Performance Summary of Bench-scale Biotower I
(70 °F) Operated to Achieve Design Conditions for
Groundwater Treatment

Operating Conditions[*]	BTEX Reduction	TOC Reduction	Acetate Reduction	BOD Reduction	COD Reduction
1) HRT 2 hrs TOC 70 mg/L	>99.2%	54%	>99%	81%	50%
2) HRT 1 hr TOC 70 mg/L	>98.9%	65%	>99%	78%	77%
3) HRT 1 hr TOC 55 mg/L	>99.2%	42%	>99%	83%	58%
4) HRT 1 hr TOC 35 mg/L	>99.9%	16%	---	10%	24%

[*] BTEX Supplemented Site Water (2 ppm)

Table 7
Performance Summary of Bench-scale Biotower II
(55 °F) Operated to Achieve Design Conditions for
Groundwater Treatment

Operating Conditions[*]	BTEX Reduction	TOC Reduction	Acetate Reduction	BOD Reduction	COD Reduction
1) HRT 2 hrs TOC 70 mg/L	>99.2%	59%	>99%	55%	61%
2) HRT 1 hr TOC 70 mg/L	Unsatisfactory Performance				
3) HRT 1.5 hrs TOC 55 mg/L	>55.2%	42%	>99%	65%	42%
4) HRT 1.5 hrs TOC 35 mg/L	>99.8%	7.2%	---	32%	13%
5) HRT 1 hr TOC 35 mg/L	>99.3%	0.9%	---	---	14%

[*] BTEX Supplemented Site Water (2 ppm)

sludge indicating these compounds do not bioaccumulate within the reactor.[11]

In addition, acetate addition and the heated water (70 °F) would only be required during the startup process. Once the biotowers were operational, the acetate feed and water heating could be gradually eliminated. The results from this study were used as the basis of the final design.

FINAL FULL-SCALE DESIGN

The final treatment system was designed to treat a maximum of 400 gpm to the cleanup criteria previously described in Table 2. The process flow diagrams for the full-scale treatment system are presented in Figures 2 and 3. The treatment system will include the following major systems:
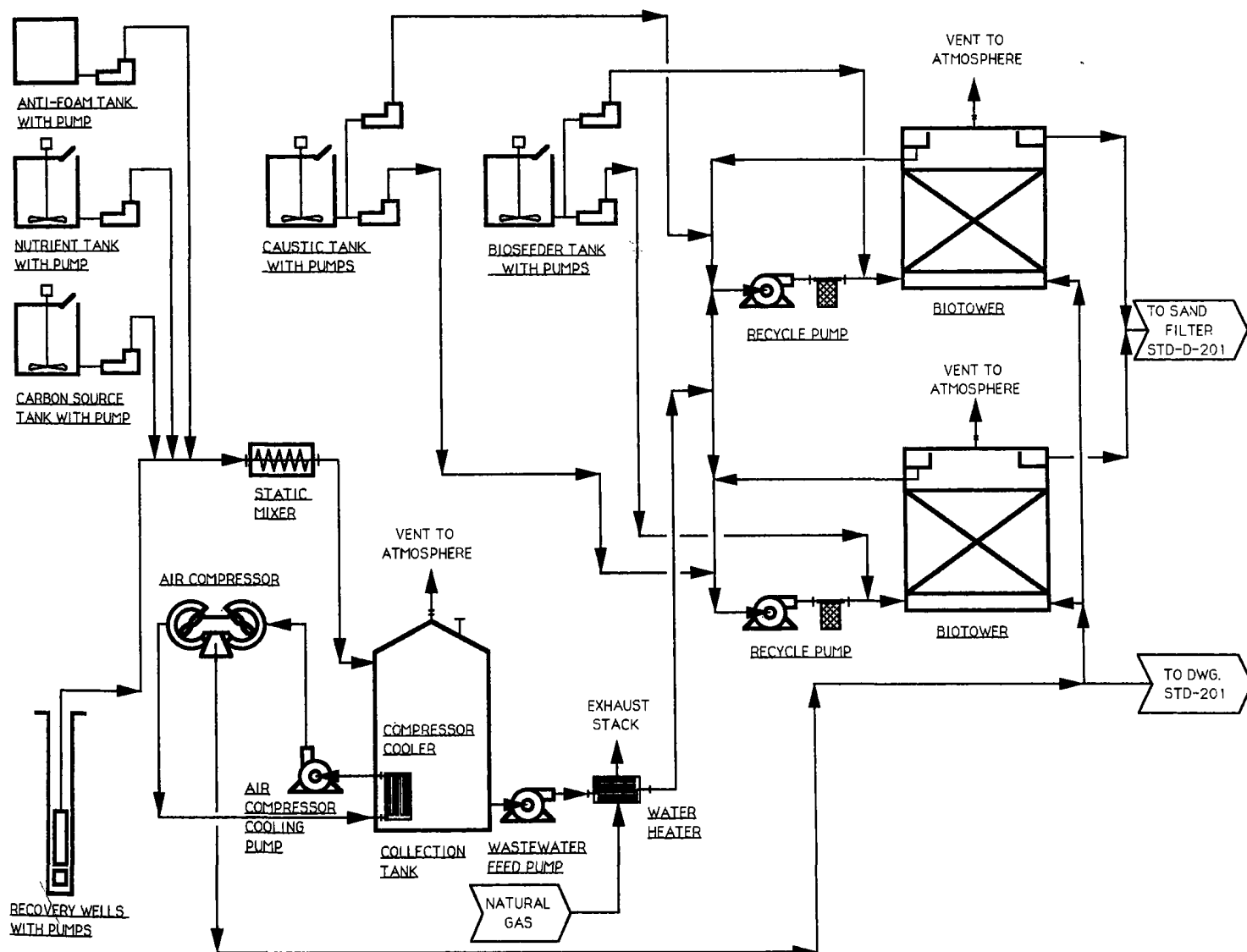
Figure 2
Process Flow Diagram

- Groundwater recovery system
- Pre-conditioning system
- Biological treatment system
- Post-conditioning system

Groundwater Recovery System

The groundwater recovery system was specifically designed to prevent off-site migration of groundwater containing dissolved PHCs at the site perimeter via a network of recovery wells. Design assumptions were based upon several years of field investigation and numerical modeling. Each of the existing site-perimeter recovery wells is a fully penetrating well screened from 10 feet below land surface to the bottom of the water table aquifer (75 to 78 feet). The maximum flowrate of groundwater extracted will be 400 gpm, with a normal flowrate of 360 gpm.

Preconditioning System

This system and all subsequent treatment processes are designed to handle a maximum flowrate of 400 gpm. The preconditioning system will receive water from the recovery wells and adjust the influent parameters to conditions more ideal for microbial growth before the water enters the recycle stream of the biological reactors. Water from the recovery wells will be delivered to a carbon steel collection tank (8,000 gallons). Nutrients (nitrogen and phosphorus), a carbon source (sodium acetate) and a defoaming agent will be added in-line prior to entering the tank. Flow equalization will take place in this tank. Water will be pumped from this tank by a horizontal, centrifugal wastewater feed pump. (The system also includes one installed spare pump.) High level and low level control in the collection tank will be connected to the groundwater well pumps and the wastewater feed pump. The groundwater will be heated in-line from the wastewater feed pump to the biotowers using a direct fired (natural gas), fin-tube water heater.

Biological Treatment System

The aerobic biological treatment system will consist of two packed biotowers. The main components of each biotower system are the biotower, the bioseeder and the recycle loop. Each system also contains support components for pH adjustment and air addition.

The total installed height of each biotower is 33 feet. The static growth attachment medium used in the biotower is specified as plastic and will have a total height of 22 feet. The BOD loading of each tower is estimated to be 20 pounds of $BOD_5/1,000/ft^3$/reactor volume/day. The HRT in each tower is designed to be 1 hour, achieved by an influent flowrate of 180 to 200 gpm per reactor. Centrifugal pumps will be used to continuously provide recycle flow in each biotower. Oxygen requirements for each biotower will be met via a blower and an air distribu-
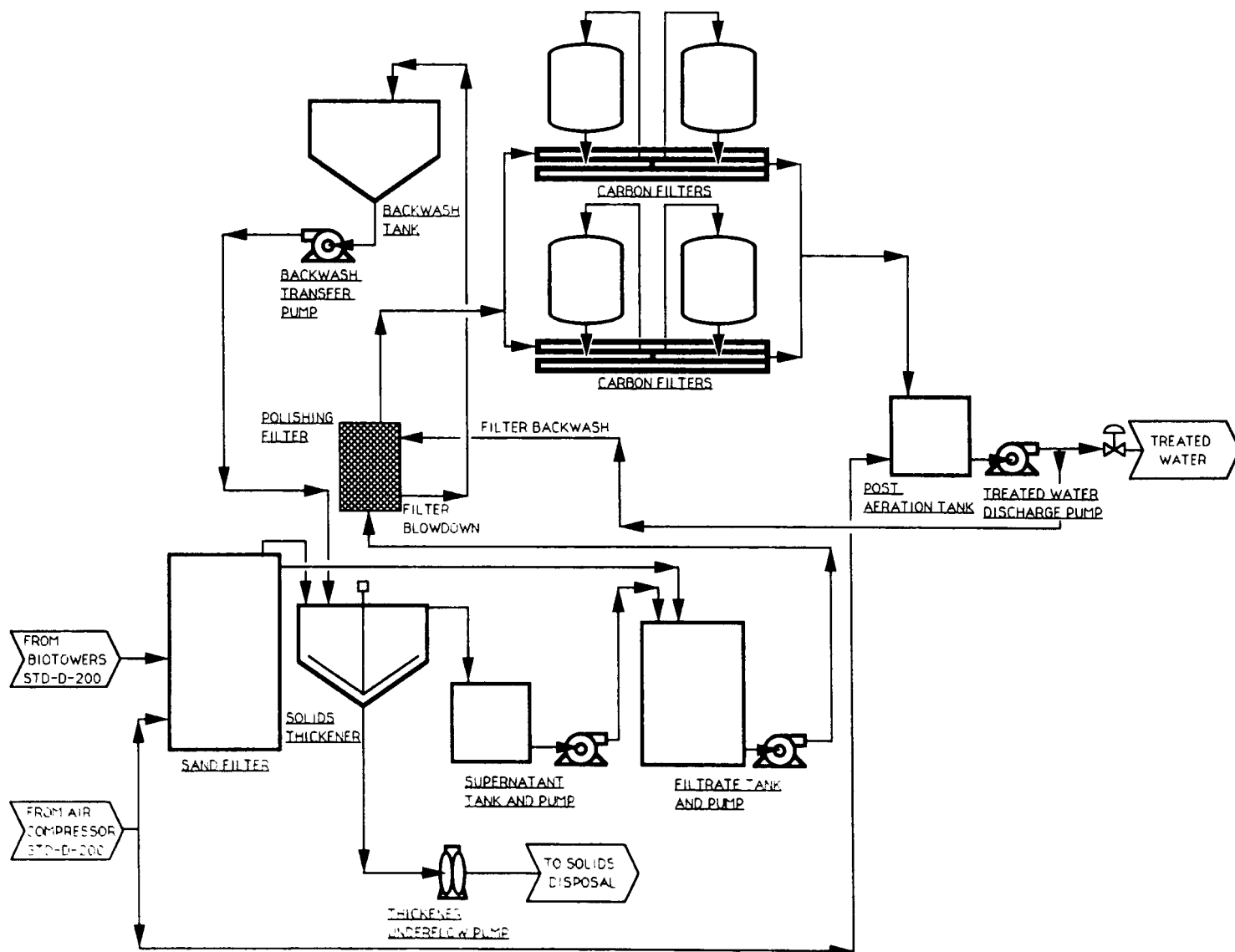
Figure 3
Process Flow Diagram

tion system at the bottom of each biotower. Approximately 60 scfm of air at 15 psig will be supplied to each biotower. Higher air flowrates will be used periodically to scour excess bacteria from the media. A system will be used to supply an initial inoculum of active biomass and to maintain a sufficient biomass in the biotower, as needed.

Post-Conditioning System

The post-conditioning system consists of a sand filter, a solids thickener, a supernatant tank, polishing filters and two 40,000-pound twin-cell carbon adsorption units.

The filter (Parkson DynaSand) will continuously remove suspended solids in the biotower effluent to an effluent quality of 10 mg/L of suspended solids. The effluent will flow from the sand filter, by gravity, into the filtrate tank.

The reject stream from the DynaSand filter, containing water and solids, will flow to a 12-foot diameter, 10-foot high, cone bottom, carbon steel solids thickener. A mixer mechanism (rake) in the thickener tank is used to enhance solids settling and to convey the settled solids to the center of the conical bottom. The supernatant from the thickener will overflow to a 900-gallon carbon steel tank. The supernatant will be pumped to the filtrate tank by a pump on level control. The solids (approximately 2% solids by weight) will underflow from the thickener and be pumped with a mechanical diaphragm pump as waste solids for disposal.

The thickener waste solids will be applied to an on-site land treatment system during months when the temperature is above freezing. The solids will be applied with a pump and a distribution system. During the winter months, the solids will be pressed in a plate and frame filter press and the pressed sludge will be stored in an outside staging area until conditions permit land application. The sand filter effluent will be collected in an 8,000-gallon carbon steel filtrate tank. Flow equalization for carbon adsorption cells will be achieved in this tank. One pump will feed the water to the polishing filters and the carbon units. Water from the filtrate tank will be filtered to remove fine particles in the range of 20 to 30 μm using an external backwashing multiplex filter rated for a flow rate of 400 gpm.

Two 40,000-pound total, dual-cell (20,000 pounds of carbon per cell) carbon adsorption units will treat the biotower effluent. The valving system will allow the units to be switched on- or off-line as needed. Each twin-cell is capable of treating 200 gpm. Each cell will be filled with 20,000 pounds of Filtrasorb 300 carbon. This carbon has a surface area of 950 to 1,050 m^2/g and a bulk density of 27 to 28 pounds per cubic foot.

The water from the carbon cells will flow into a 6-foot diameter, 10-foot high, carbon steel post-aeration tank. Approximately 20 scfm of air will be supplied to increase the dissolved oxygen to 6 mg/L in the water prior to discharge under a NPDES permit. The tank will also provide enough head to permit gravity flow to the discharge point.

A rough order-of-magnitude cost estimate (in 1989 dollars) for the design, equipment purchase, construction and operation (20 years) was completed and is summarized in Table 10. Based on an average flowrate of 360 gpm for 20 years, the cost to remediate the PHC-contaminated groundwater is approximately $0.01/gallon.

ACKNOWLEDGEMENTS

Table 10
Cost Summary for the Full-scale Groundwater
Treatment System (1989 Dollars)

Design Engineering	$	850,000
Equipment Purchase		1,760,000
Site Construction		
Field Labor		1,160,000
Material		790,000
Construction Equipment		110,000
Operation (20 years)		
Labor		8,840,000
Materials		10,200,000
Utilities		7,140,000
Analytical		7,390,000
Equipment Maintenance and Replacement		1,750,000
	TOTAL	$39,990,000

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Solid Phase Remediation of Petroleum-Contaminated Soil

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ABSTRACT

Biological processes have been used to remediate petroleum hydrocarbons, pesticides, chlorinated solvents and halogenated aromatic hydrocarbons. Biological treatment of contaminated soils may involve solid-phase, slurry-phase or in situ treatment techniques. This paper will review the general principle of solid-phase bioremediation and discuss the application of this technique for the cleanup of total petroleum hydrocarbons.

Up to 280,000 cubic yards of soil on the site of a former oil refinery tank farm are contaminated with up to 15,000 part per million (ppm) of petroleum hydrocarbons and crude oil. The site posed significant challenges due to its size as well as the depth and range of contamination. The implementation of biological remediation required the design of a Land Treatment Unit (LTU) and a remedial program which would support the treatment of a significant amount of contaminated soil within a restrictive time schedule. Once this scenario was developed, the LTU was prepared for treatment and excavation and placement of soils was initiated. Currently, the LTU area encompasses 27 acres of a 45-acre site.

A mobile laboratory has been placed on-site and is staffed with chemists and microbiologists who analyze up to 150 soil samples per day. This laboratory has been designed and equipped to provide the necessary chemical and biological analyses to fully support the excavation and bioremediation program. On-site biological treatment activities include irrigating, aerating and tilling the soil to bring microorganisms, contaminants and oxygen into contact with each other to promote biological degradation. Chemical and microbiological monitoring conducted throughout the remediation process ensure that treatment levels are being met.

A multicomponent cleanup program is currently underway at a former marketing fuel terminal in the Western United States. The site, owned by a major oil company, contains approximately 60,000 cubic yards of soil contaminated with petroleum hydrocarbons at a mean concentration of 2,660 parts per million (ppm). The primary contaminants are weathered gasoline and diesel fuel. Initial site activities involved the development of a Remedial Action Plan which served as a basis for negotiations between the client and lead regulatory agency and resulted in the signing of a voluntary Consent Order. In addition, laboratory treatability evaluations were conducted to assess treatment options and cleanup levels achievable by those options.

After demolition of existing structures on the site, the majority of contaminated Area 1 soil (approximately 20,000 cubic yards) was excavated, screened and transported via conveyor system to Area 2 for solid-phase biological treatment. Additional soil is being treated in Area 1. Solid-phase treatment involves the excavation and processing of the contaminated soil with a carefully controlled combination of oxygen, water and specific nutrient mixtures. This treatment promoted

the rapid growth of naturally occurring bacteria present in the soil to metabolize and degrade the hydrocarbon contaminants. When treatment is complete, the Area 2 soil (approximately 25,000 cubic yards) will be treated in the same manner. Some of the treated soil may be used as backfill and compacted.

These remedial programs will reduce total petroleum hydrocarbon contamination from the mean concentration of 2,660 ppm to less than the 200 ppm cleanup criterion for soil and less than the 15 ppm cleanup criterion for groundwater. Over 20,000 cubic yards of soil have been treated by solid-phase treatment to date. The in situ system operation is effectively producing biodegradation in the subsurface. The project is approximately one third complete.

INTRODUCTION

Carbon is distributed in the environment in a variety of chemical compounds that range from gases (methane and carbon dioxide) to liquids (benzene and toluene) to solids (simple sugars and polymers such as cellulose, and asphaltic components of crude oil). The biological degradation of many of these compounds is a naturally occurring reaction. The rate of this reaction, however, is highly dependent on a variety of factors including the specific structure of the compound; the availability of nutrients, oxygen and water for the microorganisms; and the nature of the soil or other matrix in which the compound resides. In some cases, certain compounds can be biologically degraded in hours, while other compounds, such as asphaltics, are virtually totally nondegradable.

The susceptibility of petroleum products to biodegradation varies with the types and sizes of the component molecules. Since there are several hundred individual component molecules in any given crude oil, which can vary with its origin, the rate and extent of degradation is not easily predictable. Thus, the overall degradability of a specific petroleum product will depend on the proportion of degradable compounds of which it is composed. For example, alkanes of intermediate chain length $(C_{10}-C_{24})$ are degraded most rapidly. However, very long chain alkanes become increasingly resistant to biodegradation, and after exceeding a molecular weight of 500 to 600, they cease to serve as carbon sources. Branching structures typical of asphaltics also reduce the rate of biodegradation, and aromatic compounds are degraded more slowly than alkanes. Some hydrocarbons and hydrocarbon biodegradation products are highly resistant to ultimate biodegradation, that is, mineralization. Condensed polycyclic aromatics and cycloparaffins, as well as high-molecular-weight alkanes, are mineralized only very slowly. Solid-phase biological treatment processes involve establishing an environment conducive to microbiological growth and degradation of organic contaminants. The availability of nutrients and oxygen have significant effects on petroleum degradation. In particular, nitrogen and

phosphorus fertilizers, as well as oxygen, accelerate biodegradation. Additionally, proper pH and temperature also produce favorable effects.

Techniques employed in bioremediation are designed to remove constraints which slow degradation rates, such as limited nutrients and oxygen, in order to bring about rapid rates of degradation. Because of the variability in the source of petroleum hydrocarbon contamination, the chemical nature of contaminated soil and other concerns, treatability studies of contaminant reduction in specific soils are the most appropriate way of establishing proper treatment conditions. Such conditions include nutrient concentrations, moisture levels and treatment duration. Treatability studies also determine the extent of degradation that can be achieved for a given compound.

Biological treatment technologies for contaminated soils and groundwater fall into four main categories: (1) solid-phase biotreatment (landfarming); (2) slurry-phase biotreatment; (3) in situ biotreatment; and (4) combined technologies with chemical or physical treatment. The specific treatment process required is a function of the physical/chemical nature of the contaminant and the matrix in which it is found. The focus of this paper is the solid-phase remediation of petroleum-contaminated soils.

Solid-Phase Biotreatment

Soil provides a rich source of microorganisms, many of which have the potential to degrade hydrocarbons. Solid-phase biotreatment relies on principles applied in agriculture in the biocycling of natural compounds. The conditions for biodegradation are optimized by regular tilling of the soil and by the addition of nutrients and water. The natural indigenous microbial populations of soil are diverse and many of the appropriate microorganisms which degrade many contaminants are found in the contaminated soils.

The rates of bioremediation of contaminated soils are enhanced by optimizing the conditions of the site for oxygen levels, moisture content, available nutrients such as nitrogen and phosphorous, pH and contact between the appropriate microorganisms and the contaminants. This technique has been successfully used for years in the managed disposal of oily sludge and other petroleum refinery wastes through a process called landfarming. Solid-phase biotreatment of contaminated soils is probably the most widely used and cost-effective biotreatment technology currently in application today. Typically, the process is used for petroleum- and creosote-contaminated soils. Typical costs for this type of treatment are $40 to $120/cubic yard but are highly dependent on conditions at the site and materials handling costs. New federal regulations (RCRA, Land Bans) may prohibit some current disposal techniques and require alterations to the system due to fugitive emissions and leaching of organics and metals. A variety of options are available to control these emissions.

A solid-phase biotreatment program involves careful manipulation of oxygen, nutrient and water levels in the soil within the treatment unit to promote optimal degradation rates. Oxygen is supplied to the soil by tilling either with disk aeration equipment or heavier recycling equipment to a depth of 18 inches. Periodic turning of the soil to deeper depths (24 inches) may occasionally be conducted. The tilling frequency is determined by a number of factors including temperature, moisture levels, contaminant concentration levels and soil type. The soil generally is tilled with a frequency of 1 to 7 days depending on time and equipment limitations.

Nutrients normally are added in an aqueous form and applied with either a spray assembly attached to the disk aerator or by specialized equipment such as a terragator. Nutrient levels are monitored and nutrients are applied as needed to maintain optimum degradation rates based on treatability data for specific con-taminants. Specific nutrient formulations are added to the soil to maintain nitrogen, phosphorus and other trace minerals.

Moisture control is critical to optimum operation of the treatment unit. Low water activity restricts biological activity and results in less than optimal treatment rates. More than optimal moisture can create a number of significant difficulties, including slow treatment rates due to lower aeration potential, difficulties in the operation of treatment equipment and recontamination of the uppermost treatment lift by con-taminants from lower lifts if tilling equipment cannot be maintained at constant depth in the soil.

Optimal moisture levels are typically in the 12 to 15% by weight range. However, presence of a clay fraction in otherwise sandy soil may result in a 12 to 15% moisture range creating a moisture content that is too high. As a result, soil moisture levels are maintained at 10 to 12% to promote optimal degradation rates in some soils and as high as 16 to 17% in other soils. A more consistent measure of water activity is field holding capacity. Maximal microbial activity occurs at approximately 40 to 50% of the maximum field holding capacity.

Moisture at the site is controlled by careful irrigation and rainfall control, if required. An irrigation system at a small site (3 to 4 acres) is comprised of a number of radial sprinkler lines that provide the appropriate water application rate. At larger sites, this approach and the logistics of implementation are not practicable and a terragator type water truck is most practical.

In areas of high rainfall, rainfall control may be achieved through the use of large plastic tarp systems that minimize the amount of rainfall that comes in contact with the soil in the treatment unit. Tarps as large as 50 feet by 650 feet have been successfully employed; they are installed by a hydraulic roller attached to the bulldozer equipment used during treatment. Modifications of typical solid-phase remediations may include systems for control of volatile emissions and leachate collection as well as composting and heap leaching. A modified solid-phase bioremediation system was used successfully by ECOVA to control volatiles and leachate. The system consisted of a treatment bed lined with a high-density liner. A perforated leachate collection system and clean sand are placed on the liner for protection of the liner and proper drainage and collection of contaminated water as it leaches from contaminated soils placed on the treatment bed. The lined soil treatment bed is completely covered by a modified plastic film greenhouse. An overhead spray irrigation system contained within the greenhouse provides for moisture control and a means of distributing nutrients and microbial inocula (as needed) to the soil treatment bed.

Volatile compounds released from the soil are swept through the structure to the air management system. Biodegradable volatile organic compounds can be treated in a vapor phase bioreactor. Nonbiodegradable volatile organic compounds can be removed from the effluent gas stream by adsorption on activated carbon. Contaminated leachate which drains from the soil is transported by the drain pipes and collected in a gravity-flow lined sump. Leachate is then pumped from the collection sump to an on-site bioreactor for treatment. Treated leachate can then be used as a source of microorganisms and reapplied to the soil treatment bed through an overhead irrigation system, after adjusting for optimum nutrients and environmental parameters.

Soil heap bioremediation is a modification of solid-phase treatment used when available space (area) is limited. In soil heap bioreclamation, contaminated soil is excavated and stockpiled into a heap on a lined treatment area to prevent further contamination. Microbial inoculum (as needed) and nutrients are applied to the surface of the stockpile and allowed to percolate down through the soil. The pile can be covered and an air emissions recovery system installed as described above. A leachate collection system is used to collect the fluid, which is recycled. An internal piping system may also be installed in order to blow air upwards through the soil and thus accelerate the biodegradation process through the addition of oxygen. During operation, pH and moisture content are maintained within ranges conducive to microbial activity. Typical costs are similar to conventional solid-phase treatment.

Composting processes are another modification of solid-phase treatment in which the system is operated at higher temperature due to increased biological activity. This technology is used for highly contaminated soils, treatment of poorly textured soils and in areas where temperature is critical to the sustained treatment process. Contaminated soils are mixed with suitable bulking agents, such as straw, bark or wood chips, and piled in mounds. The bulking agent improves soil texture for aeration and drainage. The system is optimized for pH, moisture and nutrients using irrigation techniques and can be enclosed to contain volatile emissions. Care must be taken to control leaching, to control volatile emissions, and to ensure that the bulking agent does

not interfere with the biodegradation of the contaminants (preferential carbon source).

CASE HISTORY: BIOREMEDIATION OF BUNKER C FUEL HYDROCARBONS

Soil remediation activities are being conducted at a former tank farm facility in southern California. The soil undergoing remediation consists of berm soils and soils underlying a former 20-acre concrete-lined surface impoundment which was used to store bunker fuel oil. The quantity of soil treated will be in excess of 280,000 cubic yards and is being treated in eight separate treatment cells at the site. The petroleum contamination contained hydrocarbons in the range of C-10 to C-35 carbon chain length. The oil-contaminated soil was found not to be hazardous based on the 96-hour Acute Aquatic Toxicity Bioassay tests.

Treatment Concentrations

An initial treatability evaluation was conducted to determine the optimal concentration for treatment in the land treatment unit. It was determined that a starting concentration of approximately 4000 ppm total petroleum hydrocarbon would be optimal and that it was potentially possible to treat up to 5000 to 6000 ppm TPH in these soils.

Since the excavation program required continued progress and the sequential stacking of lifts of soil to accommodate the excavation requirements, an area was set aside at the treatment site and an LTU was charged with 5500 cubic yards of high concentration (average 5595 ppm TPH) soil. The data from this LTU treatment verified the upper limit of bioremediation to meet scheduling requirements.

TPH Monitoring

The project involved treating more than 280,000 cubic yards of soil contaminated with petroleum hydrocarbons in concentrations of up to 6,000 ppm as total petroleum hydrocarbons (TPH). The analytical method used was U.S. EPA method 418.1 and the cleanup standard was 1000 ppm TPH. In order to guide the excavation of the soil and facilitate process monitoring of the solid-phase process, a mobile laboratory (Figure 1) was placed on-site and staffed with environmental chemists and microbiologists. The laboratory has analyzed up to 150 samples per day during peak periods of production from the excavation and land treatment units. More than 20,000 samples have been analyzed in the laboratory at this stage of the project.

During one phase of the project, a gas chromatograph was installed in the laboratory to guide the remediation of light kerosene-like solvent residues located in a separate disposal area on the site. For this aspect of the remediation, the analytical protocol was U.S. EPA method 8015 and the cleanup standard was 100 ppm TPH. These soils were incorporated into a separate LTU for treatment in several consecutive lifts.

The gas chromatograph also was used to qualitatively evaluate the progress of the remediation by determining what fraction of hydrocarbons had been treated and what fraction remained.

Nutrient and Biological Monitoring

In addition to contaminant chemistry, the site support laboratory supported the nutrient addition program and monitored biological activity in the LTUs. Ammonia and nitrate nitrogen as well as phosphate were routinely analyzed for in the LTU. It was found that random sampling of the LTU at approximately five samples per acre gave adequate coverage for the nutrient, moisture and microbiological monitoring.

To evaluate biological activity, total heterotrophic organisms in the treatment soils were enumerated. The microbial analysis program at the site was augmented with plating of soil onto mineral media containing specific hydrocarbons as the sole source of carbon for growth. The development trends for the hydrocarbon-degrading population could be evaluated in this way.

A variety of treatments were attempted to stimulate overall microbial activity as well as specific hydrocarbon degraders. These studies indicated that treatments selected for scale-up effectively stimulated the activity of the hydrocarbon-degrading populations.

Laboratory evaluations of the soil from the remediation and small-scale studies were conducted to more clearly establish the population of organisms involved and the community interactions responsible for the degradation of hydrocarbons. Obvious changes in the microbial population occurred over time in the LTUs. The evaluation of hydrocarbon-degrading activity has helped to clearly define the importance of these changes. A dominant organism in the remediation, distinguished by a distinctive orange pigment, was identified as possessing the ability to metabolize a wide range of hydrocarbon substrates. To better understand the full substrate range of the orange organism, media plates were made using mineral salts broth, purified agar and hydrocarbon. Clear evidence of growth was demonstrated on pentadecane (C-5), octadecane (C-18), pristane (C-15 branched), docosane (C-20) and hexacosane (C-26). A preliminary study on C-30 hydrocarbons also is being undertaken. Control plates which contained no hydrocarbons did not demonstrate growth. Interestingly, the organism produces a mucopolysaccharide when attempting growth on longer chain hydrocarbons. These types of responses are known to be important in the solubilization of heavier hydrocarbons.

To follow the occurrence and development of these organisms, soils from selected LTUs were plated on substrate specific hydrocarbons every other week. In this way, the population of specific hydrocarbon-degrading organisms was followed during the remediation. This required no additional resources or expenditure for the project.
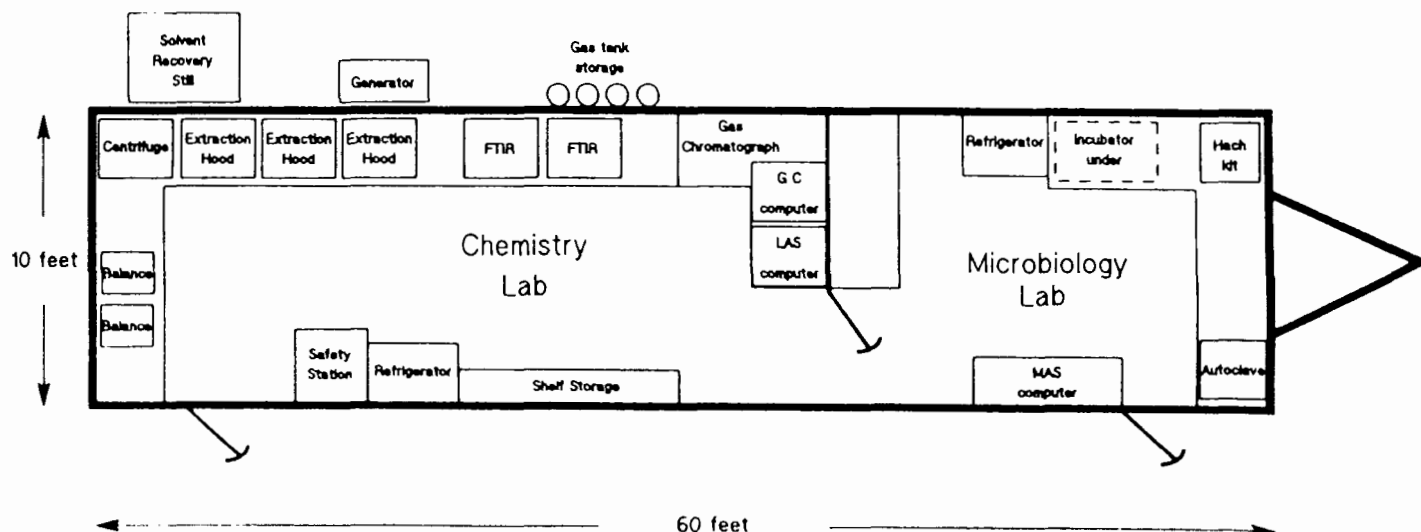
Figure 1
ECOVA Mobile Laboratory

Data Management

The Laboratory Data Management System is a PC-based software package designed and written for ECOVA mobile laboratory operations. The system provides direct data input for each sample from the moment it is taken (via a laptop-mounted computer) through the actual analysis to the final customized report. In addition, we can transfer selected blocks of data between system modules and/or commercial software packages such as spreadsheet or graphics programs.

Data integrity is assured through the use of triple-redundant data bases, automatic backup to floppy disk and a complete audit trail facility. The audit trail facility tracks and records every change made to a sample record. The audit trail data base is invisible to, and totally inaccessible by, mobile laboratory personnel.

Finally, the remote access feature uses a specialized telecommunications package which allows home office personnel to support the system even while it is unattended. This system allows quality assurance checks, data transfers or software modifications to be performed after normal working hours, eliminating system downtime for normal procedures.

Summary of Remediation Data

Figure 2 is a representative of TPH data from treatments employed during the remediation. The pattern of degradation presents a similar pattern to that observed in earlier LTU soils. A high initial rate is followed by a period of reduced rate as the composition of the petroleum hydrocarbon and microbial community changes. After these changes, the rate of remediation increases.

Figure 3
LTU 5-2
Overall Microbial Analysis

these pigmented organisms possess the ability to degrade an extremely wide range of petroleum hydrocarbons from hexane (C-6) through hexadecane (C-16), pristane (branched C-15), octodecane (C-18) and hexadocosane (C-26). The physiology and ecology of this organism may be pivotal to the control of the rate of hydrocarbon degradation in the remediation. This is currently being evaluated.

Figure 2
LTU 5-2
Performance TPH
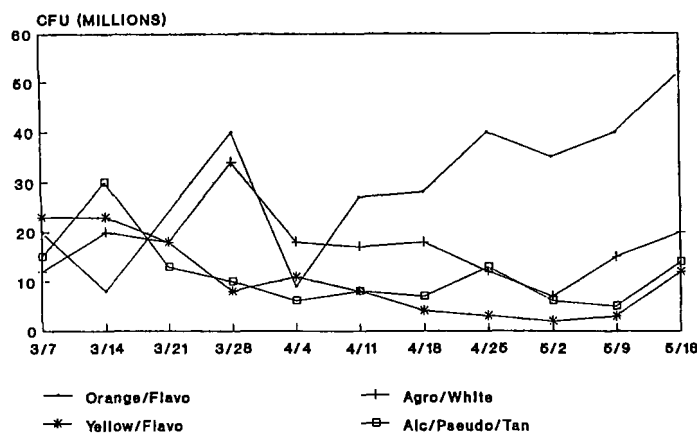
Figure 4
LTU 5-2
Analysis of Populations

There is a critical period of time in the remediation in which the rate slows. This occurs during the period of from 6 to 9 weeks in soils which have a starting concentration of approximately 5,000 ppm. This phenomenon is not observed in LTU soils which have starting TPH concentrations below approximately 3,500 ppm.

The significance of the changes in TPH degradation are borne out by the overall changes in nutrient concentrations and the heterotrophic (including petroleum hydrocarbon-degrading) microbial populations which occur during this period. The increased presence and activity of organisms that do not degrade hydrocarbons, but potentially compete for ammonia (an essential nutrient for hydrocarbon metabolism) is supported by the general, but slight, decrease in heterotrophic organisms during the course of the remediation (Figure 3) and changes in the ratio of forms of nitrogen present in the soil.

The analysis of the heterotrophic population indicates that significant changes occur after 7 weeks of treatment (Figure 4). Over the final 5 weeks of the remediation, brightly pigmented bacteria emerge from the population. Heterotrophic organisms in general decrease; the proportion of the hydrocarbon degrading organisms increases. As stated,

The nutrient concentrations attained during the study were sufficient to evaluate the effect of increased concentrations on bioremediation. The increased nutrient concentrations did not have an effect on the rate of degradation. It is also possible that increasing the concentration of nutrients may have the negative effect of stimulating populations of organisms that do not degrade TPH.

CONCLUSIONS

The solid phase remediation program implemented for this site has been extremely successful. More than 150,000 cubic yards of soil have been treated and removed from the LTUs to date. Approximately 120,000 cubic yards of soil remain to be treated. More than 20,000 samples of soil from excavation, process monitoring, verification sampling of the LTUs and backfilling operations have been taken throughout the course of the remediation. Several optimization studies are being conducted on-site during the remediation at an incremental cost to the remediation. These studies assure that the optimal rate of remediation is occurring and provide valuable information to the client for use at other sites which are candidates for bioremediation.

CASE HISTORIES: PETROLEUM MARKETING TERMINAL REMEDIATION

A former marketing terminal in the Western United States had been contaminated by losses incurred during the handling of petroleum products during 65 years of operation. More than 60,000 cubic yards of soil are contaminated with petroleum hydrocarbons at a mean concentration of 2,660 parts per million (ppm). Groundwater analyses identified benzene as the compound of concern. Ethylbenzene, toluene and xylenes are present at low concentrations.

ECOVA Corporation was hired to assist in the development of a Remedial Action Plan (RAP) for the fuel terminal site. A laboratory treatability evaluation to assess treatment options and cleanup levels achievable from those options was conducted. Options studied included excavation and off-site disposal; off-site treatment; and on-site treatment focusing on bioremediation. Activities managed in support of the RAP included preliminary design of cleanup systems and regulatory liaison and public involvement activities.

The RAP served as the basis for negotiations between the client and the lead regulatory agency which resulted in the signing of a voluntary Order on Consent. The voluntary Order on Consent was finalized in November 1988.

Two recommended treatment alternatives, on-site solid-phase biotreatment and in situ biotreatment, were selected because of the destruction of the contaminants and significant cost savings compared with off-site disposal. Bioremediation of the contaminated soil reduces the hydrocarbon contaminant level to below the agreed to cleanup level of 200 ppm. Water cleanup criteria for the contaminants are as follows: total hydrocarbons-15 ppm; benzene-40 parts per billion (ppb), and ethylbenzene-3.5 ppm. Once these levels are achieved, the site will be rendered clean and suitable for development.

ECOVA Corporation was awarded the full-scale remediation contract in February 1989 after winning a competitive bid over 30 other major environmental contractors. The multimillion dollar project is the largest biological remediation project undertaken in the State of Washington.

The first task involved preparation of a detailed Work Plan and initiation of permitting. The Work Plan contained the final design of the remedial systems and a detailed description of the installation and operation procedures to be followed during the remediation. Once the necessary permits were obtained, the remedial program was initiated.

The remedial program involved demolition, installation and operation of in situ systems and excavation and treatment of contaminated soil. This paper describes the activities and results obtained to date related to the solid-phase biotreatment component of the remedial program. A discussion of the activities and results to date related to the in situ biotreatment component of the remedial program can be found in another paper within these proceedings by Nelson and others.

The site is divided into four areas (Figure 5). The original plan called for contaminated soil from Area A to be treated in Area B and then returned to Area A for replacement and compaction. Transportation of the contaminated soil to Area B is accomplished with a conveyor system running through an existing pipe tunnel under the major street separating Areas A and B. Solid-phase biotreatment of contaminated soil in Area B would then follow. Contaminated zones in Areas C and D are treated by in situ biotreatment and soil oxygenation.

Demolition activities began in May 1989. Surface and subsurface structures were demolished and significant quantities of demolition debris, including concrete rubble, pipe, brick and wood were removed. Excavation of contaminated soil in Area A indicated that the extent of contamination was greater than the preliminary investigation determined. As a result of the increased volume of contaminated soil, Area A is used as a solid-phase treatment area as well, and the treated soil from Areas A and B is transported off-site for disposal after treatment to below the 200 ppm cleanup criteria. Solid-phase biotreatment began in Area B in September 1989 and in Area A in October 1989.

Figures 6 and 7 present some operational data for the solid-phase treatment program to date. Figure 6 indicates that the average lift volume is approximately 2,800 cubic yards. The lift volume varies due to a number of factors. The area available for treatment varies between treat-
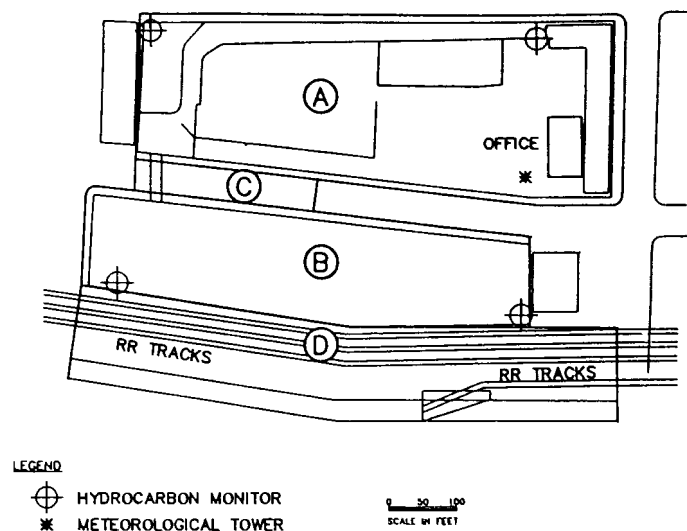
Figure 5
Site Map

ment area and the surface area which is affected by stockpile side-slope requirements and other site activities. Also, the lift size varies depending upon whether or not all cells within the lift are treated to below the treatment criteria. If there are cells that have not reached the treatment criteria, these cells remain in the treatment unit and are incorporated into the next treatment lift.
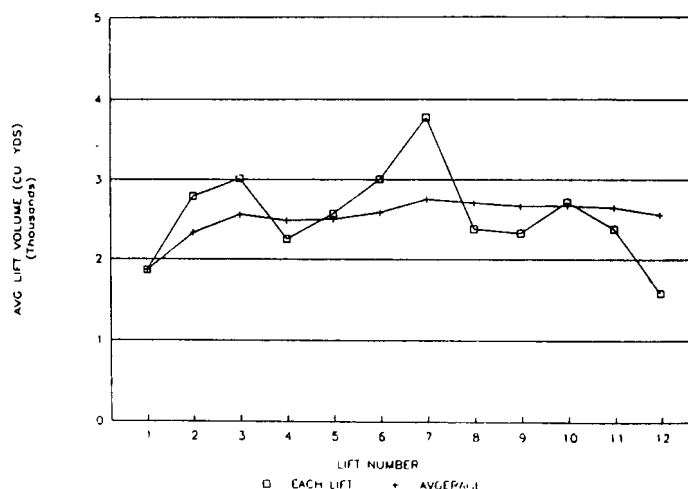
Figure 6
Average Treatment Lift Volume

Figure 7 shows the actual treatment time required for each lift and the running average treatment time for all lifts to date. The bench-scale treatability studies for the site indicated that treatment times should be in the 3 to 6 week time frame, if optimal degradation rates are maintained. This optimal treatment range is represented in Figure 7 as two horizontal lines. As can be seen in the figure, 8 of the 12 lifts completed to date are within the 3- to 6-week treatment time frame estimated by the treatability study. Four lifts have required longer treatment times.

Lifts 4 through 6 were treated during the winter months when ambient temperatures were colder than normal and snow accumulated and remained on the ground for 2 weeks. This colder temperature significantly reduced the treatment rates. The general rule of thumb is that for every 10°F decrease in temperature, there is an associated 50% decrease in degradation rates. In addition, the rainwater control tarp systems were not fully operational. As a result, the soil moisture levels
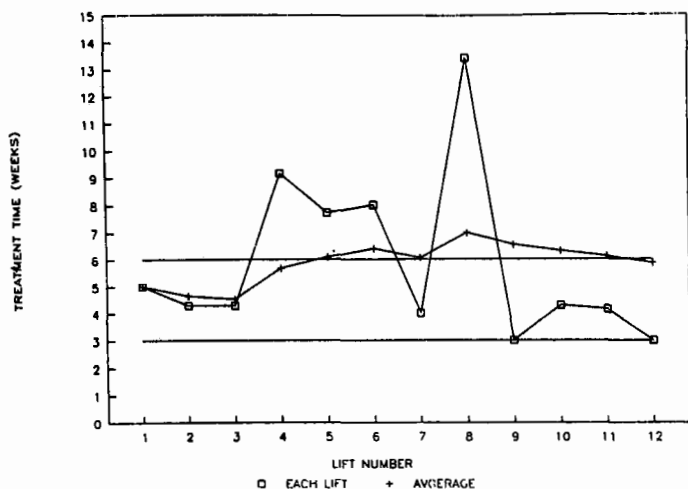
Figure 7
Treatment Time by Lift

were higher than optimal which further contributed to the decreased treatment rates and the associated increase in treatment times.

The treatment time for Lift 8 was significantly longer than the 3- to 6-week treatment time frame estimated by the treatability study. A number of factors are responsible for the extended treatment time requirements for this lift. The primary factor is excessive soil moisture.

In early June, the lift was within 1 week of reaching the cleanup criteria in more than 80% of the cells in the lift. However, before the verification samples were collected, an unanticipated storm saturated the upper 24 to 36 inches of the lift before the rainwater control tarp systems could be deployed. Efforts to reduce the amount of soil moisture by tilling resulted in contaminated soil and water from lower lifts being brought up to within the current treatment lift. As a result, the next sampling indicated that the concentrations in all cells were at or above the original starting concentrations. Therefore, the entire treatment process had to start again and resulted in a lift that had a treatment time approximately double (12.4 weeks) the maximum treatment time requirement indicated by the treatability study.

Figure 7 also indicates that subsequent treatment times have been on the lower end of the 3- to 6-week treatment time range. This improved performance is due to the warmer temperatures that occurred during the later part of the summer and early fall. The average treatment time, which has been shifted higher by the four lifts discussed above, is back within the 3- to 6-week treatment time range.

To date, approximately 32,000 cubic yards of contaminated soil have been treated to below the 200 ppm cleanup criterion and disposed off-site. An additional 25,000 to 30,000 cubic yards of contaminated soil from Areas A and B will be treated before the solid-phase component of the remedial program is concluded.

Abiotic Immobilization/Detoxification of Recalcitrant Organics

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ABSTRACT

In contrast to many remedial techniques that simply transfer hazardous wastes from one part of the environment to another (e.g., off-site landfilling), in situ restoration may offer a safe and cost-effective solution through transformation (to less hazardous products) or destruction of recalcitrant organics. Currently, the U.S. Environmental Protection Agency and U.S. Department of Energy are encouraging research that addresses the development of innovative alternatives for hazardous waste control. One such alternative is biotic and abiotic immobilization and detoxification of polynuclear aromatic hydrocarbons (PNAs) as associated with the soil humification process. This paper discusses: (1) the possibility of using abiotic catalysis (with manganese dioxide) to polymerize organic substances, (2) aspects associated with the thermodynamics and kinetics of the process and (3) a simple model upon which analyses may be based.

INTRODUCTION

Humic materials are natural organic substances that are common in the environment and are involved in a nonstop polymerization process with organic molecules. Polymerization of humus material (humification) involves the breakdown, convolution, and transformation of organic matter into long, complex, amorphous organic molecules with numerous reactive functional groups and bridges that are similar to the reactive groups added to aromatic compounds by microbial enzymatic action. Functional groups include hydroxyl, carboxyl, ketonic, phenolic, quinone, ester, ether, carbonyl, imino and amino groups, with dihydrodiol and dione (e.g., quinone) structural formations showing promise in promoting polymerization. During humus formation, reactive compounds are linked through biotic-enzymatic and/or abiotic-chemical reactions, resulting in complexes of polymerized molecules. Biotically induced polymerization, for example, can result in oxidative coupling of nonreactive organics (e.g., anilines) into active organic polymerization processes (e.g., using dichlorophenols).[1] More recently, scientists have noted that abiotically catalyzed polymerization may also represent an important aspect of humification.[2-5] For example, manganese-bearing silicates have demonstrated catalytic effects in enhancing the polymerization of polyphenols (e.g., hydroquinone).[5]

ABIOTIC CO-POLYMERIZATION

Research at Utah State University (USU) has indicated that multiple-ringed constituents might be humified. Soil samples spiked with a ^{14}C-labelled benzo(a)pyrene [B(a)P] [the structure of which is shown in Figure 1] have shown activity in humic and fulvic acid soil samples, which previously had been extracted with methylene chloride. The extraction procedure did not remove all of the radiolabelled carbon, suggesting some sort of binding process between the B(a)P molecule or a portion of it and the humus material. These results suggest that the B(a)P [or B(a)P intermediate or product] was structurally bound in some way to the humic/fulvic material and humin that was formed. These results occurred for both sterile and nonsterile samples. The results suggest that: (1) co-polymerization of multiple-ringed constituents might be possible and (2) abiotically catalyzed polymerization may also be occurring and may be as important as microbially mediated polymerization in humification. If one reviews the structures of humus (Figure 2) and those of B(a)P metabolites (Figure 3), one notes functional-group similarities. Jeftic and Adams[6] presented a general reaction scheme for the anodic oxidation of B(a)P, illustrating its transformations and polymerization properties.

Bollag,[2] whose research focuses on enzymatically induced polymerization, stated that abiotically mediated catalysis also may be important. One result of his research was the indication that most reactants appeared to move through a transitional quinone-like structure prior to the final humified product. Senesi and Schnitzer[7] have proposed similar pathways for abiotically induced polymerization. They suggested that hydroquinone $[1,4-C_6H_4(OH)_2]$ goes to the semiquinone
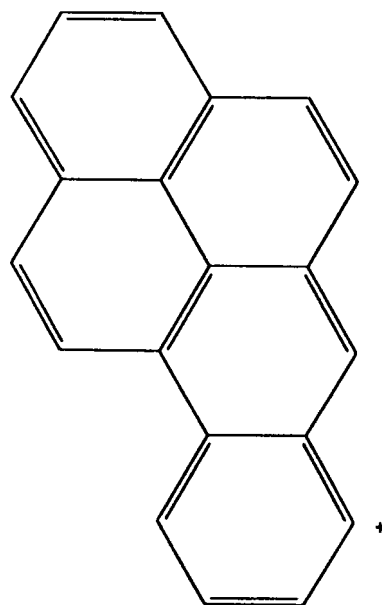
Figure 1
Structure of Benzo(a)pyrene

radical [$\bullet C_6H_4O(OH)$] and that this radical forms a quinone ($1,4$-$C_6H_4O_2$) where all reactions are reversible (Figure 4):

$$C_6H_4(OH)_2 = \bullet C_6H_4O(OH) + H^+ + e^- \qquad (1)$$
$$\bullet C_6H_4O(OH) = C_6H_4O_2 + H^+ + e^- \qquad (2)$$
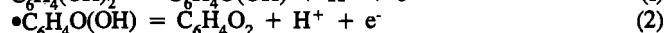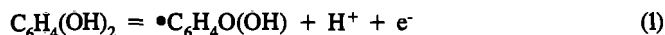
Shindo and Huang[5,8] explained the polymerization of hydroquinone in the following manner, using oxidation-reduction potentials (E°)[9,10] for manganese dioxide (MnO_2) and hydroquinone:

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad E^\circ = +1.224 \text{ V} \quad (3)$$
$$C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2e^- \quad E^\circ = -0.6992 \text{ V} \quad (4)$$
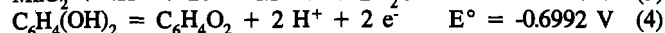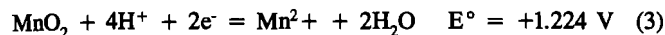
Thermodynamically, the overall oxidation-reduction reaction is $+0.525$ V, indicating that the oxidation of diphenol (i.e., hydroquinone) by manganese dioxide is favorable. Shindo and Huang[11] took a similar approach to explain the catalytic polymerization of hydroquinone by primary minerals, especially the olivine tephroite (Mn_2SiO_4). Schnitzer[12] suggested that the rate-determining step in the synthesis, by oxidative polymerization of humic acids from simple phenols and phenolic acids, is the formation of a semiquinone radical involving a one-electron transfer reaction. These relatively unstable and reactive semiquinone radicals will couple with each other to form a stable humic acid polymer. Shindo and Huang[5] noted that because the coupling of radicals requires no activation energy (in contrast to electron transfer reactions), coupling of semiquinones rather than the formation of quinones should be kinetically the preferred reaction path. Therefore, diphenols should be converted to humic acid through semiquinones during the reduction of Mn(IV) oxides. Senesi and Schnitzer[7] noted that the semiquinone radical can form a semiquinone radical ion [($\bullet C_6H_4O_2$)-] and then a semiquinone dianion [($C_6H_4O_2$)$^{2-}$], where all reactions are reversible (Figure 4):

$$\bullet C_6H_4O(OH) = (\bullet C_6H_4O_2)^- + H^+ \qquad (5)$$
$$(\bullet C_6H_4O_2)^- = e^- = (C_6H_4O_2)^{2-} \qquad (6)$$
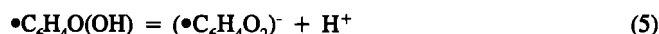
In previous work, Kononova[13] and Schnitzer and Kahn[14] made a statement similar to that of Shindo and Huang[5] regarding the polymerization of hydroquinone through a semiquinone radical.[15,16] Wang et al.[16] also reported that in the absence of an electrophilic substituent in the ring of the hydroquinone, phenolic hydroxyl groups act like weak acids, and with an increasing pH solution, the hydroquinone dissociates to a semiquinone anion {[$C_6H_4O(OH)$]$^-$}:

$$C_6H_4(OH)_2 = [C_6H_4O(OH)]^- + H^+ \qquad (7)$$
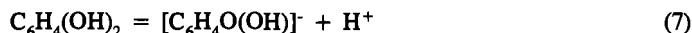
Upon oxidation by, for example, a manganese oxide [in which manganese acts as an electron acceptor and becomes reduced (acting as a Lewis acid)], the semiquinone anion is converted into a semiquinone radical (Figure 4).

$$[C_6H_4O(OH)]^- = \bullet C_6H_4O(OH) + e^- \qquad (8)$$
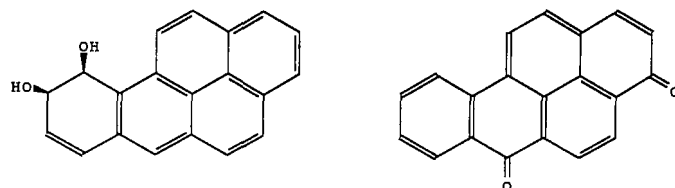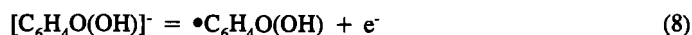
Benzo(a)pyrene-cis-9,10-Dihydrodiol   Benzo(a)pyrene-3,6-Dione

Figure 3
Structures of Biologically Mediated
Benzo(a)pyrene Intermediates

Under neutral or higher pH conditions and in the presence of air (i.e., oxygen, which acts as an electron acceptor) and MnO_2, the dissolved Mn^{2+} is rapidly oxidized to form MnO_2 through auto-oxidation:
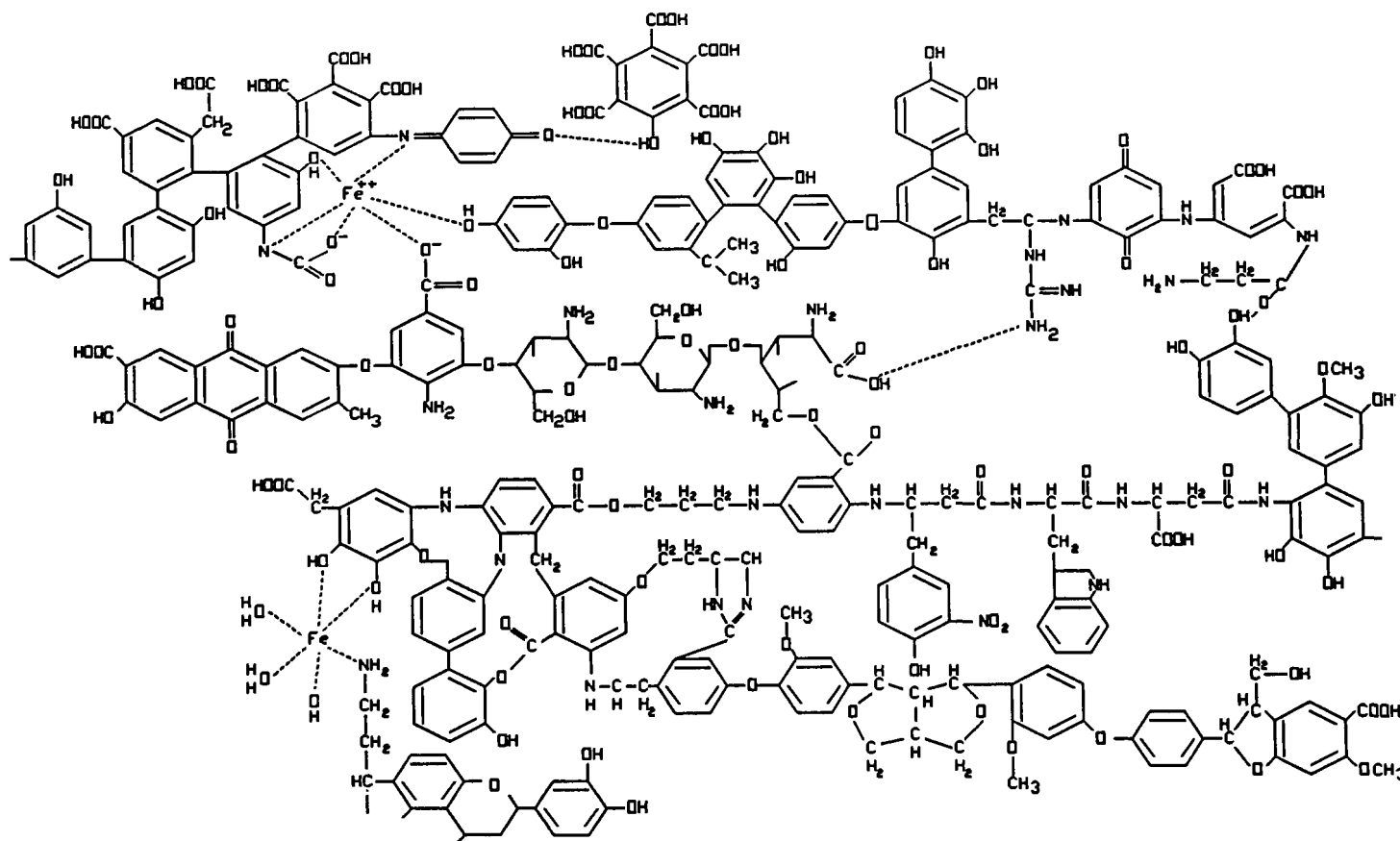
Figure 2
Illustrative Structure of Humus

$$Mn^{2+} + \tfrac{1}{2} O_2 + H_2O = MnO_2 + 2 H^+ \qquad (9)$$
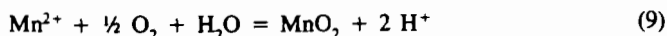
The terminal electron acceptor of the abiotic-catalytic process is free oxygen.
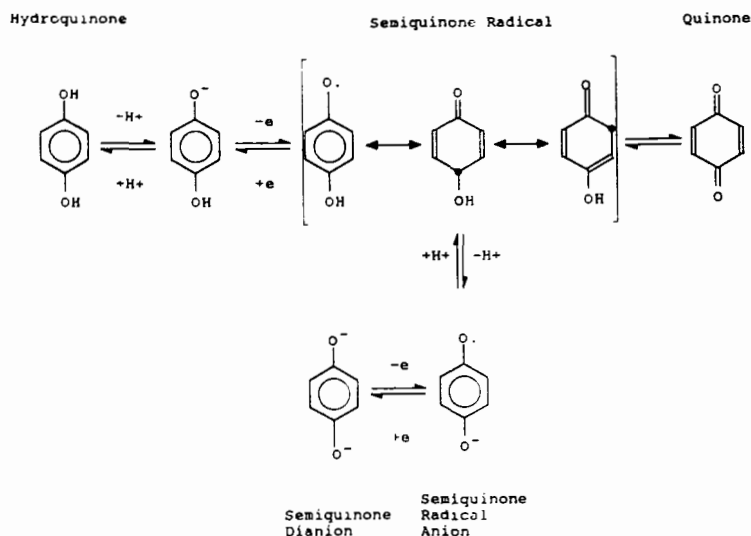
Figure 4
Proposed Relationships Between Quinone, Semiquinone Radical, Hydroquinone, Semiquinone Radical Ion and Semiquinone Dianion [After Senesi and Schnitzer[7] and Wang et al.[16]]

PROPOSED MODEL DESCRIBING REDUCTIVE DISSOLUTION AND AUTO-OXIDATION

Stone[17] notes that rates of reductive dissolution of transition metal oxide/hydroxide minerals are controlled by rates of surface chemical reactions and that transition metal oxides/hydroxides differ in their ability to oxidize organic compounds. He listed reduction potentials for nickel, manganese, cobalt and iron. Based on their thermodynamic data, their oxidant strength decreased in the following order: $Ni_3O_4 > MnO_2 > MnOOH > CoOOH > FeOOH$. Because manganese is a relatively strong oxidant that is readily found in soil, its reductive dissolution and autooxidative characteristics are reviewed.

Stone and Morgan[18] proposed a simple model for describing reductive dissolution of Mn(III) with phenol. Based on their work, a simple illustrative model is proposed herein for the reductive dissolution and autooxidation of Mn(IV) and transformation of hydroquinone. The following assumptions apply to this analysis:

- Manganese(IV) represents the oxidized form of the metal.
- The oxidized organic product is represented as a radical, because under aerobic conditions a radical represents the most likely product for polymerization reactions.[5,8,11,15-26]
- Transport-controlled reactions are assumed not to occur.[27] The dissolution rate is controlled by the rates of surface chemical reactions (assuming for this paper inner-sphere complexation) and not by diffusion.[28]
- The release of the reduced metal ion is independent of the product concentrations, indicating that the release of the reduced metal from the oxide surface is unidirectional.[27]
- The availability of the oxidized metal surface [i.e., $\equiv Mn^{IV}(OH)_2$] is not limiting in the proposed reactions, and the total number of surface sites remains constant as a new site is generated when a reduced manganese ion is released. This assumption does not address the potential for the oxide surface to readsorb reduced manganese (i.e., dissolved Mn^{2+}) or dissolved oxidized organics. Stone and Morgan[27] investigated the potential for readsorption of Mn^{2+} and determined that the loss of Mn^{2+} was less than 2% of the amount of manganese added. The number of moles of surface sites is assumed to equal 6% of the number of moles of total manganese added to

the system. Stone and Morgan[27] estimated the number of manganese oxide surface sites (based on moles) in their experimental setup to be between 3.5 and 9.0% of the total oxide added to the system.

- The organic substrate (i.e., hydroquinone) is in excess, and its mass changes negligibly in the system. The hydroquinone is assumed to represent a simple surrogate for other dione- and diol-configured organics.

This paper presents a simple model for describing reductive dissolution and autooxidation. It illustrates the importance of oxygen and the impact that autooxidation has on Mn^{2+} concentrations. The remaining portions of this paper describe the general stoichiometric equations associated with the process and present a brief analysis illustrating their application.

Half Reactions and Inner-Sphere Mechanism for Reductive Dissolution of Mn(IV)

The half-reactions associated with the reductive dissolution of Mn(IV) and the oxidation of hydroquinone (i.e., QH_2) are presented in Table 1.[29] Stone and Morgan[18] have mechanistically described these equations in four steps: (1) precursor-complex formation (i.e., reductant adsorption), (2) electron transfer, (3) release of oxidized organic product and (4) release of reduced metal ion. Precursor-complex formation may be either an inner-sphere reaction, when incoming organics bind directly to the surface metal centers, or an outer-sphere reaction, where a layer of coordinated hydroxyl groups or water molecules separate the organic from the surface metal centers.[18] Hydroxyl groups exist at the surface of the manganese dioxide mineral [i.e., $Mn^{IV}O_2(s)$]; these hydroxyl groups are used to balance the charge at the surface - water interface and can be expressed as $\equiv Mn^{IV}(OH)_2$, where "$\equiv$" refers to the oxide surface. The following four steps can be used to describe the inner-sphere complex formation between hydroquinone and the manganese dioxide surface:[18]

- Precursor-Complex Formation (Reductant Adsorption):

$$\equiv Mn^{IV}(OH)_2 + 2\ QH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \equiv Mn^{IV}(QH)_2 + 2\ H_2O \qquad (10)$$
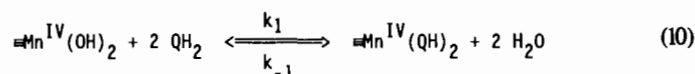
where k_1 and k_{-1} are rate constants in the forward and reverse directions, respectively.

- Electron Transfer:

$$\equiv Mn^{IV}(QH)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \equiv Mn^{II}(\cdot QH)_2 \qquad (11)$$
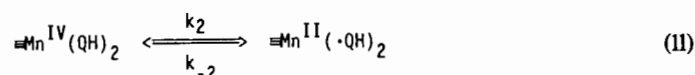
where k_2 and k_{-2} are rate constants in the forward and reverse directions, respectively.

- Release of Oxidized Organic Product:

$$\equiv Mn^{II}(\cdot QH)_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \equiv Mn^{II}OH_2 + 2\ (\cdot QH) \qquad (12)$$
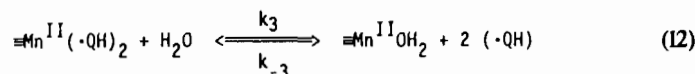
where k_3 and k_{-3} are rate constants in the forward and reverse directions, respectively, and $\cdot QH$ is a semiquinone radical. By noting that Mn(II) still resides on the oxide surface, the Mn(II) products of Equation 12 can also be written as follows, because the right- and left-hand sides of Equation 13 are equivalent:

$$\equiv Mn^{II}OH_2 = \equiv Mn^{IV}O_2 \cdot (Mn^{II}OH_2) \qquad (13)$$
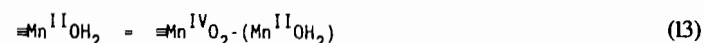
where "$\equiv Mn^{IV}O_2 \cdot (Mn^{II}OH_2)$" represents the reduced metal complex on the Mn(IV) surface prior to Mn(II) release.

- Release of Reduced Metal Ion:

Stone and Ulrich[30] noted that protons frequently assist in the metal-detachment step of dissolution reactions and that studies have generally found the number of protons involved to be equal to the valence of the detached metal (i.e., 2).[31] They continued to note that the actual number of protons involved in reductive dissolution is not known with

certainty, because the presence of two or more oxidation states on the metal surface may alter the pH dependence of the metal·release step. The release of the reduced metal ion from the surface is expressed as follows:

$$\equiv Mn^{IV}O_2\text{-}(Mn^{II}OH_2) + 2\ H^+ \xrightarrow{\ k_4\ } \equiv Mn^{IV}(OH)_2 + Mn^{2+} + H_2O \quad (14)$$
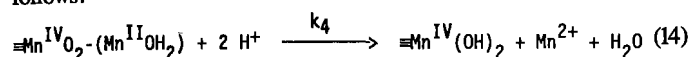
where k_4 is a rate constant. In experiments to determine the effect of varying amounts of Mn^{2+} on the rate of dissolution of $MnO_2(s)$, Stone and Morgan[27] found that the initial rates of dissolution with varying amounts of Mn^{2+} in solution had no effect on the kinetics. Based on these results, one might conclude that Equation 14 is not rate-limiting and can be considered to be unidirectional. The amount of Mn^{2+} in solution does not influence the rate of its formation. This conclusion appears to be confirmed by the fact that Mn(II) has a larger radius than Mn(IV) and does not appear to fit into the solid structure of $MnO_2(s)$ very well. As such, the Mn(II) ion is readily released from the matrix.

Table 1
Half Reactions for Reductive Dissolution

$$Mn^{IV}O_2(s) + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O \quad (1)$$

$$2\ QH_2 = 2\ (\cdot QH) + 2\ H^+ + 2\ e^- \quad (2)$$

net: $$Mn^{IV}O_2(s) + 2\ QH_2 + 2\ H^+ = Mn^{2+} + 2\ (\cdot QH) + 2\ H_2O \quad (3)$$
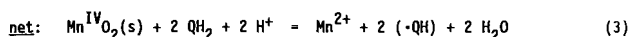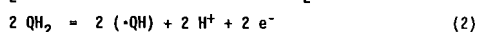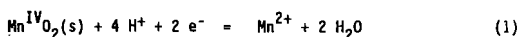
Proposed Polymeric Products of Mn(IV) Dissolution/Auto-Oxidation

Research has indicated that oxygen promotes oxidative coupling reactions, creating dimers, trimers and other less soluble, more surface-active oxidation products.[5,8,11,15-26] These reactions can be expressed as follows:

$$\cdot QH + \cdot QH \longrightarrow \text{polymeric oxidation products} \quad (15)$$
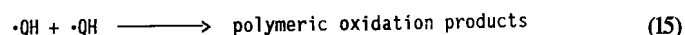
Auto-Oxidation of Mn(II) to Mn(IV)

Stumm and Morgan[32] presented reactions for the oxidation of Mn(II) to Mn(IV). They felt that the reactions might be visualized as proceeding according to the reactions presented in Table 2. They also note that the Mn^{2+} concentration decreases with time with an apparent autocatalytic effect. Based on Stumm and Morgan[32] and Morgan,[34] Benefield et al.[33] describe the autocatalytic oxidation of Mn(II) in the following manner:

$$d[Mn^{2+}]/dt = -k_5\ [Mn_T]\ [P_{O_2}]\ [OH^-]^2\ [Mn^{2+}]\ [Mn_T\ Mn^{2+}] \quad (16)$$
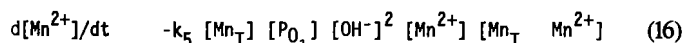
where k_5 is a rate constant, Mn_T is the total manganese in the system, and $[PO_2]$ is the partial pressure of oxygen. Although Mn(II) is oxidized according to Equation 16, it is unclear what valence that manganese is oxidized to [i.e., Mn(III) or Mn(IV)]. To be a true catalyst, Mn^{2+} would have to be oxidized to Mn(IV) to regenerate the oxidative surfaces and maintain zero net change.

KINETICS OF REDUCTIVE DISSOLUTION AND AUTO-OXIDATION

This section proposes algorithms describing the kinetics of reductive dissolution and autooxidation. The analysis presented above does

Table 2
Half Reactions for Autooxidation

$$\tfrac{1}{2}\ Mn^{2+} + \tfrac{1}{2}\ O_2 + \tfrac{1}{2}\ H_2O \xrightarrow{\ slow\ } \tfrac{1}{2}\ Mn^{IV}O_2(s) + H^+ \quad (1)$$

$$\tfrac{1}{2}\ Mn^{2+} + \tfrac{1}{2}\ Mn^{IV}O_2(s) \xrightarrow{\ fast\ } \tfrac{1}{2}\ (\equiv Mn^{IV}O_2\text{-}Mn^{II}) \quad (2)$$

$$\tfrac{1}{2}\ (\equiv Mn^{IV}O_2\text{-}Mn^{II}) + \tfrac{1}{2}\ O_2 + \tfrac{1}{2}\ H_2O \xrightarrow{\ slow\ } Mn^{IV}O_2(s) + H^+ \quad (3)$$

net: $$Mn^{2+} + \tfrac{1}{2}\ O_2 + H_2O = Mn^{IV}O_2(s) + 2\ H^+ \quad (4)$$
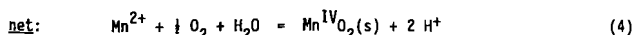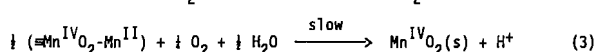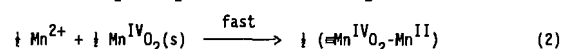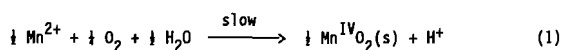
not account for the removal of radical products [Equation 12] that are consumed in the polymerization process, although Taylor and Battersby[35] note that the rate of disappearance of phenolate radicals through dimerization has been clearly shown to follow second-order kinetics.

Figure 5 presents a schematic illustration of the surface-site mass balance for reductive dissolution and autooxidation, based on Equations 10 through 14 and Equation 16. Included in this figure are formulae for the characteristic times associated with the reaction for each rate. Assuming that the only species that contribute to the surface mass balance equation are $\equiv Mn^{IV}(OH)_2$, $\equiv Mn^{IV}(QH)_2$, $\equiv Mn^{II}(\bullet QH)_2$ and $\equiv Mn^{II}OH_2$ and that other competing anions are not considered, the surface mass balance equation can be written as follows:

$$S_T = [\equiv Mn^{IV}(OH)_2] + [\equiv Mn^{IV}(QH)_2] + [\equiv Mn^{II}(\cdot QH)_2] + [\equiv Mn^{II}OH_2] \quad (17)$$

where S_T is the total moles of surface sites per liter of solution (M). Under the assumption that each reaction can be described as an elementary reaction, rate expressions are proposed for $\equiv Mn^{IV}(OH)_2$, $\equiv Mn^{IV}(QH)_2$, $\equiv Mn^{II}(\bullet QH)_2$, and $\equiv Mn^{II}OH_2$, using Equations 4 through 7:

$$d[\equiv Mn^{IV}(OH)_2]/dt = k_1\ [QH_2]^2\ [\equiv Mn^{IV}(OH)_2] + k_{-1}\ [\equiv Mn^{IV}(QH)_2] + k_4\ [H^+]^2\ [\equiv Mn^{II}OH_2] \quad (18)$$

$$d[\equiv Mn^{IV}(QH)_2]/dt = k_1\ [QH_2]^2\ [\equiv Mn^{IV}(OH)_2]\ (k_{-1} + k_2)\ [\equiv Mn^{IV}(QH)_2] + k_{-2}\ [\equiv Mn^{II}(\cdot QH)_2] \quad (19)$$

$$d[\equiv Mn^{II}(\cdot QH)_2]/dt = k_2\ [\equiv Mn^{IV}(QH)_2]\ (k_{-2} + k_3)\ [\equiv Mn^{II}(\cdot QH)_2] + k_{-3}\ [\cdot QH]^2\ [\equiv Mn^{II}OH_2] \quad (20)$$

$$d[\equiv Mn^{II}OH_2]/dt = k_3\ [\equiv Mn^{II}(\cdot QH)_2]\ (k_{-3}\ [\cdot QH]^2 + k_4\ [H^+]^2)\ [\equiv Mn^{II}OH_2] \quad (21)$$

The rate expressions for the remaining nonsurface-constituent concentrations (i.e., $[Mn^{2+}]$, $[QH_2]$, and $[\bullet QH]$) are as follows:

$$d[Mn^{2+}]/dt = k_4\ [H^+]^2\ [\equiv Mn^{II}OH_2]\ k_5\ [Mn_T]\ [P_{O_2}]\ [OH^-]^2\ [Mn^{2+}]\ [Mn_T\ Mn^{2+}] \quad (22)$$

$$d[QH_2]/dt = 2\ k_1\ [QH_2]^2\ [\equiv Mn^{IV}(OH)_2] + 2\ k_{-1}\ [\equiv Mn^{IV}(QH)_2] \quad (23)$$

$$d[\cdot QH]/dt = 2\ k_3\ [\equiv Mn^{II}(\cdot QH)_2]\ 2\ k_{-3}\ [\cdot QH]^2\ [\equiv Mn^{II}OH_2]\ \text{polymerized products} \quad (24)$$

Solutions to the Kinetic Rate Expressions

This section presents an illustrative example of the effects of kinetic rate constants and other parameters in determining the importance of reductant adsorption, electron transfer, surface release of oxidized organics, surface release of the reduced metal Mn^{2+} and autooxidation. The response to variations in parameters contained in Equations 10 through 14 and in Equation 16 are determined through solutions of Equations 17 through 24, which have been solved using Euler's method.[36] The solutions to these equations assume that the systems are well buffered (constant pH).

As noted earlier, Schnitzer[12] suggested that the rate-determining step in the synthesis, by oxidative polymerization of humic acids from simple phenolic constituents and acids, is the formation of a semiquinone radical involving a one-electron transfer reaction. This illustrative example investigates the conditions when the formation and release of the semiquinone radical is rate-limiting. To meet this condition, either the electron transfer step [i.e., formation of the radical on the oxide surface, Equation 11] or the release of the oxidized organic radical from the oxide surface [Equation 12] is rate limiting. For illustrative purposes, the latter (i.e., release of radical from the surface) is assumed to be the rate-limiting step.

The assumptions associated with this analysis are presented in Table 3. Stone and Ulrich[30] arbitrarily assigned numerical values for the parameters presented in this table, which have been modified for this example. The initial concentrations for $[S_T]°$, $[\equiv Mn^{IV}(OH)_2]°$, and $[QH_2]°$ are also given in Table 3. All other initial concentrations (i.e., $[\bullet QH]$, $[Me^{2+}]$, $[\equiv Mn^{IV}(QH)_2]$, $[\equiv Mn^{II}OH_2]$, and $[\equiv Mn^{II}(\bullet QH)_2]$) are assumed as zero.
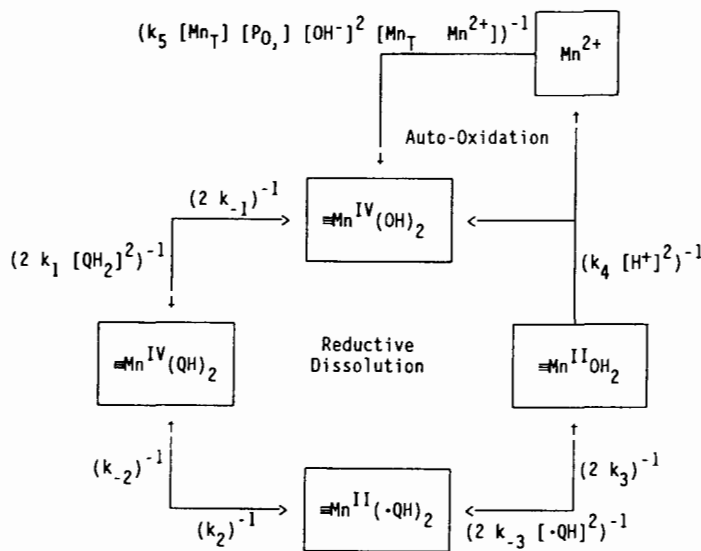
Figure 5
Schematic Illustration of the Surface-Site Mass Balance Equations (Expressions containing rate constants represent characteristic times.) [After Stone and Morgan[18]]

Table 3
Parameter Values for the Illustrative Example

Parameter	Value	Parameter	Value
k_1	1.50E+02 1/M²/min	P_{O_2}	0.21 atm
k_{-1}	5.00E-02 1/min	$[S_T]$.	4.80E-06 M
k_2	1.00E+00 1/min	pH	7
k_{-2}	5.00E-01 1/min	Mn_T	5.00E-04 M
k_3	1.00E-03 1/min	$[\equiv Mn^{IV}(OH)_2]$.	8.00E-05 M
k_{-3}	0.00E+00 1/M²/min	$[QH_2]$.	2.00E-02 M
k_4	1.00E+14 1/M²/min	k_5	1.00E+22 1/M⁴/atm/min

The results of the simulation are presented in Figure 6. When release of the oxidized organic from the metal surface is rate-limiting (i.e., small k_3), equilibrium conditions between $\equiv Mn^{IV}(OH)_2$, $\equiv Mn^{IV}(QH)_2$, and $\equiv Mn^{II}(\bullet QH)_2$ may occur. $\equiv Mn^{IV}(OH)_2$ is converted to $\equiv Mn^{IV}(QH)_2$, which in turn is converted to $\equiv Mn^{II}(\bullet QH)_2$. Under steady-state conditions, these concentrations do not change. Figure 6 also shows that the $[\equiv Mn^{II}OH_2]$ concentration is nearly zero, because once $[\equiv Mn^{II}OH_2]$ is formed it is immediately converted to Mn^{2+} [Equation 14]. The Mn^{2+} concentration (theoretically) would continue to rise with time. Figure 7 illustrates that autooxidation would counterbalance the increase until steady-state conditions were reached between Mn^{2+} formation from reductive dissolution and its disappearance due to autooxidation.

CONCLUSIONS

By understanding the environmental consequences of polymerization of aromatics and the incorporation of these compounds into the humification process, recalcitrant organics could become constituent parts of the soil humus, resulting in immobilized and/or detoxified bound residues. Immobilization and detoxification could be a valuable decontamination method for certain types of waste prod!ucts. These wastes would then be accessible to more and better engineer-designed cleanup
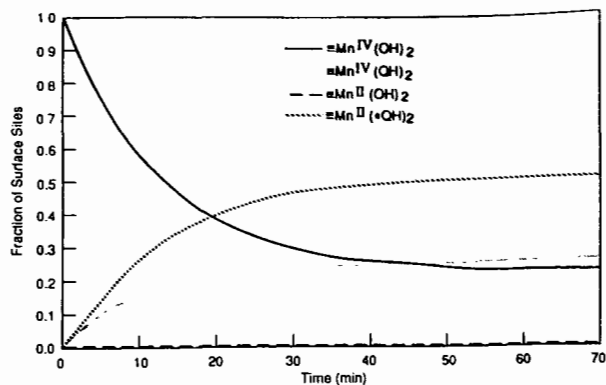
Figure 6
Fraction of Oxide Surface Sites Occupied by Various Species
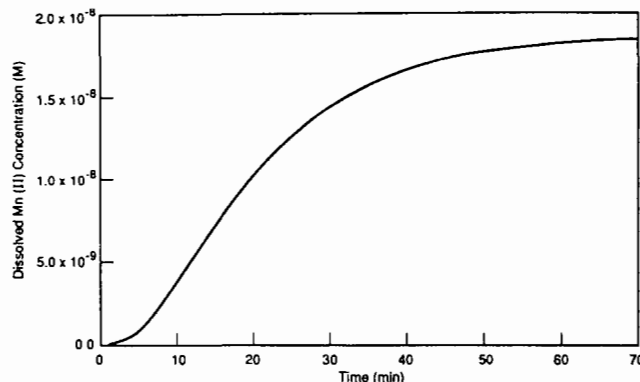
Figure 7
Temporal Variation in $Mn^{2+}[$ Concentration during Reductive Dissolution and Autooxidation when Release of the Oxidized Organic is Rate-Limiting

alternatives. This paper: (1) reviews the possibility of using abiotic catalysis to polymerize organic substances, (2) discusses aspects associated with thermodynamics and kinetics of the process and (3) proposes a simple model upon which analyses and experiments may be based.

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Enhancement of PCP and TCE Biodegradation By Hydrogen Peroxide

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ABSTRACT

Two model toxic chemicals were previously identified as recalcitrant to biodegradation by activated sludge and selected microbial consortia. Each model toxic chemical was subjected to chemical oxidation, both by hydrogen peroxide and by Fenton's reagent. Chemical oxidation rates and biodegradation rates before and after chemical oxidation were measured. Fenton's reagent was a particularly effective oxidizing agent. Subsequent microbial degradation was enhanced by Fenton's reagent pretreatment. Chloride ions were produced by both chemical oxidation and microbial degradation.

INTRODUCTION

Pentachlorophenol (PCP) and its sodium salt are widely used pesticides in the United States. The advantages of using PCP and its derivatives are that they are effective biocides and soluble in both oil and water. Although PCP and its derivatives have many uses, by far the major application is for wood preservation. Trichloroethylene (TCE) is a very useful cleaner and spot remover and is widely used as an industrial, household and military degreaser.

Economical bioremediation of contaminated soil can be carried out before a plume of toxic chemical penetrates an underground aquifer. Since recalcitrant organics in contaminated soils are degraded only slowly, pre-oxidation of recalcitrants and persistent toxic chemicals into more readily degradable substances may be useful to improve soil bioremediation techniques.

This enhancement occurs if the initial oxidation step of the sequential microbial mineralization process can be carried out chemically, rather than biologically. The initial rate-limiting step for the microbes, therefore, is bypassed by the addition of aqueous chemical oxidants and the resulting partially oxidized products become more polar, more soluble and more easily degraded than the parent toxic organic chemical. In addition, the resulting residual decreased toxic chemical concentration becomes less toxic to the microorganisms and is, therefore, more quickly degraded.

In our laboratory, a generic microbial selection process is utilized. Selected microbial consortia (SMC) for various model toxic chemicals are developed from contaminated soils obtained at nearby toxic waste sites prior to any remediation. Then reactor conditions are optimized for each aqueous solution of specific chemical and its consortium and resulting biodegradation rates are measured by a respirometer. A replicate aqueous solution of each specific chemical is then subjected to chemical oxidation by hydrogen peroxide solution and by Fenton's reagent (a mixture of hydrogen peroxide and Fe^{+2}). Respirometric measurements due to microbial biodegradation of the resulting oxidation products are then conducted as before. A replicate set of experiments is also carried out using a stock culture of activated sludge microbes

in order to determine any decrease in toxicity due to chemical pre-oxidation treatment.

BACKGROUND

In the United States, 78% of the PCP produced is used by the wood preserving industry, 12% in production of Na-PCP, 6% in plywood and fiberboard waterproofing, 3% in domestic use and 1% as a herbicide.[1] Though PCP-treated products do not appear to represent a threat to the environment, accidental spillage and improper disposal of PCP at the approximately 600 United States manufacturing plants and at wood-preserving facilities have resulted in extensive contamination of soil, surface water and groundwater aquifers.[2,3] Pentachlorophenol is presumed to be the most resistant chemical to microbial degradation; however, the feasibility of biological treatment of pentachlorophenol has been the subject of numerous research papers.[4-11]

Early studies on TCE biodegradation produced anaerobic degradation products which were toxic.[12-14] Wilson and Wilson[15] cited TCE as a compound resistant to biodegradation in aerobic subsurface environments, but Parsons, et al.[16] conducted experiments indicating that biological activity was responsible for tetrachloroethylene and TCE transformations in aerobic microcosms containing cultured bacteria. Recently, additional workers have been conducting aerobic studies with methanogenic and other bacterial cultures.[17-19]

Other researchers have investigated whether microbial degradation could be enhanced if the toxic carbon source could be oxidized to a metabolite which is more readily degraded by microorganisms. Bishop, et al.[20] conducted an experimental study on uncharacterized municipal wastewaters containing a wide variety of refractory organics using peroxide-ferrous ion solutions producing hydroxyl radical. Bowers, et al.[21] also examined the preoxidation of uncharacterized industrial wastewaters with hydrogen peroxide and found reduced toxicity of oxidation products when compared to the original wastes. The reactions to illustrate peroxide mechanisms are discussed below.

Peroxide can dissociate into water and oxygen to provide an oxygen source, as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{1}$$

In contrast, Fenton's reagent reacts to produce both the hydroxyl ion and the hydroxyl radical, as follows:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+2} + OH^- + {}^{\cdot}OH \tag{2}$$
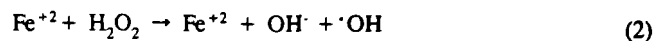
The hydroxyl radical can then attract a hydrogen atom from an organic substrate to produce an organic radical, as follows:

$$RH + {}^{\cdot}OH \rightarrow {}^{\cdot}R + H_2O \tag{3}$$
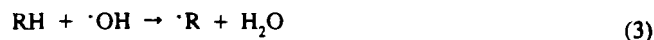
The organic radicals exist as transient intermediates and may be further oxidized by Fe^{+3} oxygen, or hydroxyl radical to form final, stable oxidation products. The oxidation products may be more easily biodegraded than the parent organic chemicals such as PCP.

The total oxidation reactions of PCP and TCE are expressed as follows:

$$PCP \ C_6OHCl_5 + 11.5H_2O_2 \rightarrow 6CO_2 + 12H_2O + 5Cl^-$$

$$TCE \ C_2HCl_3 + 4.5H_2 2O_2 \rightarrow 2CO_2 \rightarrow 5H_2O \rightarrow 3Cl^-$$
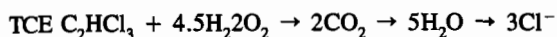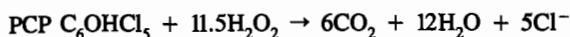
These reactions were used to determine peroxide and Fenton's reagent doses that would only partially oxidize the model chemicals for subsequent microbial biodegradation.

The chemicals were subjected to microbial biodegradation respirometric measurements before and after chemical oxidation, and reactions rates were calculated using Equations 4 and 5.

$$R = - \frac{\Delta St}{\overline{X}} = - \frac{S_t - St - t_o}{(X_o + X_t) /2} \quad (4)$$

where
S is the substrate concentration
t is time
X is microbial biomass concentration

Subscripts o and t represent initial and anytime t, respectively, and superbar denotes an average value.

The values of R at each S were then evaluated using a Michaelis-Menten function, expressed in Equation 5:

$$R = \frac{K_o S}{K_s + S} \quad (5)$$

where

k_o is the maximum substrate uptake rate constant
K_s is the half velocity constant, or substrate concentration at which specific substrate uptake, R, is half the maximum rate.

METHODS AND MATERIALS

Details of experimental procedures have been described previously.[22,23] Briefly, the following experimental variations were examined:
- Set 1. Hydrogen peroxide and PCP or TCE
- Set 2. Hydrogen peroxide, ferrous ion and PCP or TCE
- Set 3. Hydrogen peroxide, PCP, or TCE and selected microbial consortia (or activated sludge)
- Set 4. Hydrogen peroxide, ferrous ion, PCP or TCE and selected microbial consortia (or activated sludge)

Replicate reactors and controls were run for each respirometric experiment. For each analysis, a 5-mL sample was withdrawn by syringe through the rubber septum of each reactor vessel. For TCE determinations, the aqueous sample was extracted using a MIXXOR (GENEX Corporation, Maryland) in 5 mL of n-pentane with 20 strokes. Two mL of the extracted TCE in n-pentane was mixed with 2 mL of dibromodichloromethane (DBDCM) in a 10-mL vial. One μL samples of this solution were analyzed by a Varian Gas Chromatograph equipped with an FID detector at 310°C and a 30-m DB-5 (J & W Scientific) capillary column. A temperature program of 35°C (1 min), increasing to 70°C at 5°C/min temperature gradient was used. The injector temperature was 85°C. Nitrogen carrier gas flow rate was 10 mL/min. With the above conditions, the retention times for TCE and DBDCM were 3.08 and 7.80 minutes, respectively. The ratio of peak heights was converted to concentration units using previously determined calibrations. This procedure minimized TCE volatilization losses

and experimental results were compared to control runs to insure consistency.

Residual PCP concentration was determined by HPLC (Varian Model 2550) using a reverse-phase column (25 cm NUCLEOSIL C_{18} packed column) with a UV detector at 280 nm. The aqueous sample was filtered through 0.22 μm (Millipore, MILLEX-GX) before each 40 μL injection. The isocratic eluent was pumped at a rate of 1 ml/min and it was composed of 88% methanol with 1% acetic acid and of 12% deionized water with 1% acetic acid. The results were printed in analog and digital modes on a Varian integrator, model 4290.

Soluble chemical oxygen demand (SCOD) was determined by using the micro COD digestion and titrimetric procedure manufactured by the HACH Company. Chloride ion concentrations were determined with a Fisher 825 MP digital pH meter equipped with a chloride-specific electrode (Orion 94-17B). Chloride concentration was determined by using a calibration curve plotted from the molarity of a series of KCl standards versus millivolts. The potassium iodide-sodium thiosulfate titration method was used to determine residual concentration of hydrogen peroxide in each system.[24]

RESULTS AND DISCUSSION

Chemical PreOxidation

Chemical oxidation of PCP when preoxidized with Fenton's reagent was faster and more extensive than when just peroxide was added alone. The results of chemical oxidation by Fenton's Reagent are shown in Figure 1.
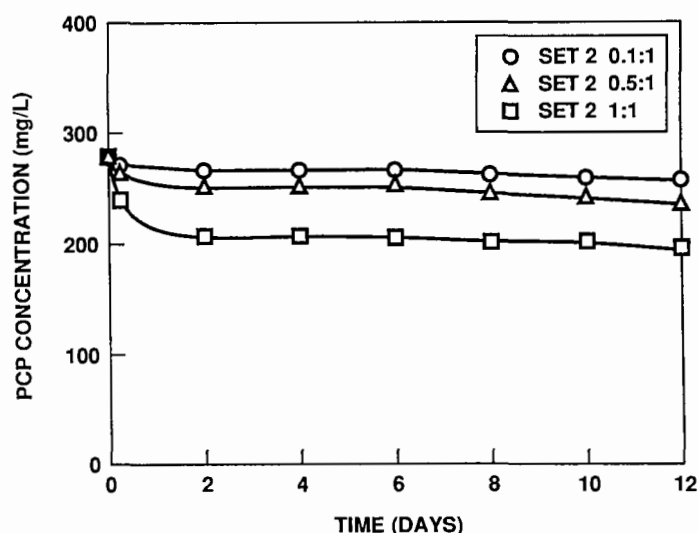
Figure 1
Residual PCP Concentration Following
Oxidation by Fenton's Reagent

By comparison, the chemical oxidation of TCE by both hydrogen peroxide alone and with Fenton's reagent was significant. Both a faster rate and higher level of oxidation with Fenton's reagent resulted, however, than when just hydrogen peroxide was used. TCE chemical oxidation using Fenton's reagent is shown in Figure 2. If Figures 1 and 2 are compared, it is evident that chemical doses were relevant to both the rate and level of oxidation occurring for PCP. For TCE, however, a minimal dose of Fenton's reagent was just as effective as a dose 10 times greater. Analyses of residual peroxide indicated that the oxidizing chemical was not detectable after four hours. These results indicated that the chemical reactions shown in Equations 1 and 2 for peroxide and Fenton's reagent occurred at approximately the same rate. Even though the disappearance of hydrogen peroxide in Fenton's reagent was very fast, the chain reaction described in Equation 3 for Fenton's Reagent occurred slightly more slowly.
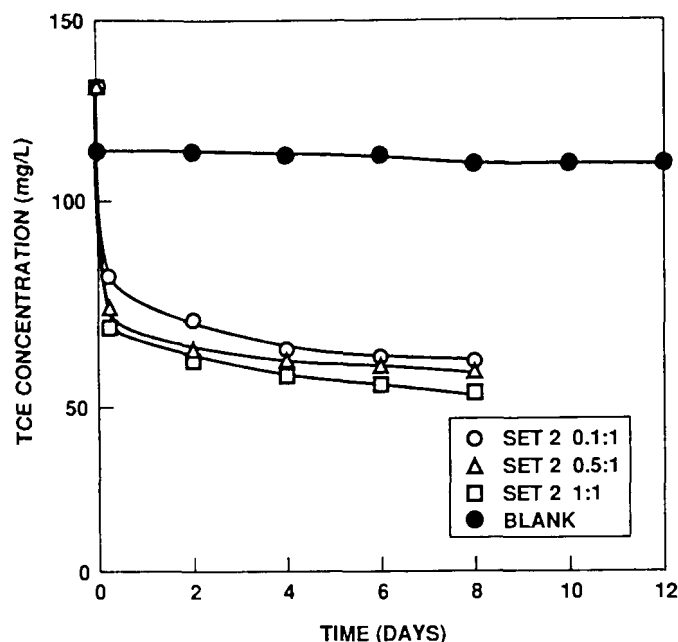
Figure 2
Residual TCE Concentration Following
Oxidation by Fenton's Reagent

Figure 3
Residual PCP Concentration Due to Biodegration
by a Selected Microbial Consortium Following
Chemical Oxidation by Fenton's Reagent

Chemical Oxidation Followed by Selected Microbial Consortia Degradation

When chemical oxidation was followed by microbial degradation, the rate of PCP disappearance was faster than when due to chemical oxidation alone. For systems to which a selected microbial consortium (SMC) were added following chemical oxidation by Fenton's reagent, the biodegradation rate constant was an order of magnitude larger than that due to chemical oxidation alone. Figure 3 illustrates the resulting degradation following Fenton's reagent preoxidation. Comparison of Figure 1 for chemical oxidation alone and Figure 3 for subsequent microbial degradation indicates that chemical dose became less relevant for the selected microbes than for just chemical oxidation alone.

For the TCE case, volatilization occurred, as indicated in the control plot of Figure 4. The loss due to volatilization was not apparent, however, until repeated aliquots were removed from the reactor. In fact, this plot defines a maximum loss due to volatilization, for in the other plots showing microbial degradation, the TCE lost early to the gas phase will subsequently be transferred back to the aqueous phase as biodegradation proceeds with time. This transfer back to the aqueous phase is caused by a shift in the chemical potential for TCE as biodegradation depletes the aqueous concentration. The decrease in aqueous chemical potential compared to gas phase chemical potential causes a spontaneous transfer from the gas phase, controlled by Henry's Law constant for TCE, in order to reestablish a constant equilibrium concentration ratio for TCE between the two phases.

The degradation plots shown in Figure 4 for the three doses of Fenton's reagent indicate that the level of biodegradation was a function of the oxidant dose. This bacterial response with respect to oxidant dose was apparently different than for PCP where oxidant dose made less difference to the degradation by its SMC. Work is being carried out in an attempt to identify both chemical oxidation products and intermediate microbial metabolites by GC/MS, but a preliminary comparison can be made by examining the microbial Cl⁻ production level, Cl⁻ production rate and oxygen uptake rate for the two compounds. A typical Cl⁻ production rate for the PCP SMC is shown in Figure 5. This figure indicates a large concentration of Cl⁻ was produced at a significant rate which was barely reaching an asymptotic value after 12 days. In addition, the Cl⁻ production appears to be independent of the Fenton's reagent dose. In contrast, the Cl⁻ production by TCE selected microbial consortium was one-fourth the amount of the PCP case, the produc-
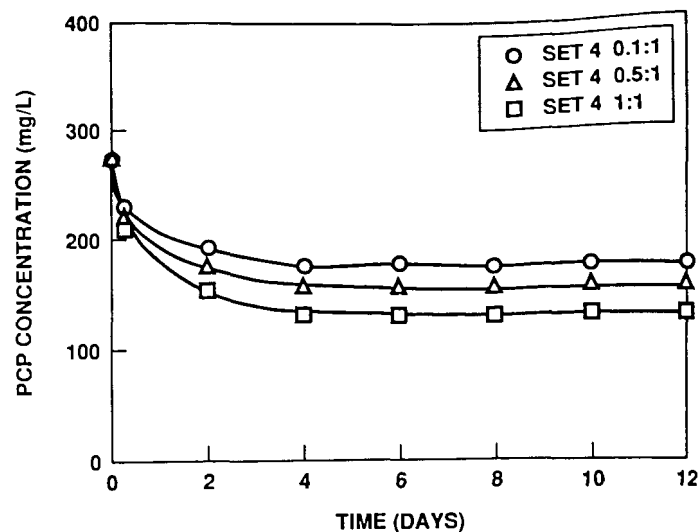
Figure 4
Residual TCE Concentration Due to Biodegradation
by a Selected Microbial Consortium Following
Chemical Oxidation by Fenton's Reagent

tion rate diminished to a very low level after Day 4 and the production rate and level were proportional to the dose of Fenton's reagent. All of these observations suggest that Fenton's reagent is a much more effective oxidant for TCE than for PCP. Examination of the chemical oxidation reactions presented previously indicate that a three-fold molar ratio increase of oxidant was required for PCP degradation compared to TCE. Therefore, even a small dose of Fenton's reagent was effective for oxidizing TCE as shown in Figure 2. The subsequent microbial response was proportional to the oxidant dose for both the degradation rate of parent TCE and the production rate and level of Cl⁻. All of these results are consistent with the hypothesis that the hydroxyl radical produced from hydrogen peroxide attacks the chloro-substituents on the hydrocarbon skeletal matrices of TCE and PCP. The results for PCP oxidation and PCP preoxidation followed by SMC degradation indicated

that comparable oxidant doses for this chemical were not large enough to cause significant oxidation. Cumulative oxygen uptake rates were comparable for both TCE and PCP SMC when each parent toxic chemical was dosed either with hydrogen peroxide alone or with Fenton's reagent. For both SMC, the oxygen uptake rates were slightly higher when Fenton's reagent was used.

TIME (DAYS)
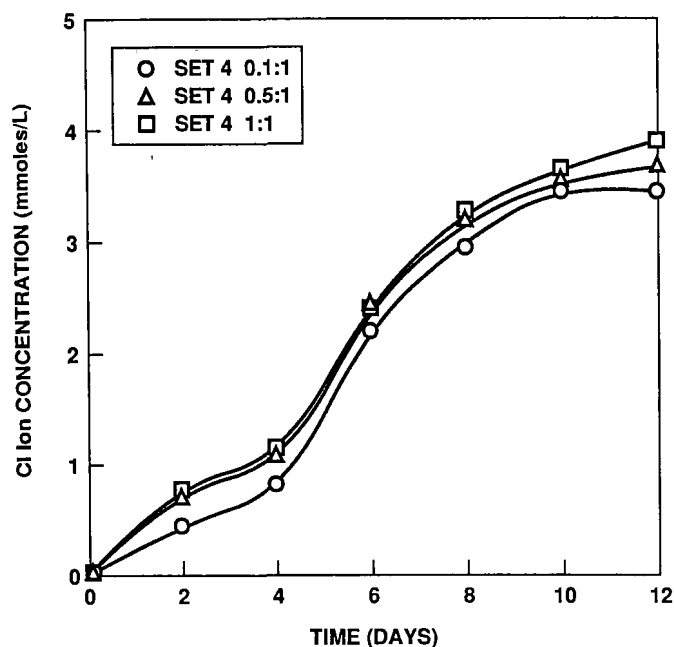
Figure 5
Chloride Ion Production Due to Biodegration
of PCP by a Selected Microbial Consortium
Following Chemical Oxidation by Fenton's Reagent

Chemical Oxidation Followed by Activated Sludge Degradation

Microbial degradation of both TCE and PCP by activated sludge was slower than by each SMC, whether the parent toxic chemicals were untreated or pretreated by hydrogen peroxide alone or by Fenton's reagent. Production of Cl⁻ and oxygen uptake rates were also slower. Activated sludge degradation of both parent toxic chemicals was fastest following Fenton's agent pretreatment. Enhancement of activated sludge biodegradation of TCE was greater than for PCP.

Table 1
Specific Substrate Uptake Rate Constants
and Half Velocity Constants for PCP Under
Varying Treatment Conditions

Environmental condition	$k_{(AS)}$	$K_{(AS)}$	$k_{(SCM)}$	$K_{(SMC)}$
Untreated system	0.00022	120.5	0.00027	114.1
Pretreated with hydrogen peroxide at molar ratios of hydrogen peroxide:PCP				
0.1:1	0.00031	126.3	0.00079	121.0
0.5:1	0.00031	126.3	0.00092	118.8
1.0:1	0.00044	115.8	0.00096	110.5
Pretreated with Fenton's reagent at molar ratios of peroxide:PCP				
0.1:1	0.00147	114.3	0.00542	91.5
0.5:1	0.00151	119.0	0.00553	80.3
1.0:1	0.00189	102.3	0.00573	72.5

$k_{(AS)}$: Biodegradation Rate by Activated Sludge
$k_{(SMC)}$: Biodegradation Rate by SMC (Selected Microbial Consortium)
$K_{(AS)}$: Substrate Concentration at Half the Maximum Velocity for Activated Sludge (Half Velocity Constant)
$K_{(SMC)}$: Substrate Concentration at Half the Maximum Velocity for SMC (Half Velocity Constant)

SUMMARY OF RESULTS

Data from all the degradation tests were used to calculate biodegradation rate constants and half velocity constants according to Equations 4 and 5. These tabulations indicate quantitative values of the differences in results described above.

Table 2
Specific Substrate Uptake Rate Constants
and Half Velocity Constants for TCE Under
Varying Treatment Conditions

Environmental condition	$K_{s(AS)}$	$K_{m(AS)}$	$K_{s(SCM)}$	$K_{m(SMC)}$
Untreated system	0.00019	78.0	0.00020	78.0
Pretreated with hydrogen peroxide at molar ratios of hydrogen peroxide:PCP				
0.1:1	0.00026	53.1	0.00027	51.3
0.5:1	0.00027	50.8	0.00030	49.6
1.0:1	0.00029	46.1	0.00031	46.1
Pretreated with Fenton's reagent at molar ratios of hydrogen peroxide:PCP				
0.1:1	0.00034	51.9	0.00043	49.6
0.5:1	0.00034	48.7	0.00040	48.5
1.0:1	0.00036	46.7	0.00059	44.7

In addition, the half velocity constants and oxygen uptake rates indicate that preoxidation treatment reduces the toxicity of the substrates for both activated sludge and both SMC. The Cl⁻ production levels and rates indicate that both the chemical oxidation and microbial degradation mechanisms sequentially remove chlorine substituents from the molecule.

CONCLUSIONS

Selected microbial consortia for TCE and PCP degraded these parent toxic compounds faster and more efficiently than unacclimated activated sludge microbes. Preoxidation of the parent model toxic chemicals enhanced the subsequent microbial degradation by both activated sludge and selected microbial consortia. Pretreatment of TCE and PCP with oxidants, particularly with Fenton's reagent, reduced the toxicity of these substrates to both activated sludge and selected microbial consortia. Chloride ion was produced as a result of both chemical oxidation and microbial degradation.

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Treatability of Contaminated Groundwater Using Biological Processes

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ABSTRACT

Treatability of contaminated groundwater from the Ninth Avenue Superfund Site, Gary, Indiana, was evaluated using bench-scale biological reactors (bioreactors). Aerobic treatment and aerobic treatment with the addition of powdered activated carbon (PAC) were evaluated. All bioreactors were configured to simulate a complete mix activated sludge system. The groundwater was contaminated with various organic contaminants including: 278 mg/L total ketones, 25 mg/L chlorinated solvents, 6 mg/L total phenols and 10 mg/L of benzene, toluene, ethylbenzene and xylene (BTEX) compounds. The groundwater also contained approximately 90 mg/L and 230 mg/L of iron and manganese, respectively.

A microbial culture collected from a local municipal wastewater treatment system was acclimated over a period of 6 wk to the contaminants in the groundwater using a 15-L bioreactor. Once the microbial culture was acclimated, biological treatability testing was performed in four 3-L bioreactors. The groundwater influent had sufficient nitrogen, but the addition of phosphate was required.

The reduced iron and manganese in the groundwater were oxidized and precipitated in the aeration chamber of the bioreactors. The precipitate caused substantial bulking of the activated sludge; however, the bulking did not seem to affect the activity of the biomass. The organic contaminants were reduced to trace levels in both treatment systems. The aerobic bioreactors without PAC addition achieved a BOD reduction in excess of 95%, but only achieved COD and TOC removals in excess of 50%. The aerobic bioreactors with PAC addition achieved a 95% BOD removal. The addition of PAC improved the percent removals of COD and TOC to over 80%. The PAC also increased microbial activity.

INTRODUCTION

The Ninth Avenue Superfund Site, which is listed on the NPL, is scheduled for cleanup under the Superfund Acts of 1980 and 1986. The site is a 17-ac inactive chemical waste disposal area located in Gary, Indiana.

Both solid and liquid wastes are reported to have been disposed at the site. Solid wastes deposited there include industrial construction and demolition wastes. Liquid wastes disposed at the site include oils, paint solvents and sludges, resins, acids and other chemical wastes. Waste disposal operations took place between 1973 and 1980.

The site groundwater is contaminated with a variety of inorganic and organic contaminants. Inorganic contaminants are mainly in the form of road salts (sodium chloride). Organic contaminants detected in significant concentrations in the groundwater are ketones, benzene, toluene, xylenes, ethylbenzene and chlorinated ethenes.

This treatability study was performed for the U.S. Army Corps of Engineers Omaha District and the U.S. EPA RI/FS Region V

This treatability study was performed for the U.S. Army Corps of Engineers Omaha District and the U.S. EPA Region V as part of the RI/FS. Four treatment technologies were evaluated by the U.S. Army Engineer Waterways Experiment Station during the treatability study. The technologies evaluated were activated carbon, air stripping, activated sludge and activated sludge with powdered activated carbon addition. The results of the evaluation of the latter two technologies are presented in this paper.

STUDY OBJECTIVE

The objective of this study was to evaluate, on the laboratory bench-scale level, the potential of biological processes to remove organic contaminants from a composite of groundwater samples collected from six site observation wells. Activated sludge (AS) and activated sludge with powdered activated carbon addition (PAC/AS) were evaluated for their ability to reduce the biochemical oxygen demand, chemical oxygen demand, total organic carbon and organic contaminants listed on the U.S. EPA's Priority Pollutant List from the groundwater composite.

DESCRIPTION OF PROCESSES

Activated Sludge

AS is a biological process that utilizes acclimated bacteria for the aerobic degradation of contaminants in wastewater. Figure 1 is an illustration of a typical AS treatment system. The term "acclimated" means that the bacteria consortium are capable of utilizing the organic contaminants in the influent as their food source.

Biological treatment processes (which include both AS and PAC/AS) are destruction technologies requiring no ultimate disposal of treatment residuals containing hazardous or toxic constituents (assuming that the waste sludges do not contain parent and/or intermediate contaminants). In contrast, activated carbon or air stripping are not destruction technologies. They are phase change technologies that simply transport the contaminants from one phase to another, with activated carbon systems requiring the disposal or regeneration of the spent carbon.

The populations of bacteria in the aeration tanks of AS systems are so great that the air-activated organic biological solids which are made up primarily of dense colonies of bacteria are referred to as activated sludge. The activated sludge/wastewater slurry in
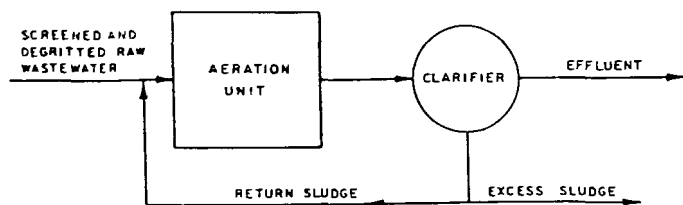
Figure 1
Activated Sludge Treatment System

the aeration tank is commonly known as the mixed liquor (ML). The ML is kept in suspension in the aeration tank by using either mechanical mixers or diffused air. Since biological solids are volatile, bacterial populations in the mixed liquor are often measured using mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS).

Influent is added to the aeration tank at a rate that is carefully controlled to achieve a specific hydraulic retention time (HRT). HRT has units of time and theoretically describes the amount of time a particle of water and theoretically describes the amount of time a particle of water is retained in the aeration tank. As fresh influent enters the aeration tank, treated water or effluent flows out of the aeration tank into the clarifier. The clarifier is a sedimentation tank used to separate the activated sludge from the effluent. To keep a constant population of bacteria in the aeration tank, a portion of the thickened sludge is returned to the aeration tank. Also, since bacteria are constantly reproducing, some of the thickened sludge must be wasted from the bottom of the clarifier or directly from the aeration tank to maintain a constant bacterial population in the aeration tank. The amount of bacteria wastes is determined based on the solids retention time (SRT) of the biological solids. The SRT or sludge age is theoretically the amount of time a particle of solid matter remains in the aeration tank. SRT also has the units of time.

Powdered Activated Carbon/Activated Sludge

PAC/AS is a treatment process that incorporates the benefits of both activated carbon and activated sludge for the removal of organic contaminants from wastewater. PAC/AS systems are usually configured identically to AS systems except that PAC is periodically added to maintain a specific PAC suspended solids (PACSS) in the mixed liquor.

The PAC/AS treatment process relies heavily on biological degradation for the removal of the majority of the organic compounds from the influent. However, if compounds that are not easily degraded are present, then these compounds can be adsorbed into the PAC, thus preventing the loss of these compounds in the effluent resulting in incomplete treatment. PAC has also been added to the AS system to reduce the amount of volatile compounds from off-gasing the treatment system via volatilization in the aeration tank. Once adsorbed, many of the adsorbed contaminants can be degraded directly from the PAC by either the suspended bacteria coming in contact with them or by attached growth microbes using the PAC as a structural substrate.

LITERATURE REVIEW

AS Treatment Process

The suitability of AS for the degradation of a variety of complex xenobiotic compounds has been demonstrated by many researchers.[8, 10, 14] Most of the research activities reviewed generally used the same technical approach selected for this study. The technical approach uses a microbial consortium containing an extremely diverse variety of microbial types, such as mixed liquor from an AS system, as a source of microbial seed for biological reactors. The microbes are slowly exposed to the contaminants in the test influent until all or a portion of the original bacterial

population become acclimated to the target contaminant(s). The chance of successfully establishing a consortium of acclimated bacteria is high because microbe populations capable of mineralizing the contaminants are usually present in activated sludge.

Sanford and Smallbeck[13] used a mixed consortium of bacteria and yeast to degrade a synthetic wastewater comprised of 100 mg/L acetone, 50 mg/L 2-butanone and 125 mg/L methyl isobutyl ketone in bench-scale chemostats. They concluded that treatment of ketones was successful within 48 hr of batch treatment utilizing a stable consortium of microorganisms and yeast.

Kim and Maier[9] evaluated the acclimation and biodegradation potential of chlorinated organic compounds in the presence of various cometabolites. They were able to acclimate a consortium of bacteria from a municipal AS plant capable of degrading 2,4-D (2,4 dichlorophenoxyacetic acid) and 3,5-DCB (3,5 dichlorobenzoate) under aerobic conditions. Combined contaminant concentrations as high as 100 mg/L were successfully degraded. Kim and Maier concluded that seed bacterial consortia should contain as diverse a population of microorganisms as possible to increase the probability of plasmid exchange. In addition, they also suggest that the acclimation phase begin with an influent containing very low concentrations of the target compounds to avoid inhibitory effects.

Bieszkiewics and Pieniadz-Urbaniak[2] evaluated the effect of benzene and xylene at concentrations as high as 75 mg/L and 150 mg/L, respectively, on the work of an AS system. They concluded that increased concentrations of the target compounds generally decreased the COD removals, increased sludge volume index (SVI), increased the number of bacteria and, finally, altered the morphology of the bacterial flocs.

Rozich and Gaudy[12] evaluated the response of an AS system to quantitative loadings of phenol. Phenol concentrations of 500 mg/L were evaluated as a base influent concentration. Initially, shock loadings of 1,000 mg/L of phenol were imposed on the AS system without significant disturbances in treatment occurring. The AS system was then shocked with 2,000 mg/L of phenol which resulted in the collapse of the stability of the system. They concluded that design engineers should design AS systems that will be treating possible inhibitory and/or toxic compounds with high SRTs; especially systems that could be subjected to periodic shock loadings of contaminants.

PAC/AS Treatment Process

There has been considerable research on the feasibility of applying PAC/AS to treat a variety of wastewaters.[4, 5] Nayar and Sylvester[11] evaluated PAC addition to an AS system for increased removal of phenol. Concentrations of phenol as high as 1,300 mg/L were successfully removed. They concluded that the addition of PAC to the aeration tank did not enhance bacterial growth); however, PAC addition could be used to prevent shock loadings of contaminants at toxic levels from disrupting the biological system.

Chao, Yeh and Shieh[3] evaluated the use of PAC/AS systems to remove total phenols and cyanides at concentrations as high as 160 mg/L and 80 mg/L, respectively. They concluded that the PAC addition did not have an appreciable effect on phenol removal; however, they did observe increased cyanide removals with PAC addition.

Hoffman and Oettinger[7] investigated the performance of a two-stage PAC/AS and activated carbon system for the removal of trichloroethylene, 1,4-dichlorobenzene and 2-chlorophenol at a combined concentration of approximately 100 mg/L from a landfill leachate. They concluded that 99.8% removal of the contaminants could be achieved using the two stage system, with only 0.31% of the contaminants removed via air stripping from the aeration tank.

TECHNICAL APPROACH

The following steps were used to implement this study:

Table 1
Chemical Analysis of Groundwater Composite

Analyte	Concentration (mg/l)
Priority Pollutants	
Methylene Chloride	11.00
cis-1,2-Dichloroethane	16.00
2-Butanone	260.00
Acetone	18.00J
Toluene	10.00
Phenol	0.27
2,4-Dimethylphenol	0.63
2-Methylphenol	0.80
4-Methylphenol	0.81
Metals	
Aluminum	1.08
Arsenic	0.01
Barium	0.32
Boron	2.11
Cadmium	0.01
Calcium	589.00
Chromium-III	0.11
Cobalt	0.06
Iron	91.40
Nickel	0.48
Lead	0.04
Magnesium	234.00
Manganese	7.41
Potassium	37.70
Zinc	0.88
Miscellaneous Analytes	
BOD5	2300
COD	4010
TOC	1260
pH	6.78
O-Phosphate	0.601
T-Phosphate	0.912
TKN	76.8
Ammonia	73.2
Nitrate	0.022
Sulfate	93.3
Chloride	566
Salinity	2400

J: Indicates concentration below statistical quantition limits
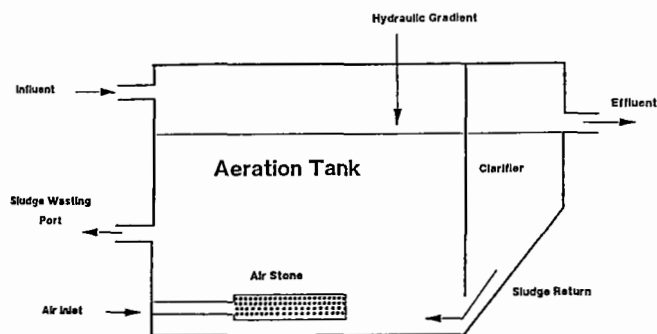
Figure 2
Activated Sludge Bioreactor Used in Study

- Acclimate a consortium of bacteria to degrade the contaminants in the groundwater composite using mixed liquor from a local activated sludge system treating municipal wastewater
- Determine an optimal SRT for an AS system using multiple bioreactors
- Examine the potential benefits of PAC addition to an AS system
- Determine an optimal PAC dose in a PAC/AS for reducing effluent pollutant concentrations.

MATERIALS AND METHODS

Materials

The contaminated water used in this study was a composite of groundwater samples collected from six site observation wells. Table 1 lists the major chemical constituents detected in the groundwater composite.

The bench-scale bioreactors used in this study are illustrated in Figure 2. Two bioreactor sizes were used. The acclimation phase used a single 20-L bioreactor having a 15-L aeration chamber and a 5-L clarifier, while the AS and PAC/AS phases of study used multiple bioreactors with 2.0-L aeration chambers and 1.0-L clarifiers. Influent was delivered to the aeration tank of the bioreactors using peristaltic pumps. Sludge wasting was accomplished through the sludge wasting port located on the side of the bioreactor (Fig. 2). The waste sludge was settled in graduated cylinders of various sizes dependent on the amount of sludge requiring wasting (determined by SRT). The supernatant from the settled waste sludge was mixed with effluent and returned to the bioreactor to make up for the volume of water lost due to sludge wasting.

A bacterial inoculum was obtained from the aeration tank of the City of Jackson, Mississippi, Wastewater Treatment System (JWWTS). This system is a contact stabilization process with a 50-mgd capacity.

The PAC used in this study was obtained from the Calgon Carbon Corporation of Pittsburgh, Pennsylvania. A pulverized version of Filtersorb 300 marketed as BL Type PAC was selected based on recommendations by Calgon personnel after review of the chemistry of the groundwater composite contaminant concentrations.

Acclimation of Bacterial Consortium

The 15-L acclimation bioreactor was completely filled with the mixed liquor from the JWWTS. The bioreactor was initially fed influent to a trickling filter of City of Vicksburg, Mississippi, Wastewater Treatment System (VWWTS). Over a 4-wk period, influent to the acclimation bioreactor was proportionally switched on a volumetric basis from VWWTS influent to the groundwater composite. The groundwater composite contained appropriate nitrogen levels in the form of ammonia; however, phosphate nutrient was added to the influent in the form of potassium monobasic phosphate to achieve a carbon to nitrogen to phosphate ratio of appriximately 100:10:5. This C:N:P ratio was considered adequate because analysis of the effluent indicated that sufficient nitrogen and phosphate nutrients were present in the effluent to prevent the biological system from becoming nutrient-limited.

Acclimation of the bacterial consortium to the contaminants in the groundwater composite was based on the acclimation bioreactor receiving a constant organic loading based on influent 5-day BOD. The rate at which the ratio of groundwater composite to VWWTS influent was increased was determined assuming that the bacterial consortium would easily acclimate to the groundwater compolsite, with little or no lag phase, when acclimated using a constant system influent organic loading. Therefore, the acclimation bioreactor was operated at different HRTs depending on influent composition and respective BOD. The SRT of the bioreactor throughout the acclimation phase was 10.0 days.

During the acclimation period when groundwater was proportionally replacing the VWWTS influent: BOD, COD and TOC removals were determined twice weekly and the MLVSS/MLSS ratio daily. This monitoring was done to ensure that the contaminants in the groundwater composite were not adversely affecting biological activity. If adverse effects such as significant reductions in BOD, COD and TOC removals or dramatic decreases in the MLVSS/MLSS ratio were noted, then these effects could be reversed or minimized by decreasing the rate of groundwater composite addition.

The VWWTS influent had an average BOD of 70 mg/L; therefore glucose was added to increase the influent BOD to approximately 200 mg/L to achieve an organic loading of approximately 0.015 lb BOD/day on the system. The organic loading was adjusted daily by changing system influent feed rates accordingly as influent BOD changed due to the increased proportion of groundwater composite making up the influent. Once the system influent consisted only of groundwater composite, the acclimation bioreactor was operated at a HRT of 3.0 days and a SRT of 10 days (these operational parameters were selected prior to testing based on a literature review of systems treating similar wastes). When

the percent removal of gross pollutants and the MLVSS/MLSS ratios were constant, then the consortium was considered acclimated. Acclimation of the bacterial consortium took approximately 6 wk.

Operation of the AS Bioreactors

After the acclimation process was considered complete, approximately 3L of mixed liquor from the acclimation bioreactor were added to the four 2-L bioreactors. Each AS bioreactor was operated at an HRT of 1.0 day. The AS bioreactors different from each other by SRTs of 2, 4, 8 and 16 days. The purpose of varying the SRTs was to determine an optimal SRT.

Operation of the PAC/AS Bioreactors

After completion of the AS study, the mixed liquors from each of the four AS bioreactors were composited into the 15-L bioreactor used in the acclimation phase of study. The compositing of the mixed liquors was done to ensure that the bacterial consortiums used in the PAC/AS bioreactors initially contained similar microbial populations (AS systems operated at different SRTs can contain different types of bacteria). The 15-L bioreactor was operated at the optimal SRT from the AS study and an HRT of 1 day. The large bioreactor was operated for a period of three SRTs, then approximately 10 L of mixed liquor were added to four of the 2-L bioreactors.

The PAC/AS bioreactors differed by PAC dose. PAC dosages of 1.0, 2.0, 5.0 and 8.0 mg/L were added to the 2-L bioreactors. The amount of PAC removed each day in the waste sludge was replaced with equal amounts of fresh PAC after sludge wasting operations were completed. New PAC was added into the PAC/AS bioreactors by slurrying the fresh PAC with enough effluent to make up for the volume of water lost from the sludge wasting activities.

Chemical Analyses

All gross pollutant, suspended and volatile solids, and oil and grease analyses were performed using methods described in *Standard Methods for the Examination of Water and Wastewater.*[1] Priority pollutant analyses were performed using U.S. EPA Methods SW 846-8270 and SW 846-8260 for volatile compounds and base neutrals/acid extractables, respectively.[6] Chemical analysis of bioreactor off-gases for volatile organic priority pollutants was performed using gas-tight bioreactors equipped with Tenax(TM) traps. Approximately 3.0% of the total off-gas flow from the bioreactors (52 mL/min) was passed through the Tenax traps at a retention time of 12.0 min. The "loaded" Tenax traps were then purged with helium to remove the contaminants. The helium gas was analyzed for volatile organic compounds using a modified version of U.S. EPA Method 846-8270.[6]

STUDY RESULTS

Acclimation of Bacterial Consortium

The operational data for the acclimation bioreactor are presented in Table 2. Table 2 also presents the solids and influent and effluent BOD concentrations over the 23 day period when the influent was proportionally being switched from VWWTS influent to the groundwater composite. The BOD loading on the acclimation bioreactor was kept at approximately 0.015 lb BOD/day throughout the acclimation phase of study (Table 2).

The impact of the groundwater addition on the biological system is illustrated in Figures 3 through 6. Influent and effluent BOD concentrations versus time are presented in Figure 3. In Figure 3, it can be seen that the effluent responded with very slight increases in BOD concentration as influent BOD strength increased; however, the effluent BOD concentration generally remained constant throughout the acclimation period. Figures 4 and 5 illustrate the variation in TOC and COD influent and effluent concentrations as a function of time. The TOC and COD data did indicate a slight increase of these parameters in the effluent, suggesting the existence of some refractory compounds in the groundwater composite. At the end of the acclimation period, the bioreactor was achieving BOD, COD and TOC removals of 97.9, 71.4 and 74.8%, respectively.

As the ratio of groundwater composite to VWWTS influent de-

Table 2
Acclimation Bioreactor Operational Parameters

Test Day	Influent Component Amounts Sewage (liters)	Ground H2O (liters)	HRT (days)	SRT (days)	MLSS (mg/l)	MLVSS (mg/l)	MLVSS/ MLSS	Influent BOD (mg/l)	Effluent BOD (mg/l)	F/M (mg/mg)	Organic Loading (lbs,800/d)
0	15.0	0.0	1.001	10	933.3	723.2	0.77	202	16	0.28	0.007
1	13.5	0.5	1.073	10	778.3	633.3	0.81	211	33	0.31	0.006
2	13.5	0.5	1.073	10	786.7	640.0	0.81	365	--	0.53	0.010
3	12.0	1.0	1.157	10	--	--	--	--	27	--	--
4	12.0	1.0	1.157	10	--	--	--	--	--	--	--
5	10.5	1.5	1.255	10	985.3	815.7	0.83	--	--	--	--
6	10.5	1.5	1.255	10	1178.3	1003.3	0.85	--	--	--	--
7	9.0	2.0	1.370	10	1308.3	1013.1	0.77	598	--	0.43	0.014
8	9.0	2.0	1.370	10	1508.3	1136.7	0.75	--	--	--	--
9	7.5	2.5	1.509	10	1668.3	1195.0	0.72	729	11	0.40	0.016
10	7.5	2.5	1.509	10	--	--	--	--	--	--	--
11	6.0	3.0	1.653	10	--	--	--	--	--	--	--
12	6.0	3.0	1.653	10	1805.0	880.0	0.49	--	--	--	--
13	4.5	3.5	1.860	10	1926.7	1198.3	0.62	--	--	--	--
14	4.5	3.5	1.860	10	2173.3	1306.7	0.60	--	--	--	--
15	4.0	3.0	2.125	10	2035.0	1158.3	0.57	1455	16	0.59	0.023
16	4.0	3.0	2.125	10	2870.0	1488.3	0.52	1455	15	0.46	0.023
17	1.5	4.5	2.480	10	--	--	--	--	--	--	--
18	1.5	4.5	2.480	10	--	--	--	--	--	--	--
19	1.5	4.5	2.480	10	--	--	--	--	--	--	--
20	0.0	5.0	2.976	10	--	--	--	--	--	--	--
23	0.0	5.0	2.976	10	5126.7	2136.0	0.42	1716	53	0.27	0.019
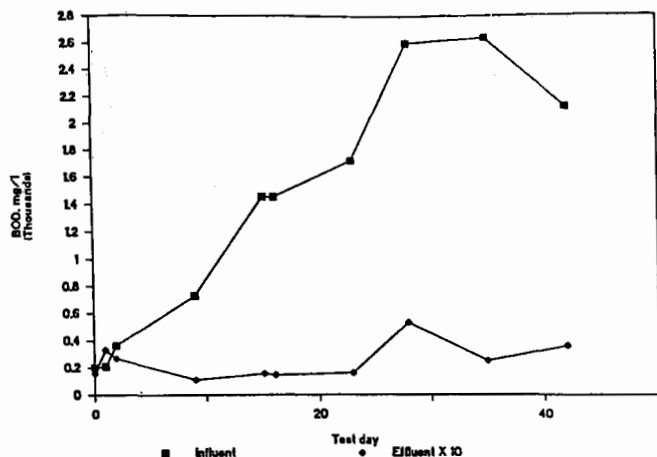
Figure 3
Acclimation Bioreactor Influent and Effluent
BOD Concentrations versus Test Time
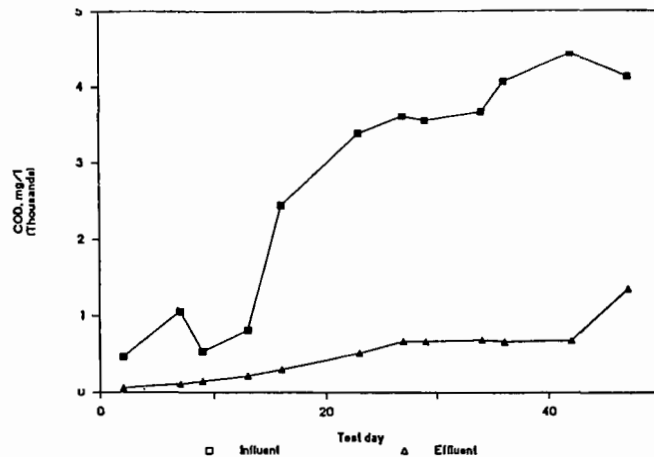
Figure 5
Acclimation Bioreactor Influent and Effluent
COD Concentrations versus Test Time
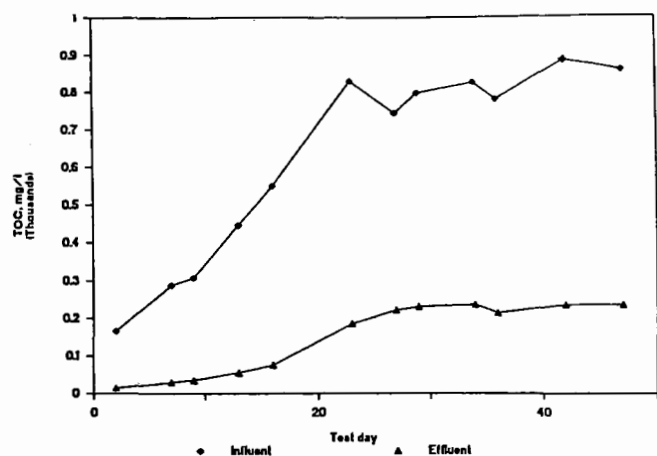
Figure 4
Acclimation Bioreactor Influent and Effluent
TOC Concentrations versus Test Time
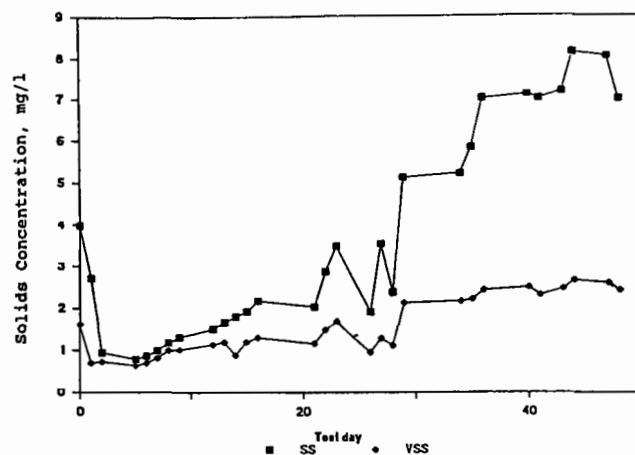
Figure 6
Acclimation Bioreactor MLSS and MLVSS versus Test Time

creased, the color of the mixed liquor changed from a light brown color to an orange-rusty color indicating that reduced iron and manganese in the influent were being oxidized and then precipitated in the aeration chamber. The accumulation of the precipitated cations in the aeration chamber caused a dramatic increase in MLSS. Figure 6 illustrates the MLSS and MLVSS of the acclimation bioreactor throughout the acclimation period. The MLVSS remained constant, while the MLSS increased approximately eight-fold. The constant MLVSS values and gross pollutant (BOD, COD and TOC) removals indicated that a lag phase in biological activity did not occur. Surprisingly, the increased fixed solids concentration did not significantly affect the gross pollutant removal efficiencies of the bioreactor. An analysis of total iron and manganese in the waste sludge indicated iron and manganese concentrations of 35,700 mg/kg and 1,510 mg/kg, respectively.

Table 3 presents the results of organic priority pollutant analysis of the acclimation bioreactor effluent. It can be seen from Table 3 that all priority pollutants previously detected in the influent were removed to levels below the analytical detection limit.

Activated Sludge Evaluation

Table 4 lists the average operating parameters for each of the four 2-L bioreactors. Also listed in Table 4 are volatile organic compound (VOC) measurements of the headspace above the aeration tanks of each of the bioreactors which were measured

Table 3
Priority Pollutant Analysis of Acclimation Bioreactor Effluent

Analyte	Concentration (mg/l)
Methylene Chloride	ND
cis-1,2-Dichloroethene	ND
Toluene	ND
Acetone	ND
2-Butanone	ND
Phenol	ND
2,4-Dimethyl phenol	ND
2-Methylphenol	ND
4-Methylphenol	ND

ND: Not detected

using an HNU™ meter which measures air phase VOC concentrations using an ultraviolet photoionization detector. All of the HNU readings were below 1.0 ppm, indicating that volatilization of contaminants (detectable by a HNU meter) was minimal. This information infers that the ambient air around a bioreactor operating in the field probably will contain little or no measurable VOCs.

Chemical analysis for organic priority pollutants in the off-gas from the eight day bioreactor (Bioreactor No. 3) using the Tenax traps was performed to determine the fraction of organic priority pollutants being removed via volatilization from the aeration tank. This analysis indicated that approximately 4.0% of the

However, the ketones could probably be further degraded if the AS system were operated at SRTs greater than 16 days (i.e., extended aeration mode) or if biological sludge digestion methods were used on-site to reduce the quantity of sludge requiring disposal, thereby further degrading the ketones.

The results of the gross and priority pollutant organic analyses of the AS bioreactor effluents indicated that the four AS bioreactors had lower contaminant removals than the acclimation bio-

Table 4
Activated Sludge Bioreactors Average Operating Parameters

Parameter	Bioreactor No.1	Bioreactor No. 2	Bioreactor No. 3	Bioreactor No. 4
HRT (day)	1.0	1.0	1.0	1.0
SRT (day)	2.0	4.0	8.0	16.0
Average DO (mg/l)	5.8	5.6	5.7	5.7
pH	8.53	8.55	8.49	8.53
Salinity (%)	1.8	1.7	1.7	1.8
Conductivity (umhos)	2912	2725	2829	2844
MLSS (mg/l)	2649.7	5260.4	7390.1	16769.1
MLVSS (mg/l)	1196.0	1831.5	2439.7	4609.6
MLVSS/MLSS	0.451	0.348	0.330	0.275
F/M ratio*	1.45	0.94	0.71	0.38
Headspace HNU Reading (ppm)	<1.0	<1.0	<1.0	<1.0

* Based on BOD

Table 5
Average Gross Pollutant Concentrations and Percent Removals in Bioreactors and Control

	Influent Concentration (mg/l)	Effluent Concentration (mg/l)	Percent Removal (%)
BIOREACTOR NO. 1:			
BOD	1729.1	122.2	92.9
COD	3279.0	1260.0	61.6
TOC	745.0	302.0	59.5
BIOREACTOR NO. 2:			
BOD	1729.1	130.9	92.4
COD	3279.0	1267.0	61.4
TOC	745.0	265.0	64.4
BIOREACTOR NO. 3:			
BOD	1729.1	131.0	92.4
COD	3279.0	1567.0	52.2
TOC	745.0	296.0	60.3
BIOREACTOR NO. 4:			
BOD	1729.1	213.7	87.6
COD	3279.0	1252.0	61.8
TOC	745.0	271.0	63.6

Table 6
Priority Pollutant Analysis of AS Effluents

ANALYTE	Bioreactor No. 1	Bioreactor No. 2	Bioreactor No. 3	Bioreactor No. 4
Methylene Chloride	0.0046J	0.0045J	ND	ND
cis-1,2-Dichloroethene	0.0032J	0.0094	0.0250	0.0069
Toluene	ND	ND	0.0069	ND
Acetone	ND	ND	1.0500	ND
2-Butanone	ND	ND	0.1500	0.0150J
T-Xylene	ND	ND	0.0062	ND
Phenol	ND	ND	ND	ND
2,4-Dimethylphenol	ND	ND	0.0217J	ND
2-Methylphenol	ND	ND	0.0105J	0.0112J
4-Methylphenol	0.1760	0.1510	0.1730	0.0287J
Isophorone	ND	ND	0.0128J	ND

J: Indicates that the concentration is below quantitational limits
ND: Not Detected

Table 7
Analytical Data on Waste Sludge from AS Bioreactors

Analyte	Concentration (mg/kg)
Methlyene Chloride	4.4
Acetone	18.2
2-Butanone	16.2
Phenol	0.71J
Phenanthrene	0.53J
Dibutylphthalate	0.12J
Fluoranthene	0.85J
Pyrene	1.2J
Chrysene	0.49J
Benzo(a)Anthracene	0.40J
Bis(2-Ethlyhexly)Phthalate	5.5
Benzo(b)Fluoranthene	0.42J
Benzo(k)Fluoranthene	0.13J

J: Indicates value is below statistical quantitation limits

Table 8
PAC/AS Bioreactors Average Operating Parameters

Parameter	Bioreactor No.1	Bioreactor No. 2	Bioreactor No. 3	Bioreactor No. 4	Control
HRT (day)	1.0	1.0	1.0	1.0	1.0
SRT (day)	8.0	8.0	8.0	8.0	8.0
DO (mg/l)	7.3	6.5	7.1	7.3	5.7
pH	8.44	8.27	8.25	8.34	8.49
Salinity (%)	0.18	0.17	0.18	0.19	0.17
Conductivity in micromhos	2776	2837	2743	2933	2829
PACSS (mg/l)	1000	2000	5000	8000	0
TSS (mg/l)	11438	10663	20399	26033	
MLSS (mg/l)	10438	8663	15399	18033	7390
MLVSS (mg/l)	4394.0	4514	10162	14228	1831
MLVSS/MLSS	0.421	0.521	0.660	0.789	0.330
F/M ratio*	0.37	0.36	0.16	0.11	0.71
Headspace HNU Readings (ppm)	<1.0	<1.0	<1.0	<1.0	<1.0

* Based on BOD
TSS: Total Suspended Solids (includes PACSS)

organic priority pollutants were being removed due to volatilization. Therefore, it was concluded that contaminant removal due to volatilization from the aeration tank was minimal compared to the amount of contaminant being biologically degraded. This conclusion was consistent with the contaminant composition of the groundwater which was comprised primarily of ketones which are relatively nonvolatile at standard temperature and pressure.

Table 5 contains influent and effluent BOD, COD and TOC analyses along with the percent removals achieved in each bioreactor. There was little difference observed in the performance of the various bioreactors for removal of the gross pollutants (BOD, COD and TOC). Therefore, at an HRT of 1 day there was no appreciable difference in BOD, COD and TOC removals for the range of SRT evaluated.

Table 6 lists the results of the priority pollutant analyses of the four bioreactors' effluents. The effluent from Bioreactor No.3 had more organic contaminants detected than the other three effluents. However, except for acetone, the concentrations detected in the Bioreactor No. 3 effluent were all near the analytical detection limits of the respective contaminants.

To complete the mass balance of organic contaminants around the AS bioreactors, a priority pollutant analysis on a composite of waste sludges from all of the bioreactors was performed. The

reactor. There are two factors that could have individually or jointly contributed to the difference in the performance of the acclimation bioreactor versus the performances of the four AS bioreactors. The first factor was that the hydrodynamic difference in terms of mixing efficiency between the large and small bioreactors affected bioreactor performance by reducing the contact frequency of the microbes with the contaminants. From visual observations made during both study phases, the larger bioreactor seemed to mix the ML more efficiently than the smaller units. The 2-L bioreactor had problems keeping the ML properly suspended. The second, and probably more important, factor was that the 2.0-L bioreactors were operated at a lower HRT, indicating that some of the contaminants may require longer treatment times.

PAC/Activated Sludge Evaluation

The operating parameters and treatment conditions for the PAC/AS bioreactors are presented in Table 8. The PAC/AS bioreactors were operated at an HRT of 1 day and an SRT of 8 days. The 8-day SRT was selected because relatively little difference in the quality of the effluents from the four AS bioreactors was observed during the AS study. Of the four bioreactors evaluated in the AS study, the 8-day SRT bioreactor (Bioreactor No. 3) had the lowest removals of TOC and COD. Since there was not an apparent optimal SRT, an 8%-day SRT was selected to evaluate the benefit of PAC addition to an AS system that was not removing extremely high percentages of the TOC and COD from the influent.

In Table 8, we report the concentrations of VOCs in the off-gases from each PAC/AS bioreactor measured using the HNU meter; all VOC concentrations were less than 1.0 ppm. Chemical analysis for organic priority pollutants in the off-gas from the 8.0-g/L PAC/AS bioreactor was performed to assess the amount of contaminant removal achieved via volatilization. This analysis indicated that approximately 2.6% of the priority pollutants were being removed via volatilization from the aeration tank of the PAC/AS bioreactor. Therefore, as was the case with the AS bioreactor, it was concluded that the majority of the priority pollutants were being removed due to biological degradation.

To fully evaluate the benefits of PAC addition to the activated sludge systems, the removal efficiencies obtained in the PAC/AS bioreactors were compared to those of the 8-day SRT AS biore-

Table 9
Average Gross Pollutant Concentrations and Percent
Removals in the PAC/AS and Control Bioreactors

	Influent Concentration (mg/l)	Effluent Concentration (mg/l)	Percent Removal (%)
PAC/AS BIOREACTOR NO. 1:			
BOD	1611.2	80.2	95.0
COD	3695	1029.0	72.2
TOC	775	297.6	61.6
PAC/AS BIOREACTOR NO. 2:			
BOD	1611.2	127.7	92.1
COD	3695	1063.0	71.2
TOC	775	281.7	63.7
PAC/AS BIOREACTOR NO. 3:			
BOD	1611.2	53.2	96.7
COD	3695	673.0	81.8
TOC	775	175.9	77.3
PAC/AS BIOREACTOR NO. 4:			
BOD	1611.2	36.9	97.7
COD	3695	490.0	86.7
TOC	775	145.0	81.3
CONTROL REACTOR:			
BOD	1729.1	131.0	92.4
COD	3279.0	1567.0	52.2
TOC	745.0	296.0	60.3

Table 10
Priority Pollutant Analysis of PAC/AS and Control Bioreactors

ANALYTE	BIOREACTOR EFFLUENT				
	No. 1	No. 2	No. 3	No. 4	CONTROL
Methylene Chloride	0.0109	ND	0.104	0.0738	ND
cis-1,2-Dichloroethene	0.0172	0.0211	ND	ND	0.025
2-Butanone	ND	ND	0.0226J	0.329	0.15
Acetone	ND	ND	ND	ND	1.05
Toluene	ND	ND	ND	ND	0.0069
T-Xylene	ND	ND	ND	ND	0.0062
Phenol	0.0012J	0.0053J	0.0035J	ND	ND
2,4-Dimethlyphenol	0.0005J	0.008J	0.0017J	ND	0.0217J
2-Methylphenol	ND	ND	ND	ND	0.0105J
4-Methylphenol	0.0027J	0.20	0.13	ND	0.1730J
Benzoic Acid	0.003J	0.0055J	0.007J	ND	ND
Isophorone	0.012	0.013	0.011	ND	0.0128J

J: Denotes concentration is below statistical quantitiion limits
ND: Not detected

actor. The 8-day SRT AS bioreactor will be referred to herein in this section as the control bioreactor.

Table 8 also lists the ratios of MLVSS/MLSS for each PAC/AS bioreactor. As PAC dose increased, the MLVSS and MLVSS/MLSS ratio also increased, indicating an overall increase in biological activity with increasing PAC dose. Several explanations for the increase in biological activity with increased PAC dosage were postulated. One explanation is that the PAC removed contaminants that were inhibiting biological activity resulting in a liquid phase more conducive to biological activity. A second explanation is that an attached growth population of microorganisms were using the PAC as a structural substrate. The attached growth consortium may be better suited for degradation of the more difficult-to-degrade compounds that were making up the TOC and COD in the effluents from the AS bioreactors. The third explanation is that the PAC was adsorbing compounds that were kinetically slower to degrade. Once adsorbed, these compounds can be utilized by the bacteria as an additional food source. As PAC dose increased, the overall adsorptive capacity of the bioreactor increased, thereby concentrating the amount of food available to the microbes.

The results of the gross pollutant analyses of the four PAC/AS and control bioreactor effluents are presented in Table 9 and illustrated in Figure 7. The removal of TOC and COD increased dramatically with increasing PAC dose. The removals of the gross pollutants also increased with increasing VSS/SS ratios which is illustrated in Figure 7. The observed increase in biological activity is further substantiated by the increased removal of the gross pollutants. The BOD removals achieved in the AS bioreactors were already high; therefore, only a slight improvement in BOD removals was observed with increased PAC dose (Fig. 7).

BODo: Influent BOD
CODo: Influent COD
TOCo: Influent TOC

■ VSS/SS   • BOD/BODo   ▲ COD/CODo   × TOC/TOCo

Figure 7
PAC/AS MLVSS/MLSS
Ratios and Gross Pollutant Removals
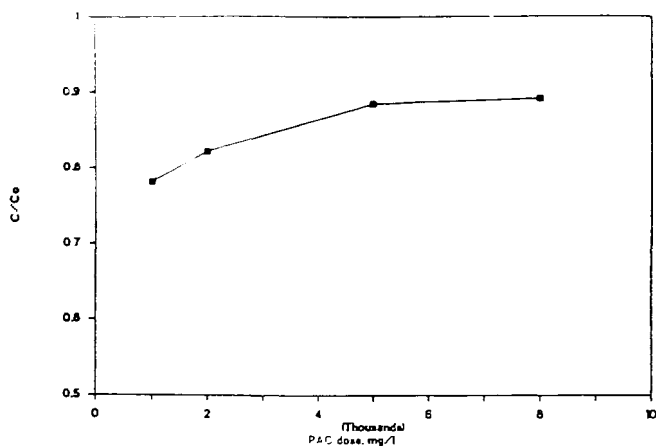
Figure 8
Effect of Increasing PACSS on Oil and Grease Removal

Table 10 lists the results of priority pollutant analyses of the four PAC/AS and control bioreactors. There was not an appreciable difference between any of the bioreactors (including the control) in the removal of priority pollutant compounds. The 8,0-g/L PAC bioreactor does indicate slightly better phenolic compound removal due to the absence of these compounds in the effluent.

Although not analyzed in the AS phase of study, the influents and effluents from the four PAC/AS bioreactors were analyzed for oil and grease concentrations. These data are summarized in Figure 8. As the PAC does increased, the removal of oil and grease also increased.

CONCLUSIONS

The acclimation phase of this study indicated that an inoculum from a suspended growth municipal wastewater treatment plant could be acclimated to the contaminants in the Ninth Avenue Site groundwater composite samples without an observed lag in biological activity. Reduced iron and manganese in the groundwater composites caused a dramatic increase in the MLSS due to cation oxidation.

Based on analysis for organic priority pollutants of the off-gases from both biological systems (AS and PAC/AS) and of a composite sample of waste sludge, it was concluded that biological degradation accounted for a majority of the priority pollutant removal achieved by both biological systems.

The activated sludge process exhibited a potential for removing contaminants in the site groundwater. BOD removals were always in excess of 95%. However, TOC and COD removals were only in excess of 50%. Few priority pollutants were detected in the effluents from the AS bioreactors. Those priority pollutants detected, except for acetone, were at concentrations very near their respective analytical detection limits.

The addition of PAC to the activated sludge did improve the removal of COD and TOC from the influent. The removal of the gross pollutants increased with increased PAC dose. A PAC dose of 8.0 g/L resulted in percent removals in excess of 80% for the COD and TOC in the groundwater composite. Also, fewer priority pollutants were detected in the 8,0-g/L PAC dose bioreactor

effluent than the effluents from the other PAC/AS bioreactors.

In summary, AS treatment augmented with the addition of PAC seemed to be more effective than the AS biological system alone for removing the gross pollutants and organic priority pollutants from the groundwater composite.

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Treatability Study of Biological Treatment System and In Situ Remediation at a Remote Superfund Site

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ABSTRACT

In January 1988, officials of a state environmental agency became concerned about an ongoing accumulation of stormwater within an inactive hazardous waste impoundment containing principally coke plant wastes. The structural integrity of the impoundment was suspect, the three million gallon stormwater accumulation was approaching the impoundment's capacity and several downstream drinking water supplies were threatened. The agency notified the U.S. EPA, which determined that a CERCLA Section 106 removal action was required. A consent decree requiring removal of the impounded water was issued in August 1988.

The initial treatment technology implemented evolved from an agency recommendation and the practicalities of a remote site lacking utilities. This technology (air stripping and activated carbon) was in place by mid-December, and treated water discharge began in late December. Discharging was stopped shortly thereafter due to elevated levels of contaminants in the discharge.

The agency was satisfied that the immediate danger had been relieved by the removal and treatment of 15% of the accumulated water. Therefore, they agreed to postpone further removal until a laboratory treatability study could be conducted by the consulting engineers retained by the PRPs. The study demonstrated that biological treatment offered the most effective and least costly treatment approach. The results from this study will be discussed.

A temporary treatment basin was constructed adjacent to the first impoundment in May and June of 1989. The wastewater was transferred and seeded with bacteria in mid-July. An additional accumulation of contaminated water was transferred in late August. Aeration/oxidation time was nine weeks. The COD reduction was in general agreement with the predicted oxygen transfer rate of the aeration equipment, and wastewater quality was in agreement with that predicted from laboratory studies. Approximately 82% percent removal of TOC was achieved.

The paper will also illustrate the effectiveness of biological treatment on a wide range of organic compounds, the predictability of full-scale performance from bench-scale testing and the expeditious manner in which biological treatment can be implemented.

INTRODUCTION

The Municipal and Industrial Disposal Company (MIDC) operated a hazardous waste disposal facility in Southeastern Allegheny County, Pennsylvania from 1979 to August 1983. Operations ceased when the Pennsylvania Department of Environmental Resources (PaDER) suspended the MIDC permit because of permit and consent order violations. The site has remained inactive since 1983. Waste materials known to have been disposed at the site include coal tar decanter sludge, spent solvents and metal-bearing wastes.

The Phase I Disposal Pit was created by constructing dike walls above the existing grade and then placing waste material within the lined diked area. Waste material was not covered when operations ceased and rainwater accumulated within the diked area. Through constant contact with the waste material, soluble chemical compounds contaminated the estimated 3.5 million gallons of accumulated water.

In 1988, PaDER officials became concerned that a dike failure would threaten several downstream drinking water supplies. PaDER notified the U.S. EPA of their concerns at MIDC. After an assessment of the situation, the U.S. EPA determined that a CERCLA Section 106 removal action was warranted.

Later that year, the U.S. EPA and the potentially responsible parties (PRPs) entered into a Consent Order and Agreement to conduct a removal action at the MIDC site. One requirement of the Order was to remove the liquid layer contained in the Phase I Disposal Pit.

The initial treatment technology implemented evolved from an agency recommendation and the practicalities of a remote site lacking utilities. The PRPs implemented the agreed technology (air stripping and activated carbon), and the treatment system was in place by mid-December. After verification of the quality of the treated water by sampling and analysis, discharge from the on-site treatment system began in late December. Discharging was stopped shortly thereafter due to elevated levels of contaminants in the discharge.

The system could not respond to fluctuating influent characteristics and overall influent concentrations which were greater than expected. More rigorous sampling and characterization of the pond water showed conspicuous stratification (Table 1) and greater organic loads than anticipated from the previously available data. Water treatment operations eventually revealed that the selected technology could not consistently meet the stipulated technology based effluent quality limitations. Acetone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) proved particularly difficult to remove to the specified limits by the selected treatment scheme. The treatment system was subsequently dismantled and demobilized.

Approximately 15% of the impounded water had been treated and discharged before cessation of operations. The agencies were satisfied that the immediate danger posed by the site had been at least temporarily relieved. Therefore they agreed to postpone further action until consulting engineers retained by the PRPs could evaluate other alternatives.

A number of on-site and off-site water management schemes were considered. Off-site methodologies investigated were incineration, the use of RCRA Treatment, Storage and Disposal Facilities and Publicly Owned Treatment Works. On-site treatment schemes investigated were incineration, solidification and biological treatment. Biological degradation of numerous solvents and of organics associated with coal coking operations, was well documented.[1-25] Table A-1 contains numerous

Table 1
Phase I Disposal Pit Impounded Water Characterization and Initial Discharge Limits
MIDC Site

PARAMETERS*	Shallow Samples mg/l	Deep Samples mg/l	Effluent limitations Applied for Stripping/Carbon Adsorption		
			Mo Avg mg/l	Daily Max mg/l	Inst Max mg/l
Suspended Solids	27	144			
Dissolved Solids	2800	11800			
Volatile Solids	1100	5600			
Total Organic Carbon	1500	4900			
Soluble Organic Carbon	1500	4900			
Chemical Oxygen Demand	5600	17000			
Phosphorus	0.19	2.2			
Ammonia	24	108			
Oil and Grease	4.4	8.4	0.15	0.3	0.3
Phenolics	13.9	17.8	115	230	285
Cyanide	0.78	3.7	0.005	0.01	0.0125
Sulfide	1	2.8			
Selected Metals:					
Arsenic	1.8	3.5	1.29	2.58	3.2
Magnesium	80	280			
Selected Organics:					
Phenol	2.3	9.1			
2-Methyl Phenol	0.3	1.3			
4-Methyl Phenol	1.4	4.8			
Pentachlorophenol	ND	2.1	0.05	0.1	0.125
Benzoic Acid	ND	51			
Butanoic Acid	2	24			
Hexanoic Acid	6.2	12			
Acetone	5.1	100	0.4	0.8	1
Methyl Ethyl Ketone(MEK)	4	57	0.4	0.8	1
Methyl Isobutyl Ketone(MIBK)	0.4	18	0.12	0.24	0.3

* The parameters and effluent limits shown are not a complete list.

The above table lists only the principal compounds and their associated limits.

ND = Not Detected

citations of wastewater treatment efficiency for specific compounds based on the type of treatment and source of the wastewater stream. The data in this table were taken from a literature search in "Estimation of Removal of Organic Chemicals During Wastewater Treatment," in 1986, for the U.S. EPA, The original data are from research conducted on pilot- and full-scale treatment systems.

The consulting engineers had participated in the successful utilization of biological treatment for the organic chemicals of concern and were satisfied of its utility and cost-effectiveness. In addition, the PRPs had had good experience with biological treatment of comparable wastewaters within their own facilities.

The preliminary review of potential treatment and disposal methodologies concluded that biological treatment processes held the most promise for successful management of the impounded water because of their ability to remove a wide variety of organic compounds from contaminated water at varying concentrations at a reasonable cost. The agencies agreed to postpone further removal until a laboratory treatability study could be conducted to demonstrate the effectiveness of biological treatment.

BACKGROUND

Sampling of the feed to the air stripper/carbon treatment system showed inconsistencies with earlier data collected by the agencies in 1988. To establish a basis for design of a new treatment system, it was necessary to accurately determine the volume and composition of the impounded water.

Liquid samples were collected from the Phase I Disposal Pit from approximately one foot below the liquid surface and from approximately one foot above the waste/liquid interface. The pit was divided into quadrants and samples were obtained at two depths in the center of each quadrant.

The samples were analyzed for the following indicator parameters and nutrients: Suspended Solids, Chemical Oxygen Demand, Dissolved Solids, Phosphorus, Volatile Solids, Ammonia, Total Organic Carbon,

Oil and Grease (Freon Extractables), Soluble Organic Carbon, and Phenolics.

These parameters were selected to:

- Determine the physical nature of the majority of contaminants (dissolved or suspended)
- Evaluate the potential for biological treatment enhancement by nutrients
- Determine initial operating parameters and loading for the biological treatability scenarios

Results of these analyses are presented in Table 1 for the shallow and deep samples.

Composite samples generated from the set of shallow samples and deep samples were subjected to these analyses: cyanide, sulfide, ignitability, Btu, metals, acid extractable organics, and base neutral extractable organics. The organic scans included the "tentatively identified compounds" library search procedure on both fractions. Table 1 also shows the analytical results.

The final group of parameters is the volatile organic compounds, including a library search. Since the U.S. EPA protocols specify that samples intended for analysis of volatile compounds are to be grab samples, two discrete samples were selected; one shallow and one deep.

These analytical data indicate that contaminants in the impounded water are generally more concentrated closer to the waste material, i.e., deeper in the liquid layer. Typically each analyte was three to five times more concentrated in the deep samples.

Concurrent with sample activities, depth soundings were taken throughout the impoundment. From depth sounding data, it was estimated that approximately 3.5 million gallons of water had accumulated within the Phase I Disposal Pit as of the date of sampling.

BIOLOGICAL TREATABILITY STUDY

Three scenarios were considered for the treatability study. The scenarios are described in the next sections of the paper.

Scenario No. 1: Blending and Biological Treatment at Nearby Coke Works

A nearby coke works, owned by a PRP, utilized an activated sludge process to treat coal coking wastewaters. Phase I Disposal Pit wastewater and the coke works wastewater were blended at a 1:20 ratio consistent with expected hauling and receiving capabilities. A bench-scale bioreactor was seeded with sludge from the coke plant and operated at an F/M (Food/Microorganism ratio defined as the gram COD applied/gram MLVSS per day) of 0.3 after blending.

Scenario No. 2: Treatment On-Site Using Mobile Equipment

For this scenario, modular, transportable equipment was envisioned for treatment of the impounded water. A low load activated sludge system was selected as the most promising approach, due to availability and proven performance. To simulate this scenario, a bench-scale activated sludge process was selected for testing at F/Ms of 0.1 and 0.2.

Scenario No. 3: In Situ Treatment

In situ treatment would consist of the introduction of surface aerators to the Phase I Pit and the addition of seed bacteria and nutrients. The seed bacteria preferably would have some degree of acclimation to the pond organics, as would occur with biological sludge from a nearby coke works wastewater treatment plant. To simulate this scenario, a small bench-scale reactor was operated.

The experimental design is summarized in Table 2.

MATERIALS AND METHODS

A laboratory treatability study was conducted to evaluate all three scenarios. Two activated sludge reactors were set up to simulate Scenarios 1 and 2. Each consisted of a stirred, aerated compartment of 5 gallons, separated by a vertical baffle to provide quiescent conditions at the overflow. Operating conditions were set to allow the reactors to operate at F/M ratios of 0.3 (Scenario 1), 0.2 and 0.1 (Scenario 2). All reactors were seeded with sludge from a local coke works biological wastewater treatment facility. Nutrients were added to the reactors to supplement the bacteria and ensure new cell growth.

Table A-1
Selected Wastewater Treatment Removal Efficiencies[a]
(22, 23, 24 and 25)

Chemical	Percent Removal	Waste Stream	Initial Chem Conc	Treatment	Scale	Temp C	Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference
Acetone	73.0			Activated Sludge	Pilot	NR	NR	8 hrs	NR	Kincannon et al, no date
Anthracene	>96.0	Coke processing plant	7.2 ug/l	Activated Sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Anthracene	>99.0	Coke processing plant	85 ug/l	Activated Sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Anthracene	98.0	Coke processing plant	15 ug/l	Activated Sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Napthalene	>99.0	Coke processing plant	560 ug/l	Activated Sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Napthalene	>99.0	Coke processing plant	180 ug/l	Activated Sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Phenol	91.00	Indust Creosote Waste	47 mg/l	Microb Treat Tower	Full	10	116 mg/l	NR	NR	Vela and Ralston, 1978
Phenol	94.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	227 mg/l	12 days	NR	Mahmud and Thanh, no date
Phenol	95.30	Refinery Wastes	16.2 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	90.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	285 mg/l	1 day	NR	Mahmud and Thanh, no date
Phenol	90.70	Refinery Wastes	22.7 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	98.20	Refinery Wastes	18.5 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	95.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983a
Phenol	86.30	Refinery Wastes	19.9 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	93.30	Refinery Wastes	13.5 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	96.70	Refinery Wastes	19.6 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	90.70	Refinery Wastes	21.1 mg/l	Aerated Lagoon	Full	NR	250 mg/l	3 days	NR	Mahmud and Thanh, no date
Phenol	0-5	Ind. Wastewater	13-19 mg/l	Activated Sludge	Full	NR	931 mg/l	NR	NR	Feller, 1979
Phenol	90.80	Refinery Wastes		Batch Activated Sludge	Full	NR	NR	10 hr	NR	Mahmud and Thanh, no date
Phenol	75.30	Refinery Wastes	20.3 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	94.10	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	245 mg/l	10 days	NR	Mahmud and Thanh, no date
Phenol	76.20	Refinery Wastes	20.6 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	81.30	Refinery Wastes	20.3 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	99.00		39.6 mg/l	Seg Batch Reactor	Full	24-26	NR	8-9 days	NR	Herzbrun et al, 1985
Phenol	97.40	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	265 mg/l	10 days	NR	Mahmud and Thanh, no date
Phenol	80.20	Refinery Wastes	21.2 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	82.70	Refinery Wastes	21.6 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date

Chemical	Percent Removal	Waste Stream	Initial Chem Conc	Treatment	Scale	Temp C	Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference
Phenol	80.20	Refinery Wastes	24.8 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	86.20	Refinery Wastes	24.5 mg/l	Cont Activated Sludge		6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	88.60	Refinery Wastes	23 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	92.80	Refinery Wastes	21.1 mg/l	Aerated Lagoon	Full	NR	290 mg/l	3 days	NR	Mahmud and Thanh, no date
Phenol	80.30	Refinery Wastes	20.2 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	93.70	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	260 mg/l	7 days	NR	Mahmud and Thanh, no date
Phenol	96.30	Refinery Wastes	18.8 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	88.30	Refinery Wastes	25.7 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	85.40	Refinery Wastes	20.3 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	93.50	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	282 mg/l	5 days	NR	Mahmud and Thanh, no date
Phenol	94.30	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	265 mg/l	5 days	NR	Mahmud and Thanh, no date
Phenol	94.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	260 mg/l	7 days	NR	Mahmud and Thanh, no date
Phenol	81.40	Refinery Wastes	18.1 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	NR	Mahmud and Thanh, no date
Phenol	90-100	Coke Plant Effluent	655 mg/l	Activated Sludge	Pilot	NR	45 mg/l	NR	NR	Osantowski & Hendriks, no date

Table 2
Experimental Design; MIDC Impoundment Water Treatability; MIDC Site

Scenario	1	2	3
Raw Waste	95% Coke Plant 5% MIDC	MIDC	MIDC
Reactor	R-1	R-2	R-3
Type	Continuous	Continuous	Batch
Description	Activated Sludge	Activated Sludge	Aerobic Digestion
F/M	0.3	0.2 0.1	N/A N/A

To determine when stable conditions had been attained at a given F/M, selected parameters were routinely monitored until constant values were obtained. Total organic carbon (TOC), methyl ethyl ketone (MEK), biochemical oxygen demand (BOD) and flow were monitored in the influent. In the mixed liquor, the concentrations of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were monitored and, in the effluent, TOC and MEK were monitored. Weeks were required for reactor conditions to stabilize; during that time the biomass acclimated to the new substrate. Large variations in sludge and mixed liquor characteristics were observed during the stabilization period.

The batch reactor study to simulate the in situ treatment, Scenario 3, was designed based on initial toxicity tests (dissolved oxygen uptakes) to determine at what concentration the pond water could be mixed with

activated sludge without toxicity. Initial testing did not indicate any toxicity problems. Seventy-five percent of the pond water and twenty five percent of the coke plant aeration tank mixed liquor were combined for the uptakes. An 8-gallon reactor was used to simulate the Phase I Pit holding the impounded water. In order to be conservative, the reactor was prepared with water samples drawn from the bottom of the impounded water layer, where the highest organic levels were observed.

The first batch reactor was seeded to a MLVSS of approximately 500 mg/L. The reactor was then vigorously aerated and monitored. A second test was conducted to check/confirm the results of the first test. The second reactor used all the settled sludge from the first reactor. After adding impounded water, the second reactor was vigorously aerated and monitored. The treatment performances for the biological reactor were monitored for BOD_5, TOC, COD, MEK and organic compounds analysis.

RESULTS AND DISCUSSION

Reactor Performance

Scenario 1: Blending and Biological Treatment at Nearby Coke Works

The organic removal increased with time due to acclimation of the bacteria to the wastewater. After approximately four weeks of acclimation, the average organic removal based on BOD was 88% (Table 3). MEK was removed by approximately one order of magnitude, but the required removal rate could not be achieved without the 20:1 dilution provided by the other wastewater streams. Overall, this reactor did not perform as well as the on-site continuous or batch reactors.

Table 3
Summary of Reactor Performance; MIDC Impoundment Water Treatability Study; MIDC Site

Scenario	R-1 (Continuous Blend)	R-2 (Continuous)		R-3 (Batch)	
	1	2a	2b	3a	3b
Raw Waste:					
TOC, mg/l	783	1950	2020	2000	1050
BOD, mg/l	1110	3100	2980	2800	1400*
MEK, ug/l	613	11800	13500	13500*	7150
Operating Parameter:					
F/M	0.3	0.2	0.1		
MLVSS	3000	4800	3700	3600	4400
Effluent:					
TOC	245	1100	524	453	333
BOD	127	960	88	26	5
MEK	79	1725	89	<10.0	17
% Removal:					
TOC	69	44	74	77	68
BOD	88	69	97	>99	>99*
MEK	79	85	99	>99*	>99

*Estimated

All data shown are averaged during steady state

Scenario 2: Treatment On-Site Using Mobile Equipment

The continuous reactor showed better performance at a reduced loading. The initial average F/M loading (gram COD/gram MLVSS/day) was 0.2. The second F/M loading was 0.1. At these loadings, the removals based on BOD were 69% and 97%, respectively (Table 3). MEK dropped to below the expected 1000 ug/L effluent limitation at the lower loading.

Scenario 3: In Situ Treatment

The batch reactor showed the best performance overall (Table 3). After 10 days of operation, the organic removal based on BOD exceeded 99% (Table 3), and the projected effluent limit for MEK was achieved. The second batch test confirmed the results of the initial test and showed that MEK removal exceeded 99% after 10 days of operation.

The operating data and the results of the batch reactor performance

are summarized in Tables 3 and 4. In all cases, the previously applied discharge limits were attained or approached. In some cases, detection limits were too high to determine whether or not discharge limits could be attained. This finding was attributed to interferences from other organics in the matrix, which often occur in high strength wastewaters.

Table 4
Operating Data for Batch Treatability Tests; MIDC site

	Test A	Test B
Volatile Suspended Solids (Avg)	3600	4400
Time for TOC removal, days	<6.0	<3.0
Time for MEK removal, days	13	13
Total test duration, days	24	13

BOD removal was computed as an average value from mean performance data. Scenario 3 offered the best removals in the shortest period of time for the least cost. Therefore, this scenario was recommended for implementation. High detection limits occurred in Scenario 3 at least once with the following parameters: cyanide, MIBK, phenanthrene, 2-hexanone, and fluoranthene. The discharge limits were not achieved for the following parameters: phenol, arsenic, boron, manganese and nickel. Therefore, one recommendation of the treatability study was to renegotiate the limits applied to these compounds.

Proposed limits were submitted to PaDER by the PRPs (Table 5). The acceptability of these limits was vigorously debated by the PRPs and the involved agencies and was not resolved until immediately before discharge of the treated impoundment water.

Table 5
Performance of Batch Treatability Tests; MIDC Site

Parameters	Test A		Test B		Proposed Effluent Limitations
	Influent	Effluent	Influent	Effluent	Inst. Max
TOC	2000	450	1050	330	
BOD	2800	26	1400	5	
Phenolics (4AAP)	6.35	0.1	4.35	0.4	0.4
Cyanide	15.5	0.05	15.5	0.87	0.05
Arsenic	2.3	1.7	1.7	1.3	3.2
Methyl Ethyl Ketone(MEK)	13.5	0.01	7.3	0.042*	1
Methyl Isobutyl Ketone(MIBK)	1.25	0.01	0.79	0.2	

Note: All concentrations are in the unit of mg/l.
* compound was detected in blank

FULL-SCALE IMPLEMENTATION

In Situ Biotreatment System Design

The bench-scale reactors yielded performance data, but no data that were readily utilizable for sizing aeration equipment. The bench-scale reactors were vigorously aerated to assure that performance would not be limited by oxygen requirements or by the quantity of biomass in suspension and to demonstrate the concept in the available time. In full-scale operation, aeration would be less vigorous to avoid disturbing the wastes at the bottom of the impoundment. The minimum recommended power level for mixing and aeration in lagoons is approximately 30 hp/mg.[14] Typical horsepowers commonly used in aerated lagoons range from 10 to 60 hp/mg. A range of anticipated performance information is shown in Table 6. Based on an anticipated waste volume of 3.5 million gallons, initial volatile suspended solids of 400 mg/L and aeration horsepower of 30 hp/mg were selected as objectives.

Table 6 indicates that MLVSS would be rate-limiting and that the required BOD removal could be accomplished in 26 to 65 days, depending on oxygen transfer efficiency and on the concentration of

Table 6
Anticipated In Situ Performance; MIDC Site

Case	Units	Expected	Worst
Total Mixing Power	HP	105	105
Total BOD in Pond (Avg. of 3000 mg/l)	lb	40000	40000
If Oxygen is Rate Limiting:			
Rate of Oxygen Delivery	lb/HP-hour	2.5	1.5
Rate of Oxygen Utilization (Estimated)	lb O2/ lb BOD Removed	1.5	1.5
Total Total Oxygen Delivery	lb/day	6300	3700
Total BOD Removal	lb/day	4200	1260
Time Required for BOD Removal	day	10	32
If MLVSS is Rate Limiting:			
Anticipated MLVSS	mg/l	500	200
Uptake Rate (Est. Avg. From Lab Data)	mg O2/l min/ mg/l MLVSS	1.1E(-4)	1.1E(-4)
Rate of Oxygen Uptake	mg/l-day	79	32
Oxygen Consumable by MLVSS	lb/day	2310	924
Total BOD Removal	lb/day	1540	616
Time required for BOD Removal	day	26	65

Figure 1
MIDC Impounded Stormwater Remediation
Process Monitoring Data

Figure 2
MIDC Impounded Stormwater Remediation
MEK Concentration vs. Days of Operation

biomass (MLVSS) maintained in suspension. Additional time would be required for the seed to acclimate, to settle the biological solids and to discharge the treated water. There also was concern that removal of organics could be anticipated to become less efficient as the BOD decreased, which would extend the treatment period. Total time from seeding to an empty pond was predicted to be twelve to eighteen weeks.

Implementing On-Site Treatment

In May 1989, another emergency condition was declared at the MIDC site due to increased seepage at the toe of the eastern dike and rising water levels within the Phase I Disposal Pit from heavy precipitation. An emergency construction project was initiated to buttress and strengthen the dikes. Although batch biological treatment within the Phase I Disposal Pit would have been the most expeditious and effective alternative to implement, two major drawbacks were evident:

- The persistent threat of dike overtopping by the rising water level would not be quickly alleviated because of the time period necessary for proper treatment and
- Leaving the impounded water in the Phase I Pit and in contact with the waste material would complicate the aeration application and possibly prolong treatment by enhancing the flux of contaminants from the solid phase to the liquid phase

The alternate plan developed to implement batch treatment involved construction of a lined treatment basin, transferring the water from the Phase I Disposal Pit into the treatment basin and proceeding with treatment. Since this plan eliminated the drawbacks of in situ treatment, it was endorsed by the agencies.

The temporary treatment basin was constructed adjacent to the Phase I Disposal Pit in approximately 6 weeks of extremely inclement weather. The aeration system consisted of ten floating aerators positioned throughout the temporary basin. Nine 10-horsepower units and one 15-horsepower unit provided a total system aeration/mixing power of 105 horsepower (Table 6). As the water level in the Phase I Pit was drawn down, a minimal amount of infiltration was observed. However, one month after the initial water removal, another one foot of infiltration and precipitation had accumulated in the Phase I Pit and was transferred into the treatment basin.

Startup

To aid mixing, nutrients and biomass were added to the temporary basin during the transfer pumping of the impounded water from July 6 to July 13. A review of the nutrient characteristics of the raw water (Table 1) suggested that the available nutrients could not support the kind of biological growth anticipated to be necessary for expedient biological degradation of the wastewater constituents. However, it was believed that a high ratio of endogenous respiration and nutrient cycling would occur.
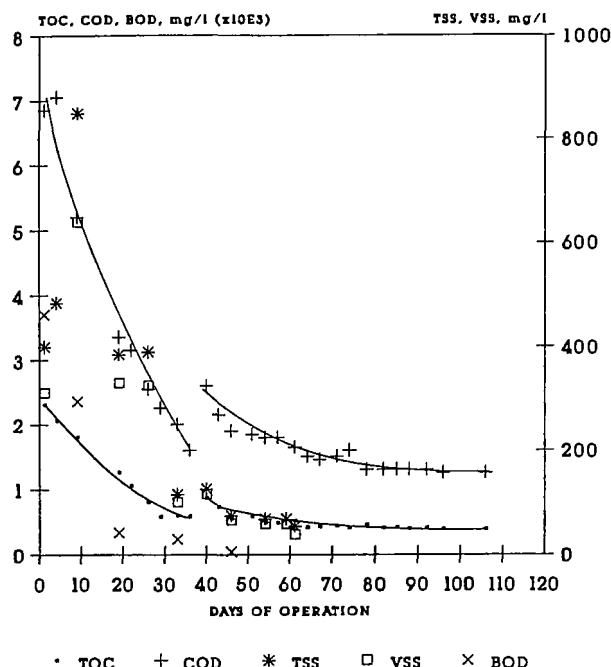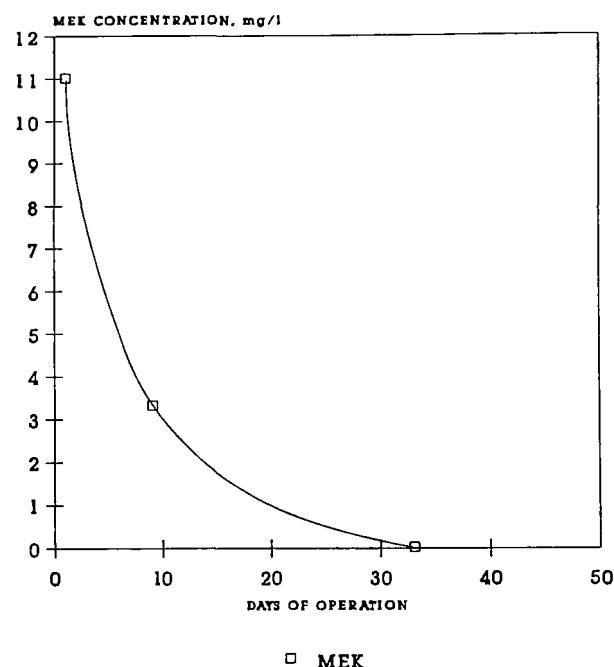
Therefore, the consulting engineers elected not to supplement the existing ammonia, but to add 110 gallons of 75% technical grade phosphoric acid. Approximately 20,000 gallons of 5% solids biological sludge were shipped from the local coke plant wastewater treatment facility and used to seed the new impoundment. Seeding took place from July 11 to 14. Aeration began on July 12.

The results of TOC, COD, TSS, VSS and BOD analyses performed are summarized in Figure 1; MEK analysis results are shown in Figure 2. A summary of the analytical data is shown Table 7. COD, TOC, BOD and MEK levels appeared to decline exponentially. Biological activity began approximately one week after seeding. Initial

Table 7
Biological Treatment Process Monitoring Data;
MIDC Site

Date	Avg. pH s.u.	Avg. DO mg/l	TOC mg/l	COD mg/l	TSS mg/l	MLVSS mg/l	BOD mg/l	MEK mg/l	Acetone mg/l	Phenols mg/l	Ammonia mg/l	Phosphate mg/l	Cyanide mg/l	Arsenic mg/l
Jul. 14	7.7	0.56	2150											
Jul. 17			2300	6850	400	310	3700	11.0			24	200		
Jul. 20			2050	7050	485						19	4		
Jul. 25		0.59	1800	5200	850	640	2355	3.3			23	4		
Aug. 4			1250	3350	385	330	1400	N.D.	0.064	0.15	31	0.08		
Aug. 7	8.9	4	1050	3150										
Aug. 11	8.2	5.8	800	2550	390	325						0.07		
Aug. 14	8.4	2.3	575	2250										
Aug. 18	8.6	7	600	2000	115	100	230	0.009	0.03	0.08	25	2.3		
Aug. 21	8.8	6.1	590	1600									<0.04	2.0
Aug. 25	8.5	0.4	860	2600	125	115					13.5	2.0		
Aug. 28	8.5	5.1	730	2150										
Aug. 31	7.5	6.7	540	1900	74	66	43	0.004	0.013	0.03	21.5	1.7	0.18	1.8
Sept. 5	7.6	8.4	590	1850										
Sept. 8	8.6	8.1	480	1800	68	58					17.5	0.16		
Sept. 11	8.9	7.6	485	1800										
Sept. 13	9.2				68	58			0.06				0.02	2.2
Sept. 15	8.5	7.8	510	1650	54	38	660	0.006	0.021	<0.05	13	7.0		
Sept. 18	8.6	8.1	415	1500										
Sept. 21			420	1450										
Sept. 25	11.2	10.1	430	1500										
Sept. 28	8.6	8.7	400	1600										
Oct. 2	9.1	10	450	1300										
Oct. 6	8.9	8.8	400	1300										
Oct. 9	9.1	11.4	410	1300										
Oct. 12			395	1300										
Oct. 16	8.9	9.3	400	1300										
Oct. 20	9.1	10.7	380	1250										
Oct. 30			385	1250										

Note: On August 23, an additional 81,000 gallons of Impounded water was transferred from the Phase I Pit to the temporary basin.

N. D. = Not Defined
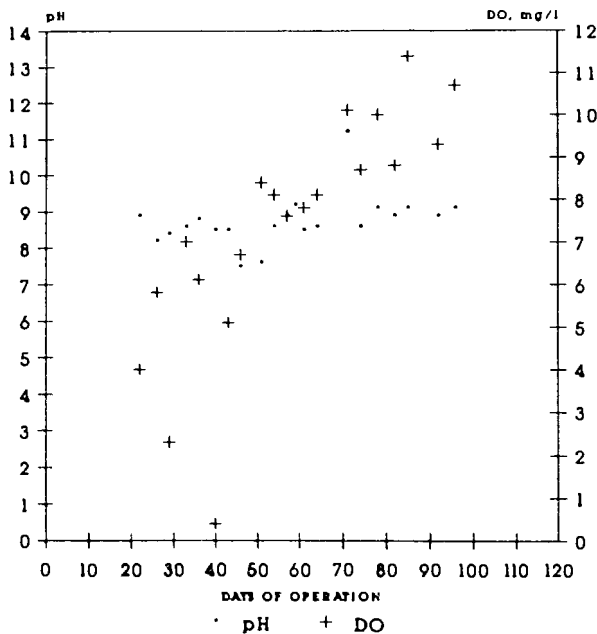
Figure 3
MIDC Impounded Stormwater Remediation
Process Monitoring Data

dissolved oxygen concentrations were positive, indicating that the aerators were adequately sized to match the initial load (Figure 3). Later dissolved oxygen levels rose as residual CODs dropped. Biological degradation was essentially complete in approximately one month.

Table 8
MIDC Site; Analysis of Biotreated Water;
Selected Parameters; Sampled September 21, 1989

PARAMETERS	TB-1	TB-2	TB-3	TB-4	TB-5*	TB-6
Total Organic Carbon	445	410	425	415	415	410
Chem. Oxygen Demand	1450	1450	1450	1450	1450	1500
Arsenic, Total	2.4	2.5	2.2	2.4	2.2	2.5
Nickel, Total	0.82	0.8	0.72	1.2	1.2	1.2
O & G	3	8	11	21	20	17
Phenols (4AAP)	0.28	0.06	0.06	0.09	0.07	0.09
Total Cyanide	<0.02	<0.02	<0.02	0.03	0.02	<0.02
Acetone	0.029	ND	0.039	0.015	0.02	0.056
Methyl Ethyl Ketone	ND	ND	ND	ND	ND	ND
Methyl Isobutyl Ketone	ND	ND	ND	ND	ND	ND
Napthalene	0.003	0.003	ND	ND	ND	ND
Acenapthylene	0.003	0.003	ND	0.003	0.002	0.002
Anthracene	0.005	0.005	0.004	0.004	0.004	0.002
Pyrene	0.001	0.002	0.003	0.002	0.002	ND
Chrysene	0.005	0.006	0.004	0.006	0.006	0.003
Benzo(b)fluoranthene	0.015	0.021	0.027	0.024	0.024	0.016
Benzo(k)fluoranthene	0.012	0.01	0.035	0.012	0.012	0.006
Benzo(a)pyrene	0.011	0.013	0.011	0.014	0.014	0.009
Phenanthrene	ND	ND	0.003	0.007	0.007	ND
Fluoranthene	ND	ND	0.003	0.007	0.007	ND

Note: All concentrations are in the unit of mg/l.
ND= Not Determined
* Duplicate of TB-4

The transfer of additional run-on and infiltration water from the Phase I impoundment (on August 25, 1989) resulted in a 63% increase in COD within the pond. Again biological degradation was essentially complete in approximately one month. The pond completely exhausted its potential for biological degradation in another three weeks. A summary of the monitoring data is shown in Table 7.

Conclusion of the treatment process was indicated by three conditions: leveling off of TOC valves, BOD below 50 mg/L, and MEK (2-Butanone) below 1 mg/L. Representative samples were then collected at five locations at varying depths (Table 8). The data demonstrated that the pond was essentially homogeneous.

Upon review of the data, the involved agencies agreed to a mass-based discharge limit based on residual levels of several polynuclear aromatic compounds. This limited the discharge rate from the pond to 100 gpm. The water was discharged in 20,000 gallon batches. Each batch was tested for soluble COD. Batches with CODs in excess of 1800 mg/L were returned to the pond. Discharge began on November 8, 1989 and concluded on January 28, 1990. Comparison of effluent analyses between the bench-scale reactor and the biotreatment process is shown in Table 9.

Table 9
Comparison of Treatability Effluent and Pond Effluent
Analyses; Selected Parameters; MIDC Site

PARAMETERS	Treatability Effluent		Pond Effluent (average)
	Test A	Test B	
Arsenic, Total	1.7	1.3	2.4
Nickel, Total	0.4	0.58	0.97
O & G	9	<5	13
Phenols (4AAP)	0.1	0.4	0.11
Total Cyanide	0.05	0.87	<0.02
Acetone		0.17	0.032
Methyl Ethyl Ketone		<0.01	0.004
Methyl Isobutyl Ketone	<0.2	<0.01	ND
Napthalene	<0.2	<0.01	0.003
Acenapthylene			0.003
Anthracene	<0.2	<0.01	0.004
Pyrene			0.002
Chrysene			0.005
Benzo(b)fluoranthene	ND	0.019	0.021
Benzo(k)fluoranthene		<0.01	0.014
Benzo(a)pyrene	ND	0.013	0.012
Phenanthrene	<0.2		0.006
Fluoranthene	<0.2	<0.01	0.006

Note: All concentrations are in the unit of mg/l.
ND= Not Determined

Evaluation of Biokinetic Constants

During the process of biooxidation of a complex substrate, the reaction rate decreases independently of the decrease in substrate concentration. As a result, efforts to describe the overall reaction rate by a first order equation is considered. At the same time, it is quite clear that the reaction rate constant (k) from the first order equations will decrease with the progress of the biochemical reaction of a complex substrate. Typically, substrate levels are represented by an indicator parameter such as BOD or COD.

While kinetic data have not been studied extensively for this study, it should be noted that the exponential decay coefficients for COD and TOC varied with initial loadings. The biokinetic constants were determined by fitting TOC and COD data to the first order kinetic equation:

$$S = S_o exp(-kt) \qquad (1)$$

where
S = substrate concentration at time t
So = initial substrate concentration
k = first order kinetic constant
t = time

Estimation of the numerical values of the biokinetic constants presents a complex problem, because one has to choose an equation which fits the data. Several investigators have utilized non-linear regression techniques to fit the data and estimate the biokinetic constants. This approach is applied with difficulty. It is possible to obtain numerical values which have little physical meaning; nonetheless, such a problem did not occur in obtaining the numerical values of first order biokinetic constants for substrate concentrations measured as TOC and COD, summarized in Table 10. The goodness of fit is also shown as correlation coefficients in the same table. The decay constants reported here seem to be comparable to one another (for both TOC and COD measurements). In Phase I, k was 0.043 day^{-1}, and 0.044 day^{-1} for TOC and COD, respectively. In Phase II, k was 0.025 and 0.018 day^{-1} for TOC and COD, respectively. MEK was removed at a faster rate of 0.19 day^{-1}.

Table 10
Biokinetic Constants; MIDC Site

TOC DATA	Phase I	Phase II
FIRST ORDER KINETIC CONSTANT (k), 1/day	0.043	0.025
INITIAL SUBSTRATE CONCENTRATION, mg/l	2050	860
CORRELATION COEFFICIENTS (r)	0.975	0.892
COD DATA	Phase I	Phase II
FIRST ORDER KINETIC CONSTANT (k), 1/day	0.044	0.018
INITIAL SUBSTRATE CONCENTRATION, mg/l	7050	2600
CORRELATION COEFFICIENTS (r)	0.997	0.93
MEK DATA	Phase I	
FIRST ORDER KINETIC CONSTANT (k), 1/day	0.228	
INITIAL SUBSTRATE CONCENTRATION, mg/l	11	
CORRELATION COEFFICIENTS (r)	0.996	

The physical, chemical and biochemical characteristics of these reported organic compounds become important during biological treatment because of the combined possibilities of stripping, adsorption and biological oxidation. Most kinetic design models available to date have originated from a substrate mass balance assuming substrate removal based on biological consumption. Stripping and biological adsorption are not included in this balance, and the amount of substrate stripped is not predicted.

Tables 3 and 7 show the comparison of the MEK removal achieved in batch reactors; one test was performed as a bench-scale experiment and the other as a biological treatment process. In a bench-scale system (Scenario 3), more than 99% of MEK was removed in 14 days; in the pond treatment process, 99% of MEK was removed in one month. This difference might reflect rate limiting conditions in the pond, i.e. oxygen transfer.

CONCLUSIONS

The batch biotreatment process achieved comparable removals to those found in the bench-scale study. Bench-scale testing was a good predictor of reactor performance.

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Innovative Biological Processes for Treatment of Hazardous Wastes

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INTRODUCTION

In this paper, the principles of biological treatment have been reviewed. This first section of the paper includes a discussion of the environmental requirements and kinetics of biological systems. This introductory material is followed by a discussion of the fundamental reasons for limitations of conventional bioprocesses in treating hazardous wastes. Identification of such fundamental reasons leads to understanding how any innovative bioprocess should be developed and evaluated for application to treatment of hazardous wastes. Some examples show how the innovative processes can enhance the successful biodegradation of hazardous organic compounds.

PRINCIPLES OF CONVENTIONAL BIOTREATMENT

Environmental Requirements

The environmental requirements shown in Table 1 must be provided for the growth of organisms to facilitate biotreatment. These requirements are only general conditions applying to all microorganisms. For a specific organism or group of organisms, knowledge of more specific requirements is required.

Table 1
Environmental Requirements for Bioprocesses

Carbon-Source
Electron Donor
Electron Acceptor
Macronutrients
Micronutrients
pH
Temperature
Absence of Toxicity
Mixing and Mass Transfer
SKT

The organic matter in wastewater is used as substrate by the organisms. These organics serve as the energy source (electron donor) and carbon-source. The organisms also need an electron acceptor for electron balance. Different groups of organisms need different electron acceptors. For aerobic bacteria, the electron acceptor is oxygen. Denitrifiers, which are anoxic organisms, use nitrate (NO_3^-) as the electron acceptor. Sulfate reducing bacteria use sulfate (SO_4^{--}) and methanogens use CO_2 as electron acceptors. The organic matter serves as both electron acceptor and elec-tron donor to fermentative bacteria.

Using thermodynamics, it can be shown that, energetically, oxygen is the most preferred electron acceptor followed by nitrate, sulfate and carbon dioxide. A simple experiment makes this concept clear. If a closed vessel contains a glucose solution (or any other easily biodegradable substrate, i.e., electron donor), oxygen, nitrate, sulfate and CO_2, the aerobic bacteria will start biodegrading glucose as long as dissolved oxygen is available. After depletion of oxygen, the denitrifying bacteria will start biodegrading glucose using nitrate as the electron acceptor. After the nitrate disappears, the sulfate reducers will start utilizing glucose. Finally, the methanogens will start consuming CO_2, leading to the formation of methane. From the hazardous waste perspective, it is important to note that various toxic organic compounds may have different adverse effects on these different groups of bacteria. One group of organic compounds may be biodegraded effectively by one group of organisms, whereas the other groups of organisms may fail to do so.

Phosphorous and nitrogen are considered as macronutrients. Some researchers consider sulfur as a macronutrient for methanogenic bacteria. Examples of micronutrients are metals (such as Fe, Mg, Ca, Co, Ni, etc.) and vitamins. In addition to the carbon source and N, P and S, the organisms need several elements in minute quantities for proper growth. Without these micronutrients, the organisms may still grow but such growth will not be "healthy" and there may be long-term adverse effects. From a biotreatment perspective, the problem is to know exactly which micronutrients are necessary and more importantly what concentrations are optimum. Quantitative information often is lacking in this area. Engineers are advised to add all these micronutrients (especially the metals) to the feed if they were not already present in the wastewater.

Most organisms require a neutral pH for optimal growth. Depending on the process, the optimum temperature may vary. For conventional aerobic treatment, the optimum temperature is normally 20 to 25° C whereas for mesophillic anaerobic treatment, the optimum temperature is 35° C. Thermophillic anaerobic treatment requires a temperature of 55° C.

One requirement for biotreatment is the "absence of toxicity." The significance of this requirement is that the hazardous organics can be treated only if they were not toxic to the organisms. But toxicity is not a simple concept. Toxicity depends on concentration, mode of application, ability to acclimate, etc. Almost any substance could be toxic if the concentrations were very high. A slug dose may have very different effects compared to a gradual increase in concentration since the latter mode of addition

gives the organisms the ability to acclimate to the toxic substances.

Adequate mixing is necessary for the transport of substrate and nutrients to the bacteria. Even if all other environmental requirements were fulfilled, lack of adequate mixing could lead to system failure. Mixer design becomes a challenge for engineers when they try to utilize biotreatment with sludge having a high solids concentration (> 5% total solids). Without an innovative process, engineers may fail when they try to apply biotechnology to the treatment of contaminated soil. Permeability and other characteristics of the soil such as particle size and type of soil also need to be considered.

The last factor in Table 1 is solids (i.e., bacterial) retention time (SRT). SRT is a measure of the length of time the bacteria spend in a bioreactor. The longer the bacteria are in a reactor, the higher the biodegradation is assuming all other requirements listed in Table 1 are fulfilled. SRT is defined as the mass of organisms in the system divided by the mass of organisms removed (wasted) per day. The engineers can control the solids wasting rate to control SRT. It is not unreasonable to say SRT is the most important variable in the biotreatment of both hazardous and nonhazardous wastewaters. The discussion of kinetics in a later section of this paper will clarify the importance of SRT.

Another important point to realize is the difference between hydraulic retention time (HRT) and SRT. For continuous-fed, complete-mix systems without solids (organisms) recycle, SRT equals HRT. For continuous-fed, complete mix systems with recycle or continuous-fed, fixed-film systems, SRT could be many times higher than HRT. In an ideal system, HRT is low and SRT is high. Low HRTs allow higher feed flow rates for the same bioreactor, and high SRTs lead to effective degradation of the organic compounds.

Scope of Innovation

Based on the discussion thus far, the areas appearing to need more R&D work are noted below.

Use of Various Types of Bacteria

It is useful to know which electron acceptor can best treat a certain organic waste (electron donor). In other words, more work is required to know which types of bacteria (aerobic, anaerobic, etc.) are most suitable for biodegrading various toxic organic compounds.

Use of Other Organisms

Recently, there is a renewed enthusiasm with white rot fungi for treatment of complex organics in wastewaters. White rot fungus belongs to a family of wood-rotting fungi found throughout the northern hemisphere. Lignin, normally resistant to decay, is the primary noncarbohydrate constituent of wood. White rot fungus naturally produces a group of enzymes that degrade lignin. White rot fungus enzymes are unique because they have a low specifity, meaning they can react with a wide variety of substances.[1]

It is expected that white rot fungus will offer a potential solution for groundwater and soil cleanup problems that currently cannot be managed using conventional methods. Although researchers expect the technology to be relatively low in cost, the pilot-scale demonstrations will define specific costs. Other organisms may prove to be very useful in biodegrading toxic organic compounds.[1]

Enhanced Bioavailability/Mass Transfer

Engineers need to find a way to increase mass transfer for treatment of wastes containing high solids and contaminated soil. No matter how simple it sounds, a successful innovative process could be to "mix" domestic wastewater or domestic sludge with contaminated soils for combined treatment. The wastewater or sludge will provide enough water content to facilitate mass transfer in the mixed waste.

Innovative Techniques to Increase SRT

During the 1980s, a significant amount of research was performed in this area. Researchers have recognized that fixed-film processes such as anaerobic filters, fluidized beds, etc., have an inherent advantage over complete-mix systems. It is important to realize that there is nothing innovative about this concept because this should be understood from the fundamentals of biokinetics. The part that is innovative is the design of a system that satisfies the fundamental requirements. Unless a process is fundamentally sound, it is not going to be of any value. For this reason, the fundamental aspects have been stressed in this paper while discussing the scope of innovation.

Kinetics of Bioprocesses

Before successful evaluation of innovative biological processes, the kinetics of bioprocesses need to be understood. The less understood areas in kinetic modeling need to be recognized.

One popular model in biokinetics is the Monod Model.[2] The organic matter (C-source and electron donor) in a waste is the substrate, S_O, for the bacteria. The bacterial mass, X, increases as S_O is utilized. The utilization of substrate and the growth of bacteria are simultaneous events. To quantify this phenomenon, a set of simultaneous differential equations is used as follows:[3]

$$\frac{dS}{dt} = -\frac{K_S X}{K_S + S} \tag{1}$$

$$\frac{dX}{dt} = Y\frac{dS}{dt} - bX \tag{2}$$

where:

$\frac{dS}{dt}$ = rate of microbial substrate utilization per unit volume, mass per volume-time

$\frac{dX}{dt}$ = net growth rate of microorganisms per unit volume of reactor, mass per volume-time

k = maximum rate of substrate utilization per unit weight of microorganisms, time^{-1}

Ks = half velocity coefficient, equal to the substrate concentration when dS/dt = 0.5 k, mass per volume.

Y = growth yield coefficient, mass per mass

b = microorganism decay coefficient, time^{-1}

X = microbial mass concentration, mass per volume

S = concentration of substrate surrounding the microorganisms, mass per volume

Each organism has a characteristic set of kinetic parameter values. For example, for acetate-utilizing methanogens, the values are: k = 2.5 day^{-1}, K_S = 10 mg/L, Y = 0.05 and b = 0.01 day^{-1}.[4] These values are constants; the engineers cannot change these values by using any innovative processes. However, when the bacteria undergo mutation, these values might change.

Mutation, which is commonly referred to as acclimation by engineers, is possible after exposing the organisms to toxic chemicals. Engineers regard mutation (or acclimation) as the ability of the organisms to develop "some resistance" to toxicity and also the ability to develop "some mechanism" (for example, growth of certain enzymes) which leads to enhanced biodegradation. When this happens, the values of the kinetic parameters might change. The engineers could successfully make such changes work to their advantage by controlling the HRTs/SRTs.

The methods for determining the values of the kinetic param-

eters are not included in this paper but are easily available in text-books on Environmental Engineering.[5]

The engineers need to know the values of the kinetic parameters for effective design of biosystems. Solving equations (1) and (2) for complete-mix, continuous systems at steady-state yields:

$$S = \frac{K_S (1 + b\,\theta_C)}{\theta_C (Yk - b) - 1} \qquad (3)$$

$$X = \frac{Y(S_O - S)}{1 + b\,\theta_C} \cdot \frac{\theta_C}{\theta} \qquad (4)$$

where:

θ_C = solids retention time (SRT), days

θ = hydraulic retention time (HRT), days

S_O = substrate (pollution) concentration in feed, mass per volume

Equation 3 is useful to calculate the effluent substrate (pollution) concentration after biotreatment. It is important to note that for complete-mix systems the substrate concentration inside the bioreactor equals the effluent substrate concentration. It is useful to be able to predict S, because when we measure soluble BOD in the effluent, we get a measure of S. Equation 4 is also useful because it gives the bacterial concentration, X, at steady state. Hence, from this equation and with known flowrates, one can calculate the amount of sludge generated from the biotreatment system.

In Equations 3 and 4, all the terms on the right hand sides are constants except θ_C, θ and S_O. Assuming no variation in the influent substrate concentration S_O, the only two parameters that the engineers need to control are θ and θ_C. The HRT (or θ) is easy to control by controlling the flowrate of the influent. The SRT, on the other hand, can be controlled by selecting the amount of sludge to be wasted from the complete-mix system. As discussed before, a successful innovative process is one which minimizes the HRT and maximizes the SRT. A short HRT will facilitate the treatment of large volumes of wastewater; a long SRT should help satisfy the effluent quality requirements.

LIMITATIONS OF BIOPROCESSES IN TREATING HAZARDOUS WASTES

Some of the organic and inorganic compounds present in a waste may be classified as hazardous. Both organics and inorganics may cause inhibitions/toxicity to bioprocesses. The toxic organics might also be biodegraded under favorable conditions.

Toxicity Kinetics

To quantify toxicity, the following models are useful:

For Noncompetitive Inhibition

$$\frac{dS}{dt} = - \frac{kSX}{K_S + S}\left(1 + T_X/K_I\right) \qquad (5)$$

For Competitive Inhibition

$$\frac{dS}{dt} = - \frac{kSX}{K_S\left[1 + (T_X/K_I) + S\right]} \qquad (6)$$

where:

T_X = concentration of toxicant, mass per volume

K_I = inhibition coefficient, mass per volume

The concepts of noncompetitive and competitive inhibition are based on biochemistry. More information on these models is available in the literature.[6,7]

At steady-state ($dS/dt = 0$, $dX/dt = 0$), the model equations reduce to simple algebraic equations which can be solved to determine the effluent substrate concentration:

Competitive:

$$S_t = [K_S(1+b\theta)(1+T_X/K_I)]/[\theta(Yk-b)-1] \qquad (7)$$

Noncompetitive:

$$S_t = [K_S(1+b\theta)]/[\theta(Yk-b(1+T_X/K_I))-(1+T_X/K_I)] \qquad (8)$$

Equation 7 can be rewritten as follows:

$$S_t = S + S(T_X/K_I) \qquad (9)$$

where:

S_t = effluent substrate concentration under toxic conditions

S = effluent substrate concentrations without toxicants

Equation 9 indicates that the effluent substrate concentration increases linearly with increasing toxicant concentration. Equation 8 can be simplified further to indicated that, unlike competitive inhibition, noncompetitive inhibition does not have a proportional effect on effluent substrate concentration. That means, when noncompetitive inhibition occurs, the effluent concentration remains unaltered up to a "limiting" toxicant concentration. When this limiting concentration is exceeded, a total system failure is possible.[7]

The inhibition coefficient, K_I, is a measure of the bacterial resistance to toxicity. The engineers cannot change this coefficient (i.e., if an organism does not have the ability to resist toxicity, no innovative process can help it). On the other hand, as indicated earlier, it might be possible for the organisms to undergo mutation (which the engineers call acclimation) which might lead to an increase in resistance to toxicity, i.e., increase in value of K_I.

If it were known how the organisms increase their resistance, it would be easier for the engineers to provide the favorable conditions to enhance such acclimation. Since the mechanism of acclimation is not understood in most cases, the Environmental Engineer's general approach should be to provide maximum possible SRT without making the HRT impractical. As discussed before, a low HRT will facilitate treatment of sufficient volume of wastewater.

A significant limitation of the application of the concept of toxicity kinetics is that more research is necessary to develop data so that the environmental professionals can find out which compounds cause which type of inhibition. Researchers have shown that organics such as formaldehyde cause competitive inhibition whereas inorganics such as ammonia and nickel cause noncompetive inhibition.[8,9,10]

Are the Concentrations of the Hazardous Organics High Enough to Cause Toxicity to the Biotreatment Processes?

The earlier discussion of toxicity kinetics is limited to scenarios where high concentrations of hazardous substances may end up in existing treatment plants designed for conventional, nonhazardous, domestic and/or industrial wastewaters. It is quite common to face a situation where the hazardous organic compounds are too low in concentration to cause any toxicity to the organisms in the treatment plant. But removal of these low concentrations of the organics could still be critical because these low concentrations which do not kill the bacteria might have a long-term effect on human health. Some organic compounds are potentially carcinogenic even at very low concentrations.

Fate of Toxic Substances in Biotreatment Processes

When the concentrations of the toxic organics are too low to cause any adverse effects on the microorganisms in the treatment system, the following factors will determine the fate of these hazardous organic substances:

- Volatilization
- Adsorption
- Biodegradation

When dealing with hazardous materials, the most desirable fate is biodegradation (assuming that biodegradation will not lead to any toxic intermediates). Volatilization of organics might create air pollution. In conventional aerobic processes, volatilization is difficult to prevent, indicating the need for closed systems such as anaerobic processes. Adsorption of the hazardous substances in the biological sludge will make the sludge hazardous. Hence, if an innovative process can control sludge efficiently, it will be of value to the client.

No innovation can change the amount of sludge that will be generated because of bacterial growth as long as the same organisms are used. However, by proper choice of bacteria, the amount of sludge can be minimized. For example, anaerobic bacteria will generate almost an order of magnitude lower amount of sludge than aerobic processes.

Biodegradation will also depend on the choice of bacteria. Engineers can do very little about biodegradation except to provide the "proper conditions" for acclimation. The problem is that in most cases the "proper conditions" are unknown.

A unified model is very useful to simultaneously predict the extents of volatilization, adsorption and biodegradation of hazardous substances. Development of such models is not easy. A General Fate Model has been proposed by Namkung and Rittmann.[11] Their work showed that for VOCs (toluene, benzene, ethylbenzene and methylene chloride), biodegradation is the most important mechanism of removal in an activated sludge plant. Volatilization and adsorption are not significant compared to biodegradation when the latter occurs. When biodegradation is not important (for example, for chloroform), volatilization is the main removal mechanism. These conclusions were based on a study of a wastewater treatment plant.[11]

Can the Organisms Biodegrade Very Low Concentrations of Hazardous Organic Substances?

We have seen that organisms use organics as their carbon and energy source. Up to what concentration levels can the organisms use the organics as their primary carbon source? This question is very important for biotreatment of hazardous organic compounds since many of these compounds could be carcinogenic at ug/L levels. That means the concentrations of these compounds might be too low for biodegradation but too high to cause toxicity to humans.

The limiting concentration at which the bacteria can use a substance as their primary carbon source is denoted by S_{min} which is the limiting condition when growth equals decay. Using the Monod kinetics discussed earlier, it can be written:

Growth	=	Decay
$\dfrac{Y k S_{min} X}{K_s + S_{min}}$	=	bX
$Y k S_{min}$	=	$bK_s + bS_{min}$

$$S_{min} = \frac{bK_s}{Yk - b} \qquad (10)$$

Equation 10 shows that the minimum substrate concentration depends on the four kinetic parameters k, K_s, Y and b. The values of these parameters are characteristics of the organisms used for biotreatment. The values cannot be changed by using innovative processes, but engineers need to realize that depending on the type of organism, S_{min} can vary considerably. The following examples will make this point clear.

Example 1

Assume:
b	=	0.01 day^{-1}
K_s	=	10 mg/L
Y	=	0.05
k	=	0.3 day^{-1}

Calculated S_{min} = 20 mg/L

Example 2

Assume:
b	=	0.01 day^{-1}
K_s	=	1 mg/L
Y	=	0.03
k	=	2.0 day^{-1}

Calculated S_{min} = 0.2 mg/L

Example 3

Assume:
b	=	0.01 day$_{-1}$
K_s	=	1 mg/L
Y	=	0.05
k	=	2.5 mg/L

Calculated S_{min} = 0.087 mg/L

These examples show that with apparently small changes in the values of the kinetic parameters, the S_{min} value can change significantly. It should be noted that most volatile compounds generally are present in very low concentrations in the wastewaters. These concentrations might be too low for biodegradation unless cometabolism occurs as discussed in the following section.

Is Biodegradation Impossible with Concentrations Lower than the Required Minimum Substrate Concentration?

Biodegradation of organics with concentrations lower than S_{min} is still possible if the organisms can use the organics as secondary substrates or cometabolites. A primary carbon source is required. In POTWs, domestic wastewater is the primary carbon source. This means that if low concentrations of toxic organic substances were discharged to POTWs, the only way these substances could be biodegraded is the use of these compounds as secondary substrates by the existing organisms in the treatment plant. However, acclimation and other fate mechanisms such as volatilization and adsorption need to be addressed.

In a recent U.S. EPA pilot-scale project, the fates of several RCRA and CERCLA compounds were studied.[12] The results indicate that stripping of volatile compounds, such as chlorinated hydrocarbons, in the activated sludge process could be significant. Some semivolatile compounds, on the other hand, could be treated more efficiently using a conventional activated sludge process. The concentration of each compound spiked to the influent domestic wastewater was 0.5 mg/L which is presumably below the respective S_{min}. Even though no mechanism study was possible in this pilot study, it might be assumed that secondary utilization was the reason for biodegradation.[12]

SELECTED INNOVATIVE BIOPROCESSES

Since it is difficult to list and discuss all innovative bioprocesses, the focus of this part of the paper will be to study how some of the innovative bioprocesses satisfy the fundamental requirements. The most important question to be addressed in this section is: "If the fundamental requirements of bioprocesses were satisfied, would a bioprocess work successfully or are there some 'other' requirements that we have overlooked so far?"

The discussion thus far has shown that an ideal bioprocess for treatment of hazardous substances should have a proper selection of organisms and adequate SRT. Table 2 lists some bioprocesses applicable to hazardous wastewater treatment.

Table 2
Selected Bioprocesses for Treatment of Hazardous Wastes

1. Aerobic Attached Growth Processes
2. Sequencing Batch Reactors
3. Anaerobic Attached Growth Processes
4. Combined Aerobic, Anoxic and Anaerobic Processes
5. Composting of Hazardous Wastes
6. In situ Bioprocesses

Aerobic Attached-Growth Processes

All attached-growth processes are generally favored for bio-treatment of toxic organic compounds. One argument in favor of attached-growth systems is that since the organisms are not wasted from the systems, "the SRTs are very high." However, one should be very careful about using the concept of SRT in attached-growth systems. SRT is applicable to suspended growth systems only. The kinetics of bioprocesses discussed earlier (Equations 3 through 10) is good for complete-mix, suspended-growth systems only. It is true that organisms are attached to the media (plastic, stones or any innovative substance could be used), but that does not necessarily mean that a very high value of SRT can be substituted in the Model Equation discussed earlier. Such an approach would be misleading. The Models for attached-growth systems are not discussed in this paper, but the information if easily available in the literature.[13]

Examples of aerobic attached-growth processes are trickling filters, rotating biological filters and aerobic fluidized bed reactors. It is well established that fluidized bed systems are more efficient than other fixed-film processes.

Sequencing Batch Reactors

A Sequencing Batch Reactor (SBR) is a self-contained treatment system incorporating equalization, aeration and clarification by using a draw and fill approach. SBRs have been used to treat wastewater from two hazardous waste sites in Buffalo, New York and Chicago, Illinois.[14] The SBR is not necessarily limited to aerobic organisms. This simple but efficient process satisfies the fundamental requirements and also is efficient for sludge handling. More applications of SBRs are expected for hazardous waste treatment, especially small-scale processes.

Anaerobic Attached-Growth Systems

Anaerobic attached-growth processes, such as anaerobic filters, anaerobic fluidized bed reactors and upflow anaerobic sludge blanket (UASB) systems, have the same inherent advantages as those of aerobic attached-growth processes. For applications of anaerobic processes, however, attached growth systems are even more useful because anaerobic organisms have very low Y values compared to those for aerobic organisms. This means that when the same amounts of a waste are independently treated aerobically and anaerobically, the amount of sludge (i.e., new organisms) generated from the aerobic process is generally an order of magnitude higher than that from the anaerobic process. It is important to note that the anaerobic organisms should not be called "slow-growers." Their k values are not low in spite of having low Y values. It is the value of k which determines how fast a waste can be biodegraded.

Combined Bioprocesses

Many Superfund sites have mixtures of organic compounds. Some of these organic compounds such as the aromatics are efficiently degraded by the aerobic organisms. However, compounds such as volatile, chlorinated hydrocarbons are not suitable for aerobic processes. It has been well established that the latter group of compounds are efficiently degraded by methanogens. Researchers have started documenting the list of respective compounds which are efficiently degradable by aerobic, anoxic and anaerobic processes. When this information becomes easily available, combined bioprocesses (involving any combination of aerobic, denitrifications, sulfate reduction and methanogenesis) will become more common.

Hazardous leachates contain a mixture of several organic compounds and heavy metals. A U.S. EPA study showed that anaerobic treatment (using an upflow anaerobic filter with plastic pull rings) followed by conventional activated sludge treatment is a feasible process for treatment of hazardous leachate.[15] More field studies are necessary before this innovative process can be implemented. However, if this process becomes successful, leachates from hazardous waste sites can be anaerobically pretreated in POTWs and can be safely discharged to the existing wastewater treatment systems.

Other anaerobic processes such as anaerobic fluidized bed systems with or without activated carbon could be more efficient and effective for such pretreatment of hazardous leachate. Several U.S. EPA pilot-scale research projects are currently being run to study these innovative processes.[16] It can be safely predicted that many problems in Hazardous Waste Treatment will be solved by innovative combinations of several bioprocesses.

One common question to be asked about combined processes is which process, the aerobic or the anaerobic, should come first. The general answer is the anaerobic process should be followed by the aerobic process for at least two reasons. First, the anaerobic process is generally more suitable for treatment of volatile compounds for both microbiological reasons and because of the fact that these are closed systems which minimize volatilization. Second, aerobic processes are more suitable as polishing systems. Effluents from anaerobic processes contain sulfide which contributes to COD. We should expect to see more anaerobic/aerobic processes than aerobic/anaerobic processes. In some cases, an aerobic/anaerobic/aerobic process could be the best option.

Composting

Even though composting is a rather "old" process, it has been listed in Table 2. Composting has generally been used for stabilizing sewage sludge. Parameters such as pathogen removal and BOD reduction were the focus of many earlier studies. Currently, there is renewed enthusiasm for composting, especially for treatment of explosive wastes. It appears that facultative systems with anaerobic pockets are more common in compost piles than a strict aerobic environment. Oxygen transfer and nutrient transfer problems need to be solved before complete success can be achieved.

In situ Biotreatment

At many Superfund sites, excavation and treatment of contaminated soils would be cost-prohibitive even for biotreatment. An in situ process could be the only solution. Bioprocesses need significant innovation before these processes can compete with successful in situ or physical processes such as In Situ Vitrification (ISV). The latter process is quick and reliable. Improved mass transfer is the key to future success of in situ bioprocesses. Properties of soil such as permeability could be the main issues to address.

CONCLUSION

The basis of evaluation of innovative bioprocesses should be the fulfillment of fundamental requirements of bioprocesses. Practical problems, such as sludge handling, need to be solved. One should not try to ignore the limitations of organisms. Proper selection of organisms is critical. Combined processes apparently are a good solution for Superfund sites with mixtures of various organics. However, combined processes do not necessarily "combine the advantages only." These processes could create new problems and should be evaluated based on pilot-scale data.

More improvements are required for applications of bioprocesses such as in situ remediation of contaminated soils.

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Energy Recovery From Waste Explosives and Propellants Through Cofiring

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ABSTRACT

The growing problem of environmentally safe disposal options for waste explosives and propellants along with the knowledge that budget reductions are the rule, not the exception, prompts the development of clean, safe, economical processes for the elimination of these wastes. While there are many potential processes for elimination of these wastes, most do not consider the energy content of the materials. While alone these materials exhibit relatively poor fuel properties, mixtures of explosives with other fuels such as oil provide suitable combustion mixtures. Initial studies of explosives cofiring processes indicate an economic advantage to explosives supplemented fuels. As supplemented fuels can be handled safely, it remains to show that they can be utilized in an environmentally sound manner. A background of the use of explosives as supplemental fuels will be presented as well as current research in the use of explosives and propellants as fuel supplements.

INTRODUCTION

Disposing of waste energetic compounds has become more difficult as a result of the end of interim status for incinerators under the RCRA. Open Burning/Open Detonation (OB/OD) of energetic wastes requires a Subpart X permit. Subpart X operations remain under interim status until Nov. 1992. OB/OD operations are of significant environmental concern and whether or not they will be allowed to continue in their current form is unknown. Means of disposing of energetic wastes have been under intense investigation since 1973. In fact, Brown[1] is convinced that sufficient knowledge has been amassed on disposing of these wastes in his 1976 study on incineration of propellants, explosives and pyrotechnics (PEP) that he felt he need only mention the following options for disposal:

- Ocean Dumping
- Open Burning (OB)
- Open Detonation (OD)
- Disassembly and Recycle
- Controlled Incineration

Brown points out that at the time of his study ocean dumping was banned, recycling was limited and OB/OD were severely restricted. The energy consciousness of the country was just emerging and the focus on hazardous waste was in the future. Even so, Brown recognized the potential for energy recovery as a possibility.

INCINERATION

While more exotic forms of elimination of waste explosives are being developed, incineration under controlled conditions will be the prevalent form of destruction. To safely incinerate a pound of TNT by currently available methods requires mixing bulk explosive in water, often with a size reduction step, followed by incineration using propane or fuel oil to vaporize the water and allow controlled combustion of the explosive. The water slurry typically consists of approximately 1 part energetic to 3 parts water. The bulk of the energy supplied externally is used to vaporize the water in the energetic slurry. Subsequently, incineration of the explosives is costly, as energy must be supplied to the system while no product is produced.

SUPPLEMENTAL FUELS ECONOMICS

Rather than destroying the explosives by incineration, some means of utilizing them for the energy they contain was sought. In 1985, Lackey[2] described scenarios whereby energetic compounds might be economically used to generate steam and/or electricity in industrial combustors. To better define the costs of using energetic compounds in this manner, he compared the costs associated with cofiring explosives in fuel oil in a boiler to other waste energetic management options including incineration and continued storage. Lackey's findings provided a rough indication of the economic competitiveness of cofiring.

An alternative approach to determining the economics of energetics-supplemented fuels is to compare them to the current manner in which they would be used, namely industrial boilers. The economic analysis can be broken down into three areas; raw materials, capital costs and labor costs.

Fuel Costs

The raw materials for the production of steam in industrial boilers are fuel and water. In the current case of supplemental fuels, the water requirements are assumed to be equal to those using nonsupplemented fuels. There are additional electrical costs for pumping and controls, but these also will be assumed to be roughly equal for this analysis. The baseline for comparison will be a 20 MM Btu/hr (5.86 MW) industrial boiler operating 6570 hours/year fired with #2 fuel oil. The boiler is assumed to be 80% efficient for both the nonsupplemented fuel and the supplemented fuel cases. Table 1 lists the physical properties and costs used in subsequent analyses. The base line fuel cost is $856,812/year from the following calculation:

2×10^7 Btu/hr x 6570 hr/yr x 1 lb #2 fuel/18,947 Btu x 1 gal #2 fuel/7.31 lb #2 fuel x $0.7225/gal #2 fuel x 1/0.8 (efficiency factor) = 856,812 $/year

A fuel oil supplemented with TNT will be compared to the baseline. Consider a fuel comprised of 55% #2 Fuel Oil, 15% TNT and 30% toluene. The cost of one pound of this fuel is $0.09311 from the following calculation:

(0.55 x $0.7225/gal #2 fuel x 1 gal/7.31 lb #2 fuel)

+ (0.30 x $0.93/gal toluene x 1 gal/7.2 lb toluene) =
0.09311 $/lb supplemented fuel

The heating value of the supplemented fuel is also necessary and is found to be 16,880 Btu/lb according to the following:

| #2 Fuel Oil | toluene | TNT |

$[(0.55 \times 18,947) + (0.30 \times 18,302) + (0.15 \times 6,454)]$ Btu/lb = 16,880 Btu/lb of supplemented fuel

The estimate above assumes heats of solution to be negligible. With these estimates, the yearly fuel cost for operating the same boiler as in the baseline case can be determined. The following calculation yields a yearly cost of $906,002/year.

2×10^7 Btu/hr x 6570 hr/yr x 1 lb supplemented fuel/16 880 Btu x $0.09311/lb supplemented fuel x 1/0.8 (efficiency factor) = 906,002 $/yr

The net cost of operating the baseline boiler using the explosive supplemented fuel is:

(906,002   856,812) $/yr = 49,190 $/yr

This figure is based on current (Mar. 1990) fuel and toluene prices. Figure 1 describes the particular sensitivity to fuel oil costs at constant toluene cost. The break-even point for fuel cost occurs at a cost for #2 fuel oil of $ 0.83/gallon at constant toluene cost of $0.93/gallon. Should fuel prices rise above this point, there would be a net profit for burning the supplemented fuel (not counting capital and labor costs).

Table 1
Physical Properties and Costs Used in Calculations

	REFERENCE	ENGLISH	METRIC
#2 Fuel Oil			
Heat of Combustion	3	18,947 Btu/lb	44.04 KJ/gm
Formula (avg)	3	C7.275H12.6	-
Density	3	7.31 lb/gal	0.8759 gm/cm3
Cost	4	$ 0.7225/gal	$0.1909/1
Toluene			
Heat of Combustion	5	18,302 Btu/lb	42.54 KJ/gm
Formula (avg)		C7H8	-
Density	5	7.2 lb/gal	0.8669 gm/cm3
Cost	6	$ 0.93/gal	$0.2457/1
TNT			
Heat of Combustion	7	6,454 Btu/lb	15.00 KJ/gm
Formula (avg)	7	C7H5N3O6	-
Density	7	12.94 lb/gal	1.55 gm/cm3
Cost			
RDX			
Heat of Combustion	7	4,101 Btu/lb	9.53 KJ/gm
Formula (avg)	7	C3H6N6O6	-
Density	7	15.08 lb/gal	1.806 gm/cm3
Cost			

Capital Cost

Capital cost estimates will be based on the assumption that the existing boiler will be used with the supplemented fuels without retrofit. This yields a zero cost for the baseline case. The feed system is the only capital equipment required to burn the supplemented fuel. A daily volume of supplemented fuel required for operating the baseline boiler is 3500 gallons. A feed tank of 5000 gallons could be specified for operations. Other equipments and estimated costs are given in Table 2. If the final capital cost is considered over a 20 year period at 0% interest, the yearly capital cost expenditure is $57,687.

Labor Cost Estimate

Finally, a labor cost estimate is required. It is assumed that a two-man operation is sufficient to prepare the supplemental fuel. A supervisor is included at one quarter of the work time. Table 3 details the labor cost estimate.
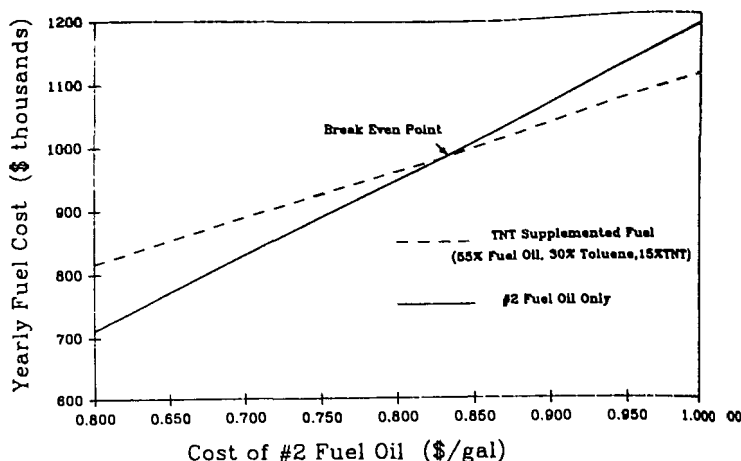
Figure 1
Yearly Fuel Cost Required to Operate a
20 MM Btu/he Industrial Boiler (80% Efficiency)

Table 2
Capital Cost Estimate for 5000
Gallon Feed System

Major Equipment Costs

ITEM	CAPACITY	COST ($)
Feed Tank	5000 gal, SS	64,200
Mix Tank	2250 gal, SS	47,900
Toluene Storage Tank	7500 gal, CS	22,800
Acetone Storage Tank	7500 gal, CS	22,800
Agitators (4)	15 hp, SS	16,400
Pumps (5)	15 gpm, SS	13,500
	TOTAL	187,600

Langs factor for solid-fluid processing plant fixed capital is 4.18

Capital Cost Estimate = $187,600 x 4.1 = $ 769,160

A factor of 1.5 is applied to the capital cost as an estimate to account for explosives requirements not included in equipment estimates

Final Capital Cost Estimate = 1.5 x $ 769,160 = $ 1,153,740

Table 3
Labor Cost Estimate

2 operators (@ $25,000/year)		$50,000
1 Supervisor (@ $40,000/year) x 0.25		$10,000
	Subtotal	$60,000
Overhead	(@75 % labor rate)	$45,000
	Labor Total	$105,000/year

Overall Cost Comparison

The total cost to operate the supplemental fuel fired boiler is then the sum of the fuel cost differential, the capital cost and the labor cost. The total is $211,877/year. The amount of TNT consumed is 1,167,792 pounds/year which results in a total cost for TNT destruction of $0.1814/pound or $363/ton. This analysis was performed on a basis of a 20 MM Btu/hr boiler to provide a realistic implementation scenario. The 20 MM Btu/hr boiler is a median size expected to be available for use at all military industrial locations. A similar calculation for Composition B (nominal 60% TNT, 40% RDX) supplemented fuel results in a per ton cost of $376. Comparison to currently available treatment methods can be made using the above per ton costs. If incineration capital and labor costs are assumed equal (an extremely conservative

assumption), the cost to destroy a ton of TNT would be a minimum of $609 using water per TNT slurry fed to a rotary kiln. The current cost of OB/OD operations is approximately $260/ton of explosive.[9] The above costs would indicate a median cost for elimination of TNT using supplemented fuels. While the costs of incinerating or open burning/open detonating of energetics are expected to rise, the cost associated with utilizing them as fuel supplements may actually decrease. As the price of #2 fuel oil increases, the value of the supplemented fuel increases. Figure 2 shows the resultant total costs associated with burning a TNT-supplemented fuel at varying toluene concentrations with change in fuel oil cost. Note that a 10% toluene, 75% #2 fuel oil, 15% TNT fuel mixture would result in a TNT destruction cost TNT less than current OB/OD costs.

EXPERIMENTAL PROGRAM

The economic estimates presented above are encouraging but need further refinement. A well designed test program is currently underway to verify assumptions and to provide design data for implementation. Previous study of the stability, handling and safety aspects of explosives-supplemented fuel mixtures has been conducted with promising results.[10] It was demonstrated that these mixtures are stable and can be handled without detonation propagation. More recently, similar studies have been conducted with nitrocellulose.[11] While these mixtures are stable and can be safely handled, the mixtures themselves become gelatinous in three-phase mixture. Further study will have to be performed to utilize propellant mixes.
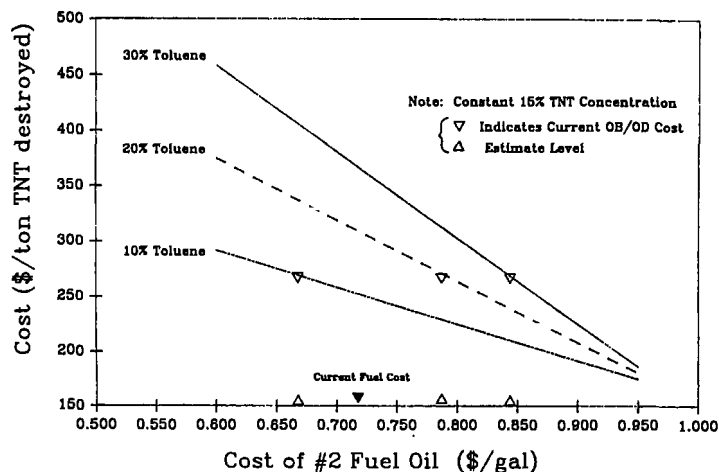
Figure 2
Cost Per Ton of TNT Destroyed in a
20 MM Btu/hr with Change in Fuel Oil Cost
Cat Varying Toluene Concentration
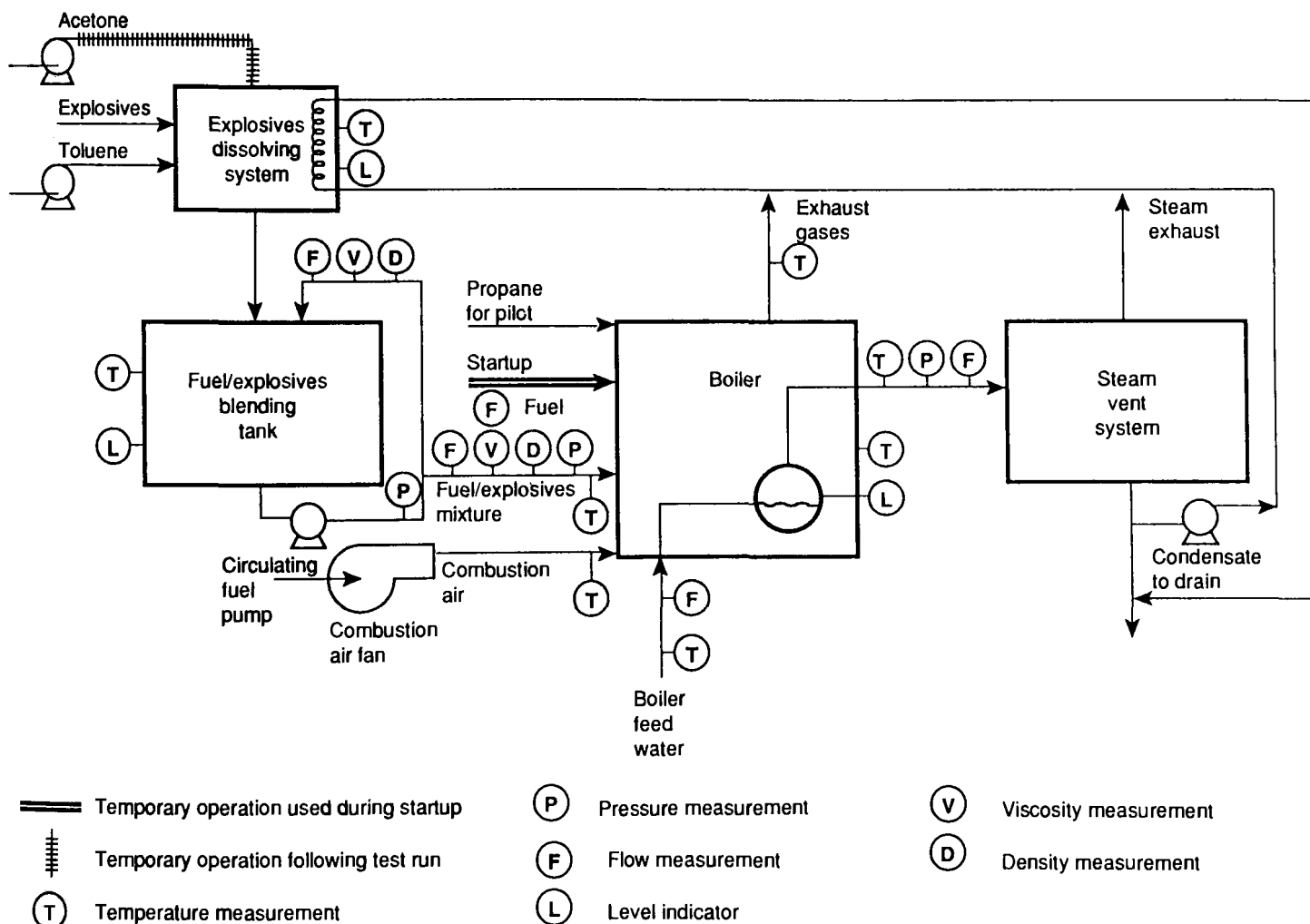
Figure 3
Schematic of Pilot-Scale
Supplemental Fuel System[13]

A proof of principle test program conducted in 1987 determined that it was "clearly feasible to cofire explosives and fuel oil."[12] The proof of principle testing also identified operational requirements for cofiring explosives which must be considered.

Current Program Synopsis

With the background testing completed, a pilot program was initiated in 1989. The objective of the pilot program is to conduct an evaluation of the use of explosives as fuel oil supplements in army industrial boilers. Equipment currently is being developed for this test program. Upon acceptance by the Department of Defense Explosives Safety Board (DDESB), TNT and Composition B will be used to supplement fuel fed to a 1.7 MM Btu/hr commercial boiler. The feed system will allow blending, heating and feeding of the fuel mixtures under complete automatic control. Automatic data acquisition will allow material and energy balances to be performed. A schematic of the pilot system is shown in Figure 3.

While the economics appear feasible, two items related to cofiring supplemented fuels appear critical. First, the resultant destruction and removal efficiency (DRE) from normal boiler operations should be above 99.99% for the explosives. Secondly, how much of NOx is formed is a key concern. Data on these operational peramaters will be obtained during extensive stack testing.

CONCLUSIONS

The concept of economically utilizing the energy content of energetic materials is being developed with the expectation of safely burning energetics mixed with fuel oil. Solvents will be used to put the explosives TNT and RDX into solution. This approach does not seem feasible for propellants at this time, but it may be possible to economically burn pure propellant slurries. Comparisons of this technology with incineration and OB/OD were made. Supplemented fuels depend on costs of the raw materials being used and may compete economically with open burning/open detonation. A testing program is currently underway to obtain the necessary data to implement this technology.

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Incineration of Contaminated Soil at a Superfund Site: From Pilot Test to Remediation

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ABSTRACT

Soil contaminants at the Bog Creek Farm Superfund site include a wide range of volatile and semivolatile organics and heavy metals. The site is currently being remediated by on-site incineration. The purpose of this paper is to discuss the results of activities leading up to this remedial action; namely, incineration pilot tests, remedial design, preparation of bid specifications and selection of the on-site incineration system.

INTRODUCTION

The Bog Creek Farm CERCLA site is located on a 12-acre tract in a rural section of Howell Township, New Jersey. It is alleged that in 1973 and 1974, paint manufacturing wastes in the form of bulk liquids and sludges, disinfectants and trash were disposed of on-site, on the ground and in trenches, by the site owners. During the period from 1983 to 1985, NUS Corporation performed an RI/FS for the site which resulted in an ROD, issued by the U.S. EPA in 1985. The ROD called for a first operable unit which would require that waste deposits, pond and bog sediment and highly contaminated soil be incinerated either on-site in a temporary unit or off-site in a RCRA facility. The ROD then called for a further study of the residual soil and groundwater contamination to determine the need for further remedy.

During 1987, Ebasco Environmental performed a supplemental RI to support the Remedial Design (RD) of the first operable unit and the second-phase FS. The RD involved characterizing the waste, soil and sediment to be incinerated, determining the volume of material to be incinerated, performing incineration testing and, finally, preparing technical bid specifications for the site cleanup to be issued by the US Army Corps of Engineers (USACOE).

CONTAMINATION AT THE BOG CREEK FARM SITE

The Bog Creek Farm Site is contaminated by a wide range of volatile and semivolatile organics and heavy metals as shown in Table 1. Soil contamination levels reported in the NUS RI ranged from 180,000 ppm for toluene, 26,000 ppm for methylene chloride, 14,000 ppm for xylenes, 8,900 ppm for benzene and 19,000 ppm for lead. Based on these results, the ROD required that all waste deposits and soil with greater than 10,000 ppm of total volatile organics (TVO) be excavated for incineration.

Ebasco Environmental's 1987 supplemental RI indicated lesser levels of organics in the waste deposits and soils and higher levels of contamination in the sediment than the previous RI. Based on these results, approximately 15,000 yd³ of soil and sediment should be excavated for incineration which would result in residual soil contamination orders of magnitude lower than 10,000 ppm TVO required by the ROD.

Ebasco Environmental's RI also included performing ultimate and proximate analyses of the waste, soil and sediment as shown in Table 2, in order to characterize these materials for incineration. Treatability tests were then designed and performed in order to provide information on the residual or ash characteristics and to support a conceptual incineration design.

Table 1
Chemical Analytical Results: Waste Samples

PP No.	CAS No.	Compound	Number of Occurrences	Concentration Range (ppm)
Organics				
	67-64-1	acetone	6	9 - 2,100
	78-93-3	2-butanone	3	16 - 5,200
44V	75-09-2	methylene chloride	2	2 - 26,000
11V	71-55-6	1,1,1-trichloroethane	3	5,300 - 8,800
87V	79-01-6	trichloroethene	3	4,700 - 5,500
85V	127-18-4	tetrachloroethene	3	840 - 6,800
10V	107-06-2	1,2-dichloroethane	1	6,800
6V	56-23-5	carbon tetrachloride	1	570
23V	67-66-3	chloroform	1	550
4V	107-06-2	benzene	4	30 - 8,900
86V	108-88-3	toluene	6	8 180,000
	1330-20-7	total xylenes	5	1 14,000
38V	100-41-4	ethylbenzene	4	30 4,700
65A	108-95-2	phenol	3	76 760
25B	95-50-1	1,2-dichlorobenzene	3	160 450
55B	91-20-3	naphthalene	3	120 - 380
54B	78-59-1	isophorone	4	39 890
	91-57-6	2-methylnaphthalene	2	21 88
61B	86-30-6	n-nitrosodiphenylamine	1	210
66B	117-87-7	bis(2-ethylhexyl)phthalate	5	10 - 1,400
68B	84-74-2	di-n-butylphthalate	4	82 1,400
67B	85-68-7	butylbenzylphthalate	2	96 - 260
Inorganics				
		aluminum	5	80 - 2,610
		barium	3	58 - 430
		calcium	6	1,120 - 36,400
		chromium	5	7 718
		cobalt	3	6 - 27
		copper	4	3 174
		iron	5	876 5,160
		lead	5	4.6 19,060
		manganese	5	7 78
		mercury	4	.27 2.2
		selenium	1	6.4
		thallium	1	(20)
		vanadium	4	4 13
		zinc	5	6 - 364

Notes: ppm (mg/kg)
PP No. Priority Pollutant Number
CAS No. Chemical Abstracts Service Number

TREATABILITY STUDIES

The treatability studies were designed to provide information to the suppliers of thermal destruction equipment to facilitate bidding for site

Table 2
Ultimate Analysis of Soils and Sediments
at Bog Creek Farm Site

	Value	
Parameter	Soil (Percent)	Sediment (Percent)
Ultimate Analysis		
Carbon (not including carbonates)	0.35	3.63
Hydrogen	0.13	0.10
Oxygen	2.66	2.71
Nitrogen	0.01	0.04
Sulfur	0.02	0.08
Moisture	13.03	51.11
Ash	83.80	42.84
Higher Heating Value	50.6 Btu/lb	632.3 Btu/lb
Bulk Density	98.4 lb/cu. ft	84.1 lb/cu. ft.
Heating Capacity of Inert Dry Solids	0.18 Btu/lb°F	

remediation. Consequently, several key technical issues were addressed in this study including the following:

- What are the time and temperature requirements in the kiln for removal of organics from the contaminated materials?
- What is the effect of different materials from the site on the time at temperature requirements of the kiln?
- What are the characteristics of the organics being removed from the materials? This issue facilitates the design of afterburner equipment.
- What is the fate of toxic metals in the site material when the materials are thermally treated? Of specific interest are the tradeoffs between removal of organics from the solid and the vaporization of volatile metals such as As, Cd, Hg and Pb which form a fine fume that is difficult to capture in particulate control devices.
- How much acid gas is produced when the materials are thermally cleaned? Again, the answer to this question will dictate what type (if any) of acid removal system will be required for the flue gas.

TREATABILITY TESTS

The testing was accomplished in a unique incinerability test facility shown in Figure 1. This facility can be used to define the time at temperature requirements necessary to decontaminate solids under realistic incinerator conditions. Specifically, the facility simulates the conditions that exist within full-scale rotary kilns including the contacting of gases and solids, the mixing of the solid beds, the time at temperatures and the gas phase conditions.

TEST FACILITY

The experimental test facility consists of a horizontal rotating refractory lined cylinder coupled with a stationary, vertical-controlled temperature tower furnace. The rotating section is designed to simulate a rotary kiln environment, while the vertical section can be used to simulate an afterburner. In this test, the afterburner was not used, but was maintained in a "hot" condition, in order to maximize the information obtained regarding kiln behavior. The kiln zone is batch fed with the test sample, and the sample is thermally treated for a specific solids residence time in the rotating high temperature environment. The time the batch spends in the simulator is translateable to the time an individual charge would remain in the kiln of a full-scale system. In the simulator, the solid temperature is monitored directly via thermocouples that extend into the bed as the rotation of the kiln brings them in contact with the test batch and indirectly via the thermocouples in the walls of the test zone. Solids can be removed after thermal treatment for specified times and temperatures and subsequently analyzed for ultimate analysis, metals, leachability of metals and hydrocarbons.
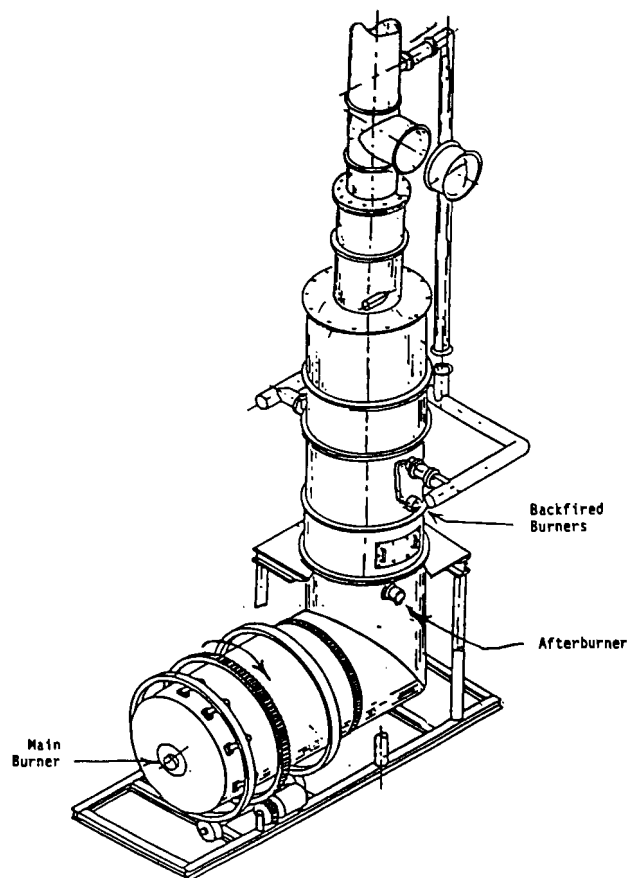
Figure 1
Rotary Kiln Test Facility

At the same time, the gaseous emissions from the kiln are monitored as the waste is thermally decomposed. The emissions of CO, O_2, CO_2, NO and total hydrocarbons are measured continuously. Low concentration volatile and semivolatile hydrocarbons are measured using Tenax and XAD traps exposed over the entire test period; standard U.S. EPA procedures are employed. Particulate samples are measured in the incinerator exhaust gas and analyzed for toxic metals. Finally, the total emissions of HCl are measured during the run by passing the incinerator effluent through a liquid scrubbing train followed by titration using ASTM procedures.

The test conditions used in this study are summarized in Table 3. The conditions were selected to allow a definition of the impacts of time and temperature, residence time and sample type. The times and temperatures were selected based upon the conditions expected to exist in full-scale equipment.

TREATABILITY TEST RESULTS

Influence of Kiln Temperature

The time at temperature required to remove organics from the waste sample was first evaluated using the ultimate analysis of samples treated in a kiln. Results of the carbon analysis as a function of time at different temperatures are provided in Figure 2. The initial sample carbon concentration (at time zero) was highly variable due to the heterogeneous nature and moisture content of the material, varying from 1.2 to 28.27. Temperature had a pronounced effect on the rate of carbon evolution. At the highest kiln temperature (1,800°F), the carbon was almost completely removed in the first 15 minutes of treatment. More than 30 minutes, however, were required to remove the carbon at a kiln temperature of 1,000°F. At any temperature, the carbon concentration could be reduced to less than 1% of the original value in less than 1 hour of thermal treatment.

Table 3
Summary of Bog Creek Incinerability Testing

Feed Material	Batch Size (lbs)	T_{kiln} (°F)	Feed Analysis	Solids Analysis 5 (min)	15	30	60	Exhaust Gas Analysis
Waste	4	1,800	u		u	u	
W	4	1,460	u		u	u	
W	4	1,000	u		u	u	
W	10	1,800	u,vo svo,m		u	u,vo svo,m		svo,vo m
W	10	1,460	u,vo svo,m	u	u	u,vo svo	u,vo svo,m	svo,vo m
W	10	1,000	u,vo svo,m	u	u	u,vo svo	u,vo svo,m	svo,vo m
W	10	1,460	u,vo svo,m	u	u	u,vo svo	u,vo svo,m	svo,vo m
Soil	10	1,460	u,vo svo,m	u	u	u,vo svo	u,vo svo,m	svo,vo m
Sed. (Bog)	10	1,460	u,vo svo,m	u	u	u,vo	u,m	svo,vo m

u = ultimate analysis
vo = volatile organics
svo = semivolatile organic
m = metals

○ 1800°F
△ ☐ 1460°F
◇ 1000°F
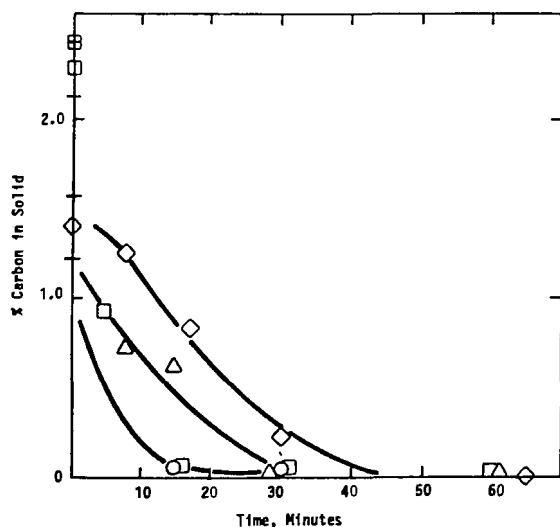
Figure 2
Influence of Time and Temperature on Carbon Content
of Residuals from Heat Treatment of Waste Samples

The continuous emission monitors also demonstrated the impact of temperature on the thermal destruction processes. Figures 3 and 4 illustrate the behavior of gas phase CO, CO_2 and O_2 as a function of time after the kiln was charged for two different operating temperatures. At high temperatures, the evolution of carbon is apparently fast enough to consume all available oxygen in the first 4 minutes after charging. There is a pronounced peak of CO in this initial period. After 5 minutes, the rapid reaction has ceased and emissions return to normal. For the low temperature run (1,000°F), the level of O_2 in the exhaust gas, is

depressed, indicating consumption of the organic carbon over a 20-minute period. This impact of temperature points out a key issue with rotary kiln incinerators. Rapid thermal decomposition of the waste can result in a "puff," and consumption of local oxygen. In practice, this phenomenon is seen as an excursion in CO in the flue gas just after a charge of material is put into the kiln. These results suggest that moderate kiln temperatures may be desirable for the Bog Creek Farm incinerator.
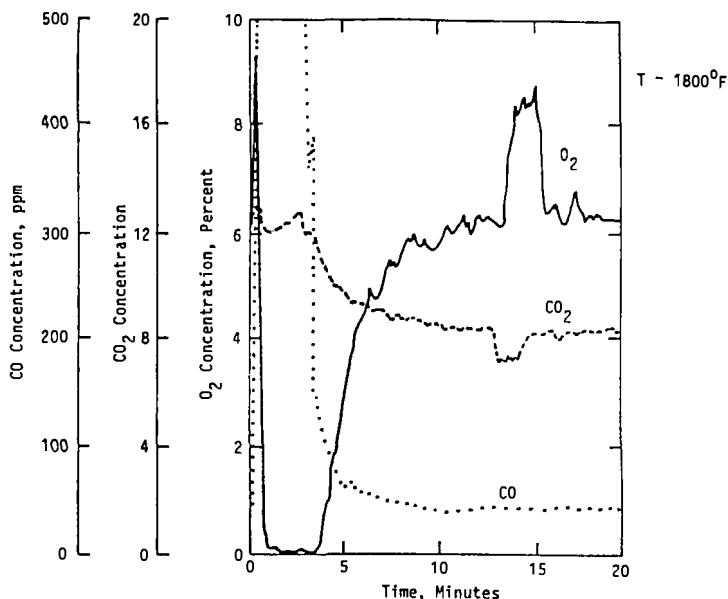
Figure 3
Exhaust Gas as a Function of Time at 1800 °F
Kiln Temperature
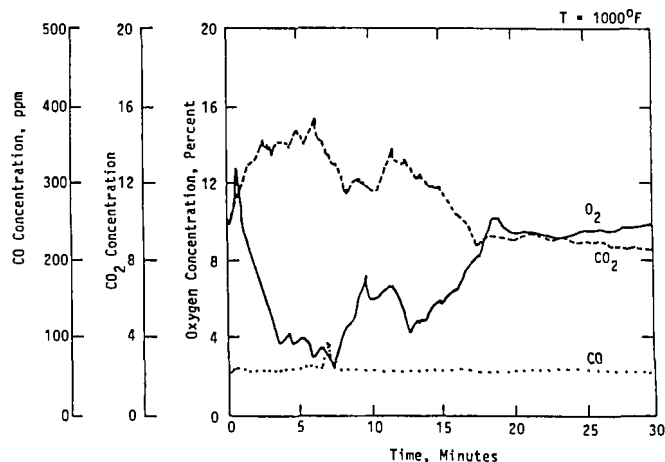
Figure 4
Exhaust Gas as a Function of Time at 1000 °F
Kiln Temperature

The Fate of Organic Compounds

The volatile and semivolatile trace organics measured in the solid before and after thermal treatment for one hour and at different temperatures are shown in Figures 5 and 6. The open bars in the diagrams represent the samples before treatment. After thermal treatment for 60 minutes, all organics were removed from the samples to below the detection limit of approximately 600 ppb as shown as black bars. This removal occurred even at temperatures as low as 1,000°F.

The results of the gas phase organic analysis as a function of kiln
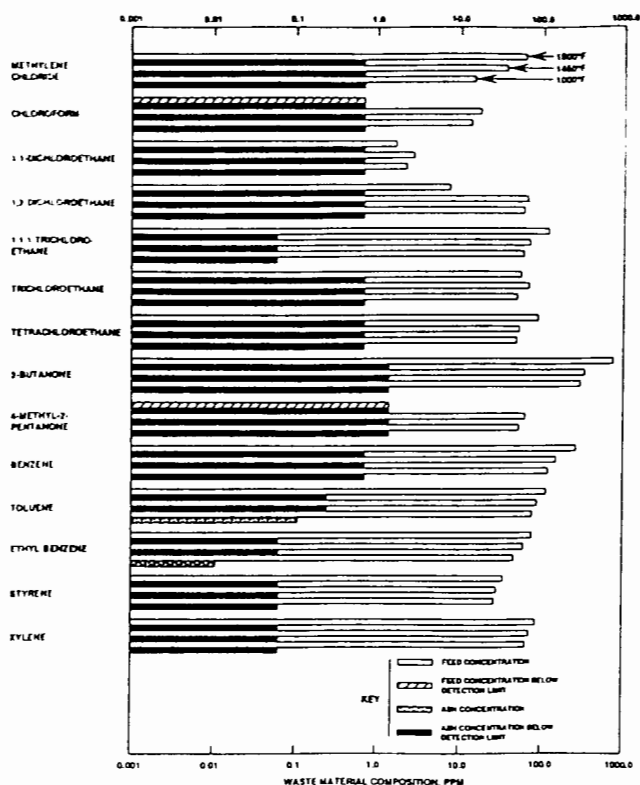
Figure 5
Trace Hazardous Volatile Organics in the Waste
Samples Before and After Treatment for 60 Minutes
at Different Temperatures

Figure 6
Trace Hazardous Semi-Volatile Organics in the
Waste Samples Before and After Heat Treatment
for 60 Minutes at Different Temperatures

or partial reactions of the compound present in the waste sample. These species, sometimes referred to as products of incomplete combustion (PICs), are generally polyaromatic hydrocarbons such as pyrene, phenanthrene and chrysene. Thus, the afterburner design must be chosen to destroy these types of organic species as will be discussed in the next section.

Figure 7
Organics Measured in the Kiln Off-gas that are
Originally in the Waste Stream as a Function
of Kiln Temperature

Figure 8
Organics Measured in the Kiln Off-gas but not
in the Waste Stream as a Function
of Kiln Temperature

The Fate of Heavy Metals

In this study the fate of the metals was determined by analysis of the test samples, analysis of the solid residuals and analysis of a total particulate catch for toxic metals. The feed and residual concentration of the metals in the bottom ash of interest are provided in Table 4.

As expected, the metals content of the ash was generally lower than the feed concentrations with higher kiln temperatures promoting greater

temperature are shown in Figures 7 and 8. As seen from these figures, most of the organics were destroyed in the kiln zone. However, several organic species were apparently produced in the kiln zone via cracking

removal of certain metals than lower term parameters. The metal enrichment in the particulates relative to the untreated waste stream is shown in Figure 9 for two different temperatures. At low temperatures, enrichment was slight and was within the bounds of the variability of metals in the waste stream. At high temperature (1,800 °F), the particulates were highly enriched in most metals except chromium. Arsenic, cadmium and lead were more concentrated in the fly ash particles. At the intermediate temperature (1,460 ° F), arsenic and cadmium were still highly enriched in the fly ash. Lead enrichment was less pronounced. Antimony, copper and zinc were no longer enriched relative to the untreated waste sample.

Table 4
Metals Content of the Feed and Residuals
for Selected Samples

Metal (ppm)	FEED (WASTE)		ASH	
	1800°F	1460°F	1800°F	1460°F
Antimony	6.7	180	1.2	11.0
Arsenic	1.56	2.33	0.287	0.302
Beryllium	0.17	<0.139	<0.098	<0.097
Cadmium	11.7	20.7	0.142	0.896
Chromium	135	942	12.9	107
Copper	18.4	209	6.36	36.5
Lead	683	3800	234	2160
Mercury	0.995	3.70	<0.047	<0.048
Nickel	5.98	9.47	<1.96	4.36
Selenium	<0.219	0.822	<0.196	<0.194
Zinc	86.8	263	31.6	59.6

Ash leaching results as a function of temperature are summarized in Figure 10. As shown, the results are generally favorable although for two samples, lead and cadmium exceeded the EP Tox standards (5 mg/L and 1 μg/L, respectively) at lower temperatures.

In summary, the kiln temperature performs two important roles in the thermal cleaning of the waste material from the Bog Creek site. In order to remove all organic carbon and hydrogen, longer times will be required at lower temperature; however, after 30 minutes even at low temperatures (1,000 °F), all organic material will be removed from the treated waste. For target hazardous organics originally in the waste, removal was complete even for low temperatures and short times. Metal vaporization and enrichment of toxic metals in fly ash was found to be a problem at higher operating temperatures, particularly for arsenic, cadmium, lead and antimony.

Influence of Material Type

In this study, four different materials wastes were tested for their thermal treatability behavior. These waste samples were taken from different locations on the Bog Creek site and were designated as waste (Sample No. 1), waste (Sample No. 2), soil and bog sediment.

The very different nature of the material and their behavior upon heat treatment are shown in Figure 11. Upon heat treatment of 1,460 °F, the waste samples and soil lose carbon very rapidly. In the first 5 minutes the carbon content for these materials was reduced to less than 1%. At 30 minutes the carbon level is below 0.1%. However, the bog sediment carbon content apparently increased (as-received basis) over the first 15 minutes of heat treatment as a function of drying and subsequently fell. The lowest level of carbon content achieved for the sediment after 60 minutes was 0.6%.

The delay in the release of organic matter from the sediment is attributable to the high moisture content of this material. The high water content of the sediment suppresses the material temperature in the bed until the moisture evaporates. For these conditions, the evaporation time can be substantial (approximately 30 minutes). Over this time period
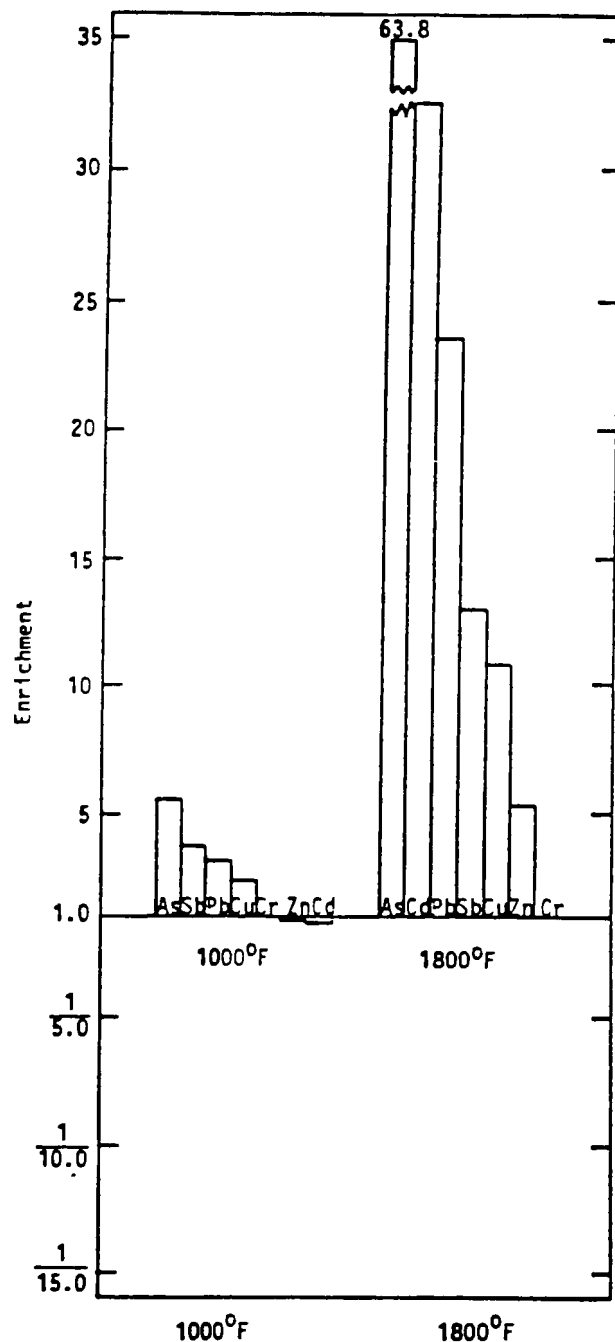
Figure 9
Metals Enrichment Relative to Waste Composition of Particulate Catch from Kiln Off-gas After Thermal Treatment at Different Temperature

there is little carbon evolution; consequently, the as-received carbon content increases due to the loss of moisture. Thus, for the high moisture material from the bog sediment, there are two apparent time scales: drying time and devolatilization time.

CONVERSION OF TREATABILITY TESTS INTO A CONCEPTUAL DESIGN

The treatability test results demonstrated that:

- Primary reactor temperatures of 1,400 °F and 2,200 °F (bed temperatures of 1,000 °F to 1,800 °F) with residence times of 30 to 40 minutes are adequate for devolatilization of Bog Creek Farm materials
- Moderate primary reactor temperatures will minimize the potential
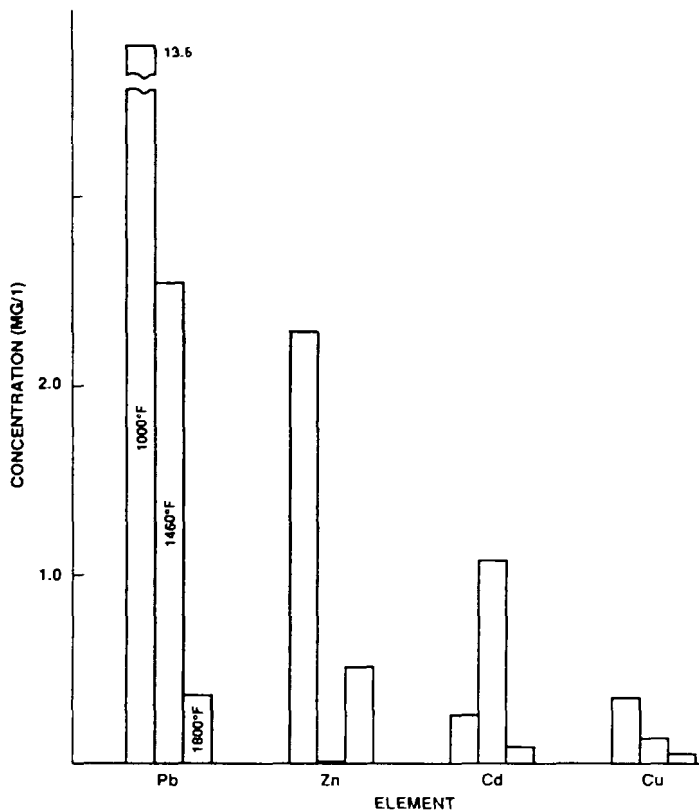
Figure 10
Influence of Treatment Temperature on Leaching
of Metals from Residual Ash
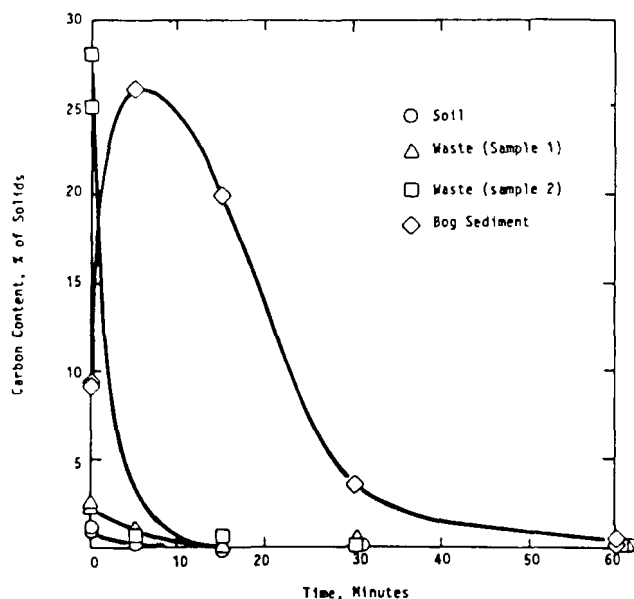
Figure 11
As Received Carbon Contents of Solids as a Function of
Time in the Rotary Kiln Simulator for Different Materials
(T = 1460°, 10 lb Charges)

for "puffs," and consequent overloading of the afterburner

• Afterburner temperatures in excess of 1,650°F are adequate for final destruction of contaminants

On this basis, the conceptual design was developed by Ebasco Environmental as nonbinding guidance for bidders and as a basis for cost

estimation. Critical elements in the conceptual design included selection of the basic system, selection of the incineration regime, development of process flowsheets and heat and material balances, determination of post-combustion air quality and solid residue treatment systems and then the development of equipment lists.

THE BASIC INCINERATION SYSTEM

The conceptual design focused upon a transportable rotary kiln based thermal destruction unit. The basic elements of this system included the kiln, secondary combustion chamber or afterburner, quench tower, air quality control system and ash quench system. The kiln installation for this site does not require its own wastewater treatment system due to the presence of a larger wastewater system for remediation of other site groundwater. A rotary kiln was chosen as the basis for thermal destruction unit conceptual design, while recognizing that vendors of all incinerator types could bid to performance specifications.

PROCESS FLOW DIAGRAMS AND HEAT BALANCES

Once the basic incineration process was selected, process flow diagrams were developed highlighting the thermal destruction unit itself, the air quality control system and the interfaces between the incinerator and the other site remediation activities. The development of a process flowsheet led to the calculation of heat and material balances around the thermal destruction unit and about the air quality control system. The heat and material balance about the incinerator was based upon the following assumptions:

• No. 2 distillate oil would be used as fuel for the incinerator
• Air atomization would be used rather than steam atomization
• Soil and sediments would be fed separately
• Unit capacity would be 5 tons/hour

The heat balance was used to assist in determining an appropriate incineration regime. As shown previously, the treatability tests demonstrated that any bed temperature greater than 1,000°F will volatilize the organics in the Bog Creek Farm materials. Consequently, kiln and afterburner heat balances were constructed for bed temperatures ranging from 1,000°F to 1,600°F and with afterburner temperatures ranging from 1,600°F to 2,000°F. Finally, the calculations were based upon 50% excess air for combustion in the kiln and 25% excess air for combustion in the secondary combustion chamber.

The results of preliminary heat balance calculations showed that the optimum fuel consumption (Btu/ton) occurs with a kiln bed temperature of 1,200° F, a kiln gas temperature of 1,600°F and an afterburner temperature of 1,800° F. Since the treatability studies demonstrated that such temperatures are adequate for thermal treatment of the Bog Creek Farm soils and sediments with significant "insurance" margin, they were chosen for the conceptual design. The final heat balances for the conceptual design are shown in Figures 12 and 13. Post-combustion controls for the facility were selected based upon the mobile nature of the installation, the low concentration of acid gases expected in the
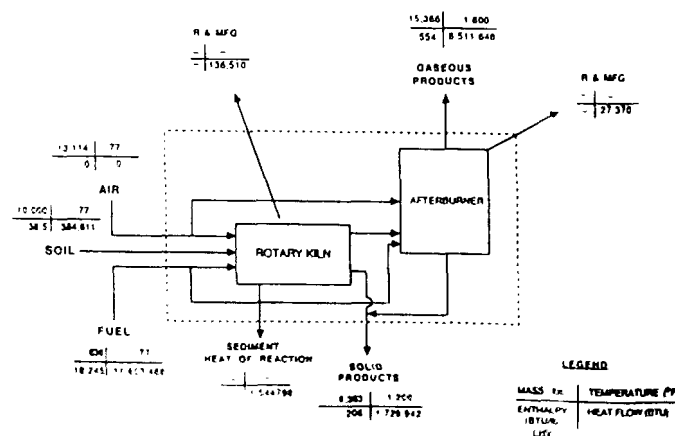
Figure 12
1 Hour Heat and Material Balance: Soil

Figure 13
1 Hour Heat and Material Balance: Sediment
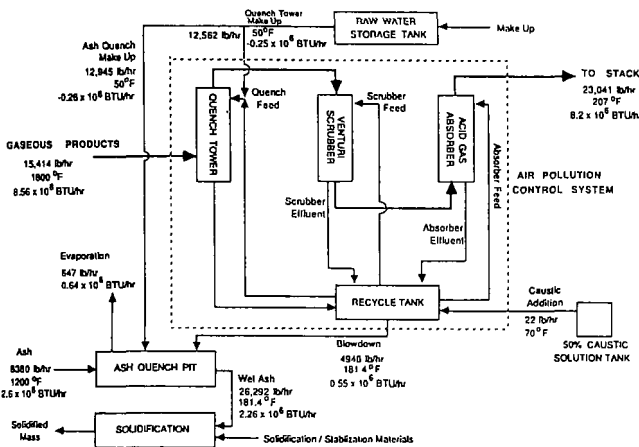
Figure 14
Soil Incineration: Simplified Material and Heat Balance
for Air Pollution Control and Ash Handling Operations

Table 5
Technical Specification Standard Section

Section No.	Description
	DIVISION 1 - GENERAL REQUIREMENTS
01000	Definitions, Codes and Abbreviations
01005	Specification Outline
01010	Summary of Work
01011	Site Description
01025	Measurement and Payment
01050	Field Engineering
01060	Regulatory Requirements
01065	Health and Safety Requirements
01201	Pre-Construction and Pre-Work Conferences
01202	Project Progress Meetings
01300	Submittals
01305	Letters of Commitment
01400	Site-Specific Quality Management Plan
01410	Construction Quality Control
01420	Material Laboratory Services
01430	Chemical Quality Control
01440	Chemical Testing Laboratory Services
01450	Spill Control
01505	Mobilization/Demobilization
01510	Temporary Site Utilities
01540	Security
01560	Temporary Controls/Environmental Protection
01563	Erosion and Sediment Control
01600	Equipment and Material Handling
01720	Project Record Documents
01725	As-Built drawings
01735	Project Closeout
	DIVISION 2 SITE WORK
02040	Dust and Vapor Control
02090	Off-Site Transportation and Disposal
02095	Drum Removal and Handling
02100	Site Preparation
02140	Aqueous Waste Handling
02200	Earthwork
02360	Steel Sheet Piling
02830	Fences and Gates
02900	Landscaping
	DIVISION 13 SPECIAL CONSTRUCTION
13180	Incineration
13350	Aqueous Waste Treatment System

products of combustion and the behavior of metals as shown in the treatability studies and discussed previously. This system is shown in Figure 14.

The system, as configured for advisory purposes, is a relatively simple process. Based upon the test burn/treatability studies, this incinerator should achieve the objectives of the site remediation program. Further, it should be readily integrated into the overall site remediation effort.

TECHNICAL BID SPECIFICATIONS

Ebasco Environmental's RD effort resulted in a complete bid document which was issued by the USACOE in early 1988. The entire remediation program requires that incineration be integrated with numerous other on-site activities. The technical bid specifications therefore covered not only incineration, but also all aspects of the site remediation including soil and sediment excavation, dewatering, dewatered groundwater treatment, site restoration, health and safety and quality assurance.

A complete list of the standard sections of the bid specification package prepared by Ebasco Environmental according to USACOE format is shown in Table 5. Section 13180—Incineration contained performance-type specifications for either on-site or off-site incineration. The treatability test results and conceptual design report were appended to the specification package for informational purposes only.

Performance requirements and bid information for both the on-site and off-site incineration options were provided in the following categories:

• General requirements

• Applicable regulations
• Construction submittals which included a system backup report and emergency response manual
• Waste, soil and sediment characteristics
• Equipment requirements specifics for the waste feed, ash handling and air quality control subsystems
• Process development and demonstrated performance
• Erection/installation for on-site incineration
• Disposal/treatment of residuals
• Incineration performance requirements
• Procedures to verify performance
• System rectification
• System operation and maintenance

Of particular interest is the issue of disposal/treatment of residuals, particularly the on-site treated soil/sediment or ash. Since the treatability tests indicated that the ash could possibly be suitable as backfill without further treatment, such as stabilization, the specifications cited on-site backfilling as the preferred disposal method for on-site incineration but did not require ash treatment prior to backfilling on-site. Rather, Ash Acceptance Criteria, shown in Table 6, were developed to set acceptable ash contaminant levels, and the TCLP limits were cited as the compliance levels that must be demonstrated prior to backfill.

The specifications also provided considerations relating to on-site trial burning after installation in order to verify performance, including selection of POHCs based on the site contamination; specifically, benzene and tetrachloroethylene were suggested as the volatile POHCs and di-n-butyl phthalate was included as the semivolatile POHC. Also,

Table 6
Ash Acceptance Criteria

Constituent	Concentration (ppm)
Arsenic	20
Barium	400
Beryllium	1
Cadmium	3
Chromium	100
Copper	170
Lead	100
Mercury	1
Nickel	100
Petroleum Hydrocarbons	100
Polychlorinated biphenyls	1
Selenium	4
Silver	5
Total Base Neutrals	10
Total Cyanides	12
Total Volatile Organics	1
Zinc	350

suggestions were made with regard to spiking the feed with a surrogate, such as carbon tetrachloride or hexachlorobenzene, to demonstrate DRE (Destruction and Removal efficiency).

ON-SITE INCINERATION

As a result of the bidding process, a remediation contractor was selected by the USACOE and construction was initiated in 1989. An on-site, temporary incinerator was installed and successfully operated. Remediation of the on-site waste, soil and sediment was essentially completed at the time of the writing of this paper (in August of 1990).

A schematic diagram of the on-site incineration system is shown in Figure 15, and some operating parameters are given in Table 7. The selected incinerator was a rotary kiln system which included a cyclone prior to the afterburner to remove solids from the off-gas, a quench tower, baghouse and acid gas scrubber and a wet ash quench system. This system was modified during construction to include oxygen enrichment in order to meet the New Jersey particulate emission requirement of 0.03 gr/dscf (N.J.A.C. 7:26-10.7).

During operation, ash was stockpiled until test results confirmed acceptability for backfilling. At the time of writing this paper, all the tested ash had passed the acceptance criteria although some data were still outstanding. Treated groundwater obtained from the dewatering operation during soil and sediment operation, was used for off-gas and ash quenching and scrubber water was recycled back to the groundwater treatment system. This process eliminated the need for any treated effluent discharge. Approximately 15,500 yd^3 of waste/soil and sediment were incinerated in approximately 3 months of operation.

CONCLUSION

Ebasco Environmental's remedial design effort, which culminated in the on-site incineration of contaminated soil and sediment at the Bog Creek Farm site, included thermal characterization, treatability testing and conceptual design. These activities were proven useful in the subsequent preparation of bid specifications as well as providing site-specific information to potential remediation system selection and on-site operation.
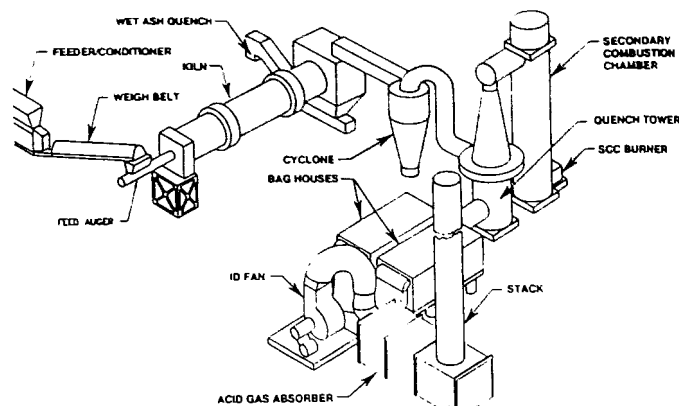
Figure 15
Thermal Destruction Unit

Table 7
On-site Incinerator Process Specifications

Item	Value
Waste soil rate, TPH wet basis @ 15% moisture	15-20
Solid residence time, minutes	>35
Kiln size, dia x Length, feed	7.5 x 45
Kiln outlet gas temperature, F	1450
Secondary combustion chamber outlet temperature, F	1700
Secondary combustion chamber outlet oxygen concentration, measured in stack, % dry	>3%
Secondary combustion chamber res. time @1700 F, sec	>2
Fuel for burners	propane
Burner rated cap., MM Btu/hr	82
Baghouse inlet temp. measured at quench tower exit, F	350
Particulate loading after baghouse, gr/dscf	<0.03
HCl removal efficiency, if > 4 lb/hr	>99%

Remediation of Gasoline-Contaminated Groundwater:
Spray Aeration/Internal Combustion Oxidation

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ABSTRACT

The use of a heated vacuum chamber for spray aeration enhances the rate of evaporation of gasoline from contaminated groundwater. The gasoline vapors are thermally oxidized by feeding them to the intake of an internal combustion engine, where they are burned as part of the combustion process.

A vacuum will increase the rate at which the gasoline evaporates, as does the addition of heat. Separating gasoline from the groundwater is the first obstacle; the gasoline vapors in the air stream must also be treated before release to the atmosphere. Both problems can be solved by thermal oxidation. The vapors in the air stream are below the flammability level, thus it is not possible merely to burn them. However, by feeding the vapors to an internal combustion engine which is powering the system pump and creating the vacuum, the vapors are consumed as part of the combustion process. The emission exhaust levels of the engine are unchanged because the vapors become part of the fuel. Thus, this system efficiently treats the effluent stream from the spray aeration unit.

This system is a fully self-contained remediation system that uses thermal vacuum spray aeration and compressive thermal oxidation. It costs considerably less than conventional systems of air strippers with carbon absorption or catalytic thermal oxidation.

INTRODUCTION

Gasoline-contaminated soil and groundwater have become major concerns in recent years as more and more leaking underground storage tanks have been discovered. Currently, two methods are typically used to remediate groundwater before it is discharged to a reinfiltration gallery, sewers or storm drains: carbon filtration and air stripping. Carbon filtration is not desirable on highly contaminated sites, as the costs of carbon and its associated handling and disposal become prohibitive. With air stripping, if direct venting is allowed, the cost to replace fouled packing is the only major maintenance expense. However, in areas where emissions are controlled and risk assessments based on benzene concentrations are the governing factor, as is the case in the metropolitan areas of California, vapor phase carbon treatment for air polishing after air stripping is required. On highly contaminated sites, carbon costs again become prohibitive.

A logical alternative for eliminating gasoline vapors is to burn them. On most sites the level of hydrocarbons present in the vapor stream is insufficient for combustion to be maintained by these vapors alone. Either additional fuel must be added to sustain combustion, or a catalyst must be used to maintain combustion. A system has been developed to utilize the energy of the heat of combustion of the vapors and supplemental fuel. Part of the heat is converted to work to operate the pumps of the system while the remaining heat is utilized to enhance the separa-tion of hydrocarbons from the water.

This system combines a thermal oxidation unit with a unique spray aeration unit. Although the aeration unit operates on the same principle as an air stripper, it has no packing, thereby eliminating efficiency problems due to fouled packing. The spray aeration system sprays heated water in a vacuum chamber. The engine develops a vacuum on the spray aeration tank and also provides a vacuum on the well(s) for vapor extraction.

PRINCIPLES OF OPERATION

The entire system is self-contained and needs no additional power source. The engine furnishes all power to drive the other components. The technologies behind this system are spray aeration enhanced by heat and vacuum and internal combustion of hydrocarbons in an engine. Both of these are well proven concepts. Spray aeration has been proven effective on both large and small scales to separate dissolved hydrocarbons and water. The technology for controlling internal combustion engine emissions has been effectively demonstrated by the automotive industry.

This remediation system combines three separate methods of remediation and is more efficient than any of the methods alone:

- Vapor extraction from soil
- Spray aeration
- Thermal oxidation using an engine for combusting hydrocarbon-laden vapors and a catalytic converter to control the exhaust

The soil vapor extraction system uses a vacuum pump driven by the internal combustion engine; alternatively, the vacuum may be developed by the engine itself. The vacuum on the well causes the hydrocarbons to volatilize and flow with the air into the well and up to the vacuum pump.

Water contamination is remediated using a spray aerator. In this system, water-hydrocarbon separation is enhanced by both vacuum and heat; by lowering pressure, the temperature at which the hydrocarbons vaporize decreases; increasing the temperature further increases the potential for the hydrocarbons to vaporize. The spray aerator takes advantage of both these principles by spraying heated water in a vacuum (Fig. 1).

Spray aeration works on the same principle as an air stripper. In an air stripper, air is moved quickly over the surface of the hydrocarbon-laden water to volatilize the hydrocarbons. In spray aeration, hydrocarbon-laden water droplets move quickly through the air causing the hydrocarbons to volatilize; however, in the spray aerator, there is no packing to foul or replace. In the spray aerator, heated water is sprayed in a vacuum. Lowering the pressure in the spray tank increases the rate of evaporation of the hydrocarbons. Heat has the same effect. By adding

heat and lowering the pressure, the hydrocarbons are boiled or flash-evaporated off the water droplet surface. A vacuum of 12 inches of mercury is developed on the tank and the water is heated with waste heat from the engine's cooling system. There are limits to the level of vacuum on the tank and the quantity of heat added to the water which must be maintained to avoid evaporating a large quantity of water along with hydrocarbons. As an example, at 110°F and 27 inches of mercury, all the water would evaporate and be passed to the engine. To ensure sufficient hydrocarbon removal, the water is recirculated through a second set of spray nozzles (Fig. 2).

vapors. In the prototype test, water mixed with 1,700 ppm of hydrocarbons was fed to the spray aeration unit at approximately 3 gpm. Vacuum on the tank was maintained at 12 in. of mercury and the recirculating water was heated to 100°F. The vapor flow rate was 40 cfm. The discharge had an average total petroleum hydrocarbon (TPH) concentration of 32 ppm, the cleanup efficiency was 98%. These results are 18% higher than spray aeration without vacuum or heat.

Figure 1
Spray Aerator
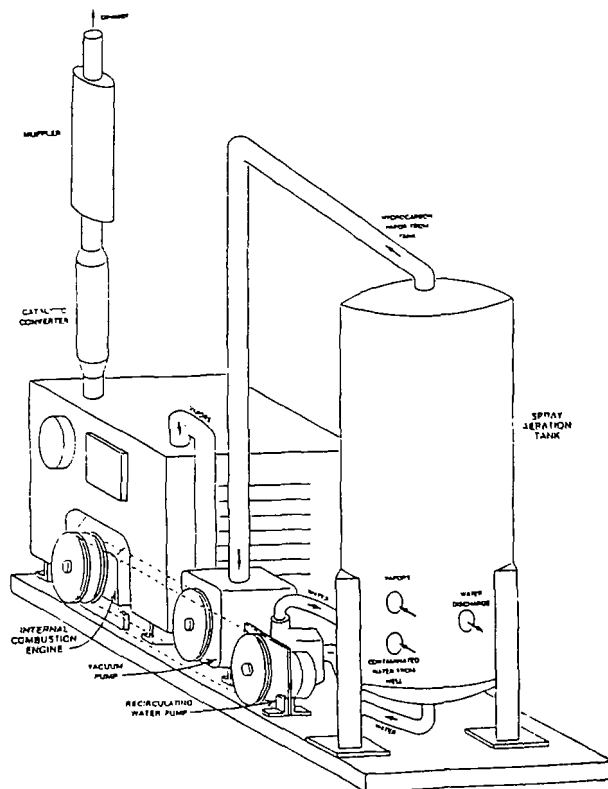
Figure 2
Remediation System

The vapors drawn by the vacuum are directed to the intake of the engine where they are mixed with the primary fuel and then combusted in the engine, thus consuming the total hydrocarbon mixture. The engine's air:fuel ratio is adjusted to maintain efficient combustion when the vapor from the wells and the spray aerator are combined with supplemental air or fuel, thus resulting in minimum emissions from the engine. The exhaust from the engine is passed through a small automotive catalytic converter to ensure complete combustion (Fig. 3).

Because the entire system is under vacuum until the vapors enter the cylinders of the engine for combustion, any possible leaks of seals or connections are into the system, with no loss of hydrocarbons to the atmosphere. If there is no combustion, the engine stops running. The engine is the power source for all other equipment; all systems stop when the engine stops, thus preventing uncontrolled releases of hydrocarbons to the atmosphere. The well pumps are pneumatically powered from an air compressor driven by the engine; therefore, well pumping also ceases if the engine shuts off. In addition, the engine has shutoff devices triggered by loss of vacuum, low oil pressure or engine overheat.

TEST RESULTS

Currently there are more than 25 units permitted and operating on the west coast.

Initial tests were conducted on the prototype spray aeration system and the engine to determine the basic efficiency of the equipment in remediating gasoline-contaminated water and thermally oxidizing the

Figure 3
I/C Engine and Catalytic Converter

The engine exhaust was analyzed for hydrocarbons using a continuous infrared meter and by taking samples and analyzing them in a gas chromatograph. These tests showed the emitted hydrocarbons to be, on the average, below 70 ppm in the exhaust stream. At this level, less than 1 lb/day of hydrocarbons is emitted from the exhaust while more than 125 lb of hydrocarbons are consumed by the engine during the same time period. The benzene concentration in the exhaust stream

was near 1 ppm. By adjusting the air-fuel ratio, the benzene level was lowered to less than 0.1 ppm, resulting in emissions of less than 0.003 lb/day of benzene. This level is low enough to pass risk assessment criteria in the Los Angeles area. Current sites have hydrocarbon vapors as high as 140,000 ppm going into the engine with only 15 ppm TPH being measured in the exhaust steam and benzene at less than 1 ppm.

The following are the results from a typical site. The system was connected to three wells. Free product was present in two of the wells; the third well had no free product. A vacuum was placed on the first well and the air:fuel ratio was adjusted.

This first well produced enough vapors to run the engine with no additional fuel; moreover the flowrate from the well had to be restricted to avoid running in an over-rich state of combustion. The well, which had been bailed of free product before the system was started, had 1 foot of free product in it after 1.5 hrs. of operation. Prior to the introduction of a vacuum on this well, a 1 foot recovery of free product would take 48 hrs. or longer. The well was restarted and the same results occurred; free product flow to the well increased.

No free product is pumped to the spray aerator. The free product is evaporated in the well by the vacuum and this vapor is extracted by the vacuum on the well and fed directly to the engine. Water out of the well was tested and found to have 8.9 ppm TPH with benzene at 3.5 ppm. Initially, there was approximately 90% reduction of contaminants. The discharge from the system was tested and found to be below the detection limits of 0.1 ppm TPH and 0.7 ppb benzene. These results are typical for the 25 sites at which the systems are in operation. These particular units are designed for 8-10 gpm. This system has shown itself to be effective on typical service station size lots for remediating soils and groundwater. The system is capable of remediating up to 150 lb of hydrocarbons per day.

COSTS

Currently this system costs approximately $60,000. It is ready to operate when unloaded from the delivery truck and needs only to be connected to the wells from which water and air are to be extracted and supplied with supplemental fuel of propane or natural gas fuel.

However, operating at the maximum combustion of the extracted vapors, the engine needs no supplemental fuel. Operations and maintenance for the system costs are the costs of weekly oil and filter changes, a monthly tuneup and an annual overhaul on an engine running 24 hours per day. These maintenance expenses require approximately 4 hours of labor per week (at approximately $50 per hour) and approximately $50 in parts and supplies per week, resulting in a total operations and maintenance cost of $250 per week.

An equivalent system using carbon adsorption for vapor and water phase would require 1500 lb of carbon per day. Comparable operations and maintenance costs for a carbon system would include carbon replacement costs; the costs for electricity to operate three down well pumps, a circulation pump and vapor extraction pump; and labor costs. Carbon replacement costs would be approximately $21,000 per week; 625 kilowatt hours of electricity would be used per week at $0.15 per kilowatt hour to run the pumps in the system; and weekly labor (at $50/hr) would be approximately 3 hours, including carbon changeout time. This results in weekly costs of: $108 for electricity; replace 1500 lbs of carbon per day at $2 per lb; and $150 for labor yields a total cost $21,258 a week for operations and maintenance of the carbon system. Obviously there is a significant cost savings in using the combustion system at a heavily contaminated site.

Even at low vapor concentrations, this new system is more economical than a carbon system. For a site for which only 1% of the fuel for the engine is supplied by extracted vapors, the cost of supplemental fuel (99% natural gas) is approximately $50 per week, resulting in a new total operations and maintenance cost of $300 per week for the combustion system. Comparing this system again to a carbon treatment system for such a site, we find that the carbon usage rate would be approximately 15 lbs per day, while all other costs for the carbon system remain the same. At this carbon usage rate, the weekly cost of carbon would be $210 per week, resulting in a total operations and maintenance of $418 per week, over $100 more than for the combustion system.

Comparison of this system to an air stripper/vapor extraction unit with a catalytic oxidation system for vapor control results in the following operations and maintenance cost analysis. Assuming no supplemental heat is needed to maintain the catalytic reaction, power requirements are approximately 1 kw per hour for water pumping to the air stripper, 4 kw per hour for air and water pumping through the air stripper and 3 kw per hour for the vapor extraction pumps resulting in 8 kw per hour or 1340 kilowatt hours per week. At $0.15 per kilowatt hours, the electrical costs would be $1,201 per week. Add three hours of technician time and weekly operations and maintenance costs would be $1,351. Again the spray aeration/internal combustion system is significantly more cost-effective than an air stripper/vapor extraction system with a catalytic oxidation unit.

CONCLUSIONS

Vacuum enhanced spray aeration with thermal oxidation has been demonstrated to be an effective method of removing hydrocarbons from contaminated groundwater and oxidizing the contaminants so that they are no longer a significant health hazard. The vacuum to the well effectively increases the flow of free product to the well as it extracts vapors from the well for combustion. This system has been demonstrated to be an economical and practical alternative to carbon canisters and their associated costs.

The vacuum spray aeration tank has been demonstrated to have an effectiveness equivalent to a packed-tower air stripper, without the problems of packing fouling or the expense of packing replacement costs. Savings are realized in both the initial cost of equipment and the operating costs of a conventional system using vacuum extraction, a packed-tower air stripper and carbon polishing.

While optimization of operating parameters is being further defined, this system has been shown to be both practical and cost-effective for remediation of gasoline-contaminated groundwater and contaminated soil vapors.

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Hazardous Waste Minimization and Control at Army Depots

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ABSTRACT

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) recently conducted visits to eight Army depots involved in the maintenance of tactical equipment. The purpose of these visits was to identify research needs related to hazardous waste minimization in addition to control of volatile organic compounds VOCs emitted during operations. The focus of the information collected related to methods of paint application and removal, degreasing operations, and wastes generated from electroplating operations. The information was used to identify several research projects that are currently being conducted to address specific waste minimization issues at selected facilities.

A total of sixty-nine potential waste minimization and VOC reduction/control projects were identified at the depots visited. Three of these projects were selected for research/demonstration projects that will be conducted and implemented at appropriate depots. The three projects selected involve: (1) The evaluation of paint application systems to increase transfer efficiency to reduce VOC emissions and paint waste generation, (2) the extension of chromic acid bath lives via electrodialysis, and (3) the extension of the lives of alkaline paint-stripping baths to reduce the amount of generated wastes.

Findings of the depot visits and subsequent technical efforts described in this paper.

INTRODUCTION

U.S. Army depots are involved in the maintenance of tactical equipment. Maintenance operations generate large amounts of hazardous waste and air pollutants as a result of paint application, paint removal, degreasing and plating processes. Control, treatment and/or disposal of air pollutants and hazardous waste are expensive.

Preventing the generation of hazardous waste at the source reduces the amount of waste materials that must be tracked, treated and/or disposed of, and often results in significant cost savings for the depots. Waste minimization also reduces the long-term liability associated with the generation of hazardous waste.

U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) personnel are conducting research and development projects pertaining to hazardous waste minimization (HAZMIN) at Army depots. Hazardous waste minimization is a viable method for solving some of the problems created by the generation of hazardous waste. Additionally, HAZMIN can create a safer work environment.

Anniston (Alabama), Corpus Christi (Texas), Letterkenny (Pennsylvania), Red River (Texas), Sacramento (California), Sharpe (California), Tobyhanna (Pennsylvania) and Tooele (Utah) Army Depots were visited between April and July 1989. The purpose of these visits was to identify research needs related to HAZMIN and/or control of volatile organic compounds (VOCs) emitted during depot operations. The information was used to define several research projects that are currently being conducted as part of USATHAMA's Pollution Abatement and Environmental Control Technology (PAECT) program.

A total of sixty-nine potential waste minimization and VOC emissions control projects were identified at the eight depots visited. Of these, 24 were identified as short-term, high priority projects. The projects ranged widely in technical effort and scope of work required. Three projects were selected for demonstration testing based on the current scope of work, interest of depot personnel, applicability of the projects at several depots and potential for hazardous waste and/or VOC reduction. Each of the three projects is currently being initiated at an appropriate Army maintenance facility. Testing and evaluations will be conducted during the fall of 1990.

This paper presents the some of the findings of the depot visits and describes subsequent technical efforts in hazardous waste minimization and VOC control/reduction.

PAINT APPLICATION

Paint application is a major source of hazardous waste generation and VOC emissions at Army depots. Each waste generation problem of this operation is addressed separately.

Generation of Hazardous Waste

Painting operations at Army depots produce large amounts of hazardous waste. Waste results from excess paint, paint overspray, use of cleaning solvents and the capture of paint particulates to prevent their release into the atmosphere. Paint wastes are hazardous because components of the paints are often toxic and/or flammable.

All the depots visited used dry filters on some paint booths to capture the particulates from overspray during painting operations. The filters become clogged as the overspray accumulates and must be replaced. Some of the depots dispose of all filters as hazardous waste, whereas other depots have determined that some of their filters are nonhazardous waste.

The water-wash paint booth is another type of control device used by the depots to remove paint particulates from overspray. In these booths, water flows down a wall at the rear of the paint booth and over an air vent through which the booth exhaust flows. The air containing the paint overspray is vented through the water and the particulates are captured. The resulting water and paint mixture (sludge) is collected in a trough.

Paint sludge from water-wash booths is a major hazardous waste problem at many of the installations. Some of the depots are attempting to reduce the amount of sludge by separating the paint residue from water through the use of cyclone separators combined with the addition of detackifying agents. Several facilities have expressed interest

in using filter presses to decrease the volume of collected sludge.

Other methods of minimizing the generation of hazardous waste during depot painting operations are being implemented by the installations:

- Development of alternative methods for capturing particulates
- Recharacterization of waste materials
- Segregation of hazardous from nonhazardous waste
- Replacing paints which have hazardous characteristics
- Increasing transfer efficiencies of paint application systems

VOC Emissions

Most depots are undertaking steps to reduce VOC emissions to levels required by state or federal statutes. The depots located in California and Pennsylvania are under regulatory pressure to decrease VOC emissions. Even in states without stringent VOC regulations, depots are expected to attempt to reduce VOC emissions and to complete a health and safety evaluation before regulatory authorities will permit new VOC sources.

VOC control technology is very expensive and may not be practical because the sources of VOC emissions often are located in different sections of the installation. Most depots are focusing on reducing VOC emissions by switching to paints with low VOC contents and improving the transfer efficiencies of paint application systems.

Paint application operations at Army depots are production oriented. Consequently, painting as rapidly as possible often is essential. Increased rates of production often are achieved by increasing nozzle pressure and/or using a wider paint gun nozzle angle. Overspray also increases as a result of these changes, resulting in higher VOC emissions and lower transfer efficiency. The use of high efficiency painting equipment will reduce the amount of overspray and VOC emissions. Consequently, less hazardous waste in the form of spent dry filters and sludge from water-wall paint booths will be generated.

One of the USATHAMA HAZMIN projects presently being initiated is the evaluation of transfer efficiencies of paint application systems at Sacramento Army Depot (SAAD). Several high volume low pressure (HVLP) spray guns will be purchased and tested to determine their effectiveness in decreasing VOC emissions. The information obtained from this project will be used by depot personnel to identify and implement high efficiency painting systems.

The test equipment will be evaluated on an actual production line at SAAD. The following variables will be measured to assess the effectiveness of the paint application equipment:

- Transfer efficiency
- Speed of paint application to achieve a high quality coating
- Ability to meet coating specifications

A final report will be available in early 1991.

PAINT REMOVAL

Paint stripping operations generate large amounts of hazardous waste at Army depots. They are also a significant source of VOC emissions.

The method of paint removal depends on the tactical equipment being processed and often varies between depots. Chemical and mechanical paint removal will be discussed separately.

Chemical Paint Removal

Chemical stripping compounds commonly used during paint removal are either methylene chloride- or alkaline-based formulations. Methylene chloride-based strippers are targeted for replacement because of health and safety concerns. Many chemical strippers also contain VOCs.

Equipment parts to be stripped of paint usually are submerged in a tank containing the stripping solution. This method of paint removal generates large amounts of hazardous waste in the form of spent stripping solutions and paint sludge. Paint removal operations at Army depots are also large generators of wastewater.

Army depots are exploring several methods for hazardous waste minimization during paint stripping operations:

- Replacement of strippers containing hazardous components

- Increasing the lives of stripping solutions
- Decreasing the volume of sludge via filter press

The removal of paint residues generated during stripping operations from paint stripping baths may be a viable method for extending the useful life of chemical stripping solutions. The solid residue remains in the bath after paint is removed from equipment parts and continues to chemically react with the stripping reagents. Eventually, these reactions will deplete the stripper. Removal of the residues may result in longer bath lives, fewer tank changes and a reduction in hazardous waste generation.

Another project selected for USATHAMA demonstration testing is to extend the life of a chemical stripping solution by removing solid residues from the stripping bath. The project will be conducted on an alkaline paint stripping bath at Letterkenny Army Depot. During this project, the reduction in waste generation will be quantified. Process variables of the filtration system will be determined and factors that may affect the life of the process bath will be studied. Data obtained during this demonstration test will help implement the technology at other depots. A final report detailing the results of this task will be available in early 1991.

Abrasive Paint Stripping

Many different abrasive blast media are used at Army depots. Types of media used include walnut shells, steel shot, aluminum oxide, peridot, sand, glass and plastic beads. Spent media usually are disposed of as hazardous waste because of heavy metal contamination from paint pigmentations and surface finishes removed from equipment during blasting operations.

Several waste minimization efforts were identified during the visits to the depots:

- Implementing or improving recycling of blast media
- Use of media with longer usable lives
- Alternative blast methods
- Optimization of blast parameters

Some of the depots indicated a desire to replace methylene chloride-based chemical strippers with plastic media blasting (PMB). PMB generates less hazardous waste than chemical strippers. Indications are that plastic media do not damage sensitive substrates and are more recyclable than many other types of blast media.

DEGREASING OPERATIONS

Army depots use various chemicals in degreasing and cleaning processes. These compounds are sources of VOC emissions and hazardous waste generation at the installations. The primary degreasing solvent used at the depots 1,1,1-trichloroethane.

Several depots have tried to recycle 1,1,1-trichloroethane. However, efforts to recover the spent solvent have been plagued by equipment failure, acidification of the solvent and low recovery rates.

Some of the installations are investigating the use of heated fluidized beds to remove paint and degrease equipment. In the fluidized bed process, paints and grease are pyrolized and the gaseous emissions from the bed are destroyed in an afterburner. Fluidization of the bed medium results in efficient heat transfer.

PLATING AND SURFACE FINISHING OPERATIONS

Normal surface finishing operations at Army depots include cadmium and chromium plating, anodizning and metal electrostripping processes. Other metals such as brass, copper, gold, nickel, silver, tin and zinc also are plated.

Several waste streams are generated during these operations at Army depots. Process solutions, such as chromic acid and chromate conversion coatings, are frequently replaced and disposed of as hazardous waste. Rinse water becomes contaminated due to carryover from the process baths and must be treated as hazardous waste. Treatment of the rinse water results in the generation of sludge. The plating baths are rarely dumped and are not a large source of hazardous waste.

Hazardous waste minimization efforts can be targeted at the process

tank, at wastewater from rinse tanks, or at the sludge from wastewater treatment. The HAZMIN target areas are discussed separately.

Hazardous Waste Minimization for Process Solutions

Army depots are undertaking efforts to minimize waste from plating and surface finishing operations at the source - the process solutions. Several depots have eliminated cyanide-based cadmium electroplating by using other types of process baths. Some installations have expressed interest in replacing some cadmium plating operations with aluminum ion vapor deposition (AIVD).

Another method directed at the process tank is to increase the life of the process solution. Contaminants that shorten the lives of the process solutions generally consist of metals introduced by carryover. The effectiveness of using an electrodialysis unit to remove metal contaminants from a chromic acid bath will be demonstrated as an USATHAMA HAZMIN project. Chromic acid may be continuously rejuvenated during the process by oxidizing trivalent chromium to its hexavalent form. The electrodialysis unit will be installed and tested on a process tank at Corpus Christi Army Depot (CCAD). A final report will be available in 1991.

Reduction of Wastewater Generation

The amount of wastewater generated during plating and surface finishing operations can be decreased by reducing dragout from process tanks. Some depots use a spray rinse to remove and return most of the dragout to the process tank. The water from the spray rinse can be used in the process tank to replace water lost through evaporation. Other depots rinse parts directly over plating baths and use drainage boards between process and rinse tanks.

Army depot personnel have expressed interest in reclaiming metals from the rinsewater. Metals can be efficiently recovered from wastewater and returned to process tanks by such methods as ion exchange, evaporation, reverse osmosis and electrodialysis. CCAD personnel, for example, are presently trying to implement a closed-loop process that will use ion exchange and electrodialysis to remove chromium and other metals from rinsewater. The rinsewater could be recycled and the chromium converted to its useful form for reuse in a chromic acid bath. This system, in conjunction with the USATHAMA test system, has the potential for zero discharge of hazardous waste.

Reduction of Hazardous Sludge Volume

Wastewater from Army depot plating and surfacing operations requires treatment before discharge to the environment. Generally, metals in the wastewater are precipitated out as metal hydroxides at the installation's industrial wastewater treatment plant (IWTP). The resulting sludge usually is disposed of as hazardous waste. Consequently, HAZMIN efforts can be applied to the treatment of wastewater once the water reaches the IWTP.

Several methods have been, or are now being, implemented to minimize hazardous sludge generation. Some depots combine wastewater streams, and all sludge generated from wastewater treatment is considered hazardous. Segregation of hazardous and nonhazardous wastewater streams will reduce the amount of sludge classified

as hazardous waste. At some of the facilities, the heavy metal concentrations may be low enough that the sludge produced is not EP toxic. The sludge is being recharacterized and may be delisted if it is not EP toxic. Several depots have achieved sludge volume reductions through the use of filter presses.

OTHER USATHAMA HAZARDOUS WASTE MINIMIZATION EFFORTS

Commercially available, state-of-the-art technology is being evaluated in support of the Army depots' hazardous waste minimization efforts. Three additional USATHAMA demonstration projects are outlined below.

Alternative Chemical Paint Strippers

The identification of commercially available chemical paint strippers which may be viable alternatives to methylene chloride-based strippers is presently being conducted. The evaluation of the stripping performance of one of the formulations identified is under way on an operational paint stripping line at SAAD.

The elimination of methylene chloride-based chemical paint stripping solutions will aid in the reduction of total toxic organics (TTO) and VOC emissions. The use of less hazardous strippers will also significantly decrease the generation of hazardous waste at the depots.

Fluidized Bed Paint Stripper/Degreaser

The feasibility of using a heated bed of fluidized aluminum oxide to remove grease and paint from tactical equipment parts is being evaluated at Red River Army Depot. The results of this demonstration test will be available in mid 1991.

A fluidized bed can directly replace chemical degreasers and paint strippers for parts that can tolerate temperatures up to 850° F. This system can substantially reduce the generation of hazardous waste and provide a safer work environment.

Aluminum Ion Vapor Deposition

The feasibility of using aluminum vapor plating in lieu of cadmium plating is being evaluated at Anniston Army Depot. Cadmium plating is a large source of hazardous waste generation at most Army depots. A report detailing the results of this project will be available in mid 1991.

During aluminum vapor plating, the metal is deposited directly on the part to be plated. Aluminum ion vapor deposition does not require the use of hazardous materials and does not generate hazardous waste. Aluminum also has been shown to provide a superior corrosion resistance compared to cadmium.

CONCLUSION

U.S. Army depots are making progress towards the Army's goal of a 50% reduction of the total hazardous waste generated in fiscal year 1985 by the end of 1992. The technologies currently being evaluated by USATHAMA may assist the depots in meeting the Army HAZMIN goal. However, significant obstacles still remain, including lack of resources available to implement proven technology and lack of sufficient technical information transfer among the installations.

The Installation Restoration Program Information Management System (IRPIMS) and An Overview of Air Force Hazardous Waste Investigations

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ABSTRACT

The Installation Restoration Program Information Management System (IRPIMS) was developed by the Air Force Human Systems Division, IRP Program Office to support the data management needs of its Air Force hazardous waste program. The system was designed in 1986 and was operational in 1987. Approximately 80% of the technical data stored consists of analytical sampling results. Data continue to be loaded into the system as IRP project data become available. More than 600,000 analytical records have been entered into the system.

The system stores information on more than 2000 hazardous waste sites that are distributed across 196 Air Force installations and 14 Major Commands. More than 7000 sampling locations (monitoring wells, soil borings, etc.) are identified from which analytical results can be retrieved and evaluated. In addition, the system stores and processes data related to general site and sampling location information, lithologic descriptions, monitoring well completion information, groundwater levels and sampling test methods.

The intent of this paper is: (1) to provide an overview of the roles and capabilities of IRPIMS and (2) to describe the Air Force's Installation Restoration Program in terms of the investigative effort performed, the types and concentrations of contamination found and the association of contaminants detected in groundwater at a variety of hazardous waste site types.

INTRODUCTION

The Air Force Human Systems Division Installation Restoration Program (IRP) Program Office (HSD/YAQ) is one of three service centers providing IRP technical and contract administration support to Air Force installations and Major Commands (e.g., Strategic Air Command, Tactical Air Command, etc.). IRP projects generate technical reports containing large volumes of hydrogeological and chemical data that are difficult to manage with manually maintained systems. Mere storage and availability of these reports containing large amounts of hard-copy data does not represent information, in the modern sense, without the ready access and computational capability of a main frame computer equipped with the query tools of a relational data base. It was with these factors in mind that the Installation Restoration Program Information Management System (IRPIMS) was designed for use by the IRP Program Office and its customers.

IRPIMS was designed by a multidisciplinary team of professionals consisting of hydrogeologists, chemists, applied statisticians, system analysts and IRP project managers. The major emphasis in designing the system in 1986 was to provide an application tool to assist technical, contract-administrative and program managers. The design of the system took approximately one year and the first generation system was operational in 1987. Major changes in system architecture were made in 1988

and the second generation system was developed within a year. Since 1989 there have been relatively minor changes in the data structure and more attention has been drawn to technical applications.

IRPIMS hardware consists of a Digital Equipment Corporation VAX 8650 Computer. Data are entered into, stored and managed by Oracle, a commercially-available relational data base. Other application software, existing both in the VAX and personal computer (PC) environment, supports the system relative to data entry, graphics, statistics, reporting and groundwater modeling.

Component Data Bases

IRPIMS consists of three component databases: (1) the Technical Information Management System (TIMS), (2) the Contract Administration Management System (CAMS) and (3) IRPTRACK, a Project Timeline Management System. IRPTRACK is presently undergoing major modifications and will be replaced by a second generation full-functioned program-management/program-control system. All three of these existing data bases share data. TIMS and CAMS represent the two most important data bases, both in terms of size and functional capabilities. Figure 1 provides an overview of the IRPIMS database and the relationship that exists between the two major data bases. The TIMS data base, however and the technical information associated with it will be the primary focus of this paper.
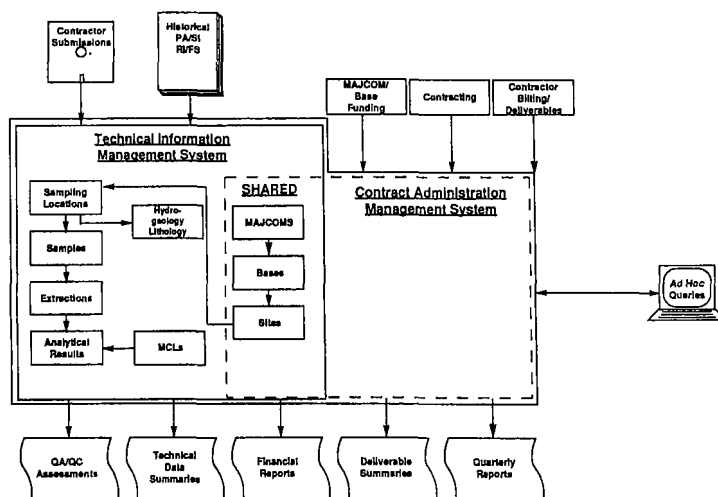
Figure 1
IRPIMS Data Archive

Technical Data

The types of data stored can be broken down into major categories as shown in Figure 2. These main data categories represent the foundation of the data structure and are the keys by which data are queried and retrieved from the system.

Operating Unit	Substance Class	Sampling Medium	Location Types	Site Types	Dates	Other Categories
AF-WIDE MAJCOM BASE SITE LOCATION	Organics Inorganics Metals Substance Group Chlorinated solvents Fuels JP-4 Pesticides Herbicides DNAPLs APLs LNAPLs Any other group of interest Individual Substances Trichloroethylene Benzene Cyanide Copper Beryllium Chlorobenzene	Water Groundwater Surface water Ocean water Potable Water Soil Depth ranges Soil types Sediment Air Tissue Plant Animal Other ALL	Wells Lakes Streams Estuaries Test pits Borings Springs Tanks Faucets & Taps Background Upgradient Down-gradient Cross-gradient On-site ALL	Drum storage Waste pits & lagoons Landfills Spill sites Munition disposal Radioactive disposal Fire protection training pits Other ALL	Specific ALL	Sample type Laboratory Location On/Off Base Analytical method Physical properties REGULATED SUBSTANCES

Figure 2
Major IRPIMS Data Categories

More than 125 different types of technical data (data fields) are stored in TIMS. The bulk of this information, more than 80% of the total data base, relates to analytical sampling results and data pertaining to sampling events, analytical methods, or miscellaneous tests performed. Hydrogeological data consist primarily of monitoring-well completion information, groundwater level data, lithologic descriptions and hydraulic parameters. Other data relate to general site and sampling location information. Figure 3 shows the relative size of the various data tables stored in IRPIMS. A detailed discussion of the various types of data stored in IRPIMS can be found in the IRPIMS Data Loading Handbook.[1]
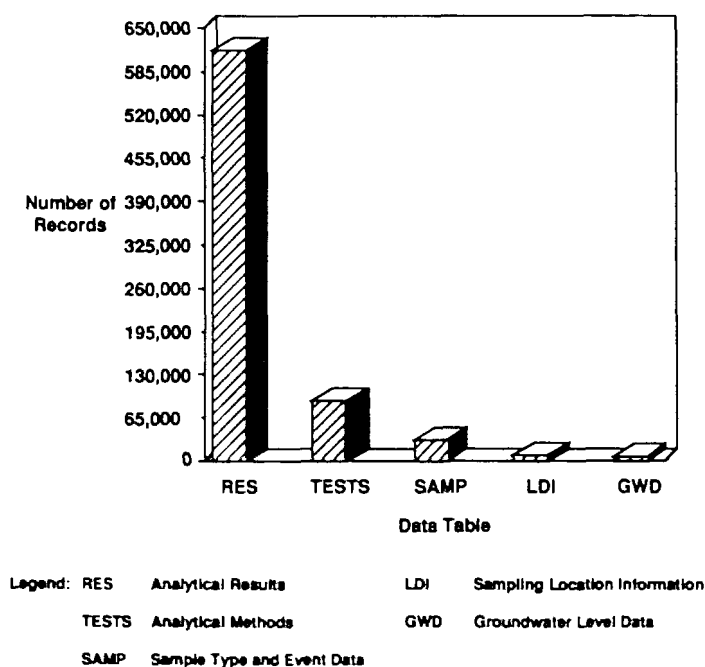
Figure 3
IRPIMS
Size of Component Data Tables

Legend: RES Analytical Results
TESTS Analytical Methods
SAMP Sample Type and Event Data
LDI Sampling Location Information
GWD Groundwater Level Data

When designing an information management system, it is the forethought that is dedicated to developing the data structure (i.e., the types of data captured and how the information will be categorized for access) where most of the time and effort should be spent. Great flexibility should be built into the data structure to accommodate a myriad of "what if" queries and information requests from the user community. Once the data structure has been defined and the system developed, any changes to the data structure can pose major impacts and complications to the management and operation of the system. Therefore, great attention and detail should be paid to the principles of configuration management when a change in data structure is being considered.

Data Entry

Data enter the system through two mechanisms: (1) manual entry from hard-copy reports ("keyed" data) and (2) batch entry from floppy disk or magnetic tape (Fig. 4). Manually-entered data generally are associated with historical IRP reports that were generated from completed hazardous waste investigations. These data were captured originally from Preliminary Assessment/Site Investigation (PA/SI) and Remedial Investigation/Feasibility Study (RI/FS) investigations. Data-entry staff key the hard-copy data into terminals that are configured with data entry screens. The batch-entry system is designed for ongoing projects where IRP contractors are tasked to prepare data submissions. Data from these submissions are uploaded into IRPIMS via a series of batch-loading software utilities. Before data are uploaded, they undergo a series of QA/QC checks to verify data integrity and format compliance.
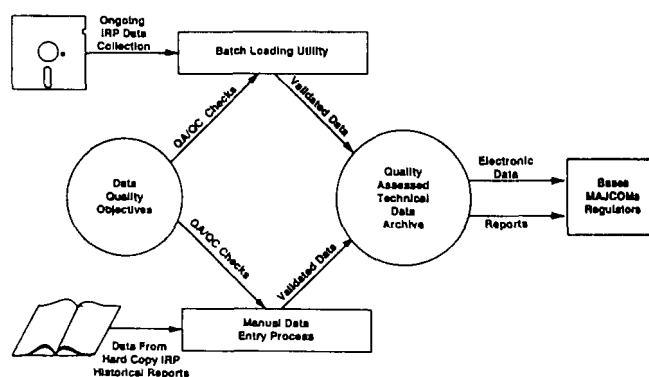
Figure 4
IRPIMS Data Entry

As the data are entered into the system, they are inserted into a series of 10 data tables where they are ultimately stored for access. One data table, for example, may consist of general site location information, whereas another table may consist of the analytical results that are associated with the site locations of interest. Many of the routine data queries require that tables be electronically joined to retrieve the necessary information. This process is done through standard techniques available to the query language in Oracle.

Capabilities

Aside from functioning as a data archive, IRPIMS was designed to be used extensively for technical data analysis and information transfer. Current capabilities involve QA/QC of analytical data, risk assessment support and technical oversight of IRP contractors. The assistance that IRPIMS provides to the Air Force IRP staff to oversee technical interpretations made by contractors is especially critical since the IRP Program is heavily dependent on contractors.

Several menu-driven reports exist to support routine technical data queries. The information generated by these reports varies from general program-wide inquiries (across all Air Force installations) to reports specific to a particular Air Force installation, site or sampling location. Sampling results can be retrieved over a particular point in time as well as in space (both in the horizontal and vertical sense). Con-

taminant analysis reports are available to retrieve sampling data that exceed a particular health-risk threshold such as a Maximum Contaminant Level (MCL). Menu-driven reports are developed after the user community has expressed a need for accessing a routine data query.

Ad hoc reports also are possible, and they are generated when special information needs arise. Recently, ad hoc queries have been developed to identify sites that would be suitable to certain remedial technologies based on the types of contaminants present, constituent concentration levels and the particular conditions posed by the hydrogeologic setting (e.g., depth to groundwater). This capability affords a particularly powerful approach to identifying sites for remediation across the entire Air Force IRP program.

Other capabilities involve sophisticated three-dimensional graphics, statistical data analysis and groundwater modeling. These types of applications have proven critical to supporting Air Force litigation proceedings in the past and have been responsible for rendering a favorable legal decision that saved the government an estimated $10 million in monitoring and remediation expenses.

Statistical procedures are used to assess the precision and accuracy of analytical data submitted by support laboratories. Statistical analysis also is used to identify data outliers (anomalously high or low data values) that may have escaped other data validation checks.

A Defense Priority Model (DPM) interface currently is being developed. DPM is the hazard ranking model currently adopted by all military services in the Department of Defense (DoD) for purposes of prioritizing cleanup and remediation at hundreds of IRP sites. This interface will allow DPM scorers to access IRPIMS to retrieve the front-end data necessary to run the hazard ranking model. This interface will save the operators needless hours in preparing raw data before running the model, particularly since the data-preparation phase has been identified as the most time-consuming aspect of running the model and generating DPM scores.

A Geographical Information System (GIS) supporting sophisticated graphics for spatial analysis and volumetrics is planned for the near term. This system will support users who have the expertise to perform their own interpretations using the spatial data found in the IRPIMS archive.

Regarding the future of IRP in the Long-Term Monitoring and the Remedial Design/Remedial Action arenas, IRPIMS is designed to accept data from these investigations as they become available. IRPIMS will serve as the obvious technical tool to verify that remedial actions have effectively improved the environment. This process will be accomplished by analyzing trends in constituent levels detected in affected media prior to, during and after remediation.

User Community, Support and Access

The IRPIMS' user community consists of staff located at the IRP Program Office, at individual Air Force installations and at Air Force Headquarters where program managers determine broad policy and oversee the direction of IRP. Currently, information is transferred to organizations outside the IRP Program Office via hard-copy; however, direct remote access to the system is now being planned for the entire Air Force community. This expanded access is due to recent decisions that have identified IRPIMS as the central data repository for the Air Force.

Various scenarios for access have teen identified, and it is likely that the level of access will vary depending on the needs of the user organization. Some of the larger Air Force installations which have enormous data management needs, for example, may require a replicated data base installed on-site. This arrangement essentially clones IRPIMS for use on an on-site computer at that particular installation. In other instances at installations where IRP activities and technical staff are limited, hard-copy access to the system may suffice.

Users are supported by various documents such as user's manuals, data loading manuals and, in the near future, a quarterly newsletter. On-site training will be provided as the user community expands to other outside organizations. Government contractors will be trained on data format requirements and on the use of software to assist data loading and QA/QC of analytical data.

OVERVIEW OF AIR FORCE IRP INVESTIGATIONS

The discussions that follow will provide an overview of Air Force IRP investigations based on data that are currently stored in IRPIMS. Emphasis will be placed on environmental data that are associated with the groundwater media. The discussions that follow are qualified by the fact that the data base is not entirely complete and, at this writing, represents a subset of data collected from one of three Air Force technical service centers. The amount of data stored, however, is so large that statistically significant conclusions can be drawn, particularly in regards to quantitative estimates and summary information of constituents detected in the environment. An ongoing program, nonetheless, is in place to load IRP data for the entire Air Force IRP program. Funding for this effort has been approved for the 1991 fiscal year.

Data Base Size

The data universe at this time (Table 1) represents information on more than 2000 hazardous waste sites that are distributed within and outside the contiguous United States across 196 Air Force installations and 14 Major Commands. More than 7000 sampling locations have been entered into the data base for which more than 630,000 sampling results can be retrieved for analysis. More than 725 chemical substances compounds are identified in the system and can be associated with analytical results. As of this writing, 260 compounds have been detected in various sampling media. Approximately 3500 monitoring wells have been installed and the borehole footage exceeds 231,000 feet.

Table 1
Air Force IRP Data Universe and Sampling Effort
IRPIMS Data Summary
as of August 30, 1990

Air Force Bases	196
Sites	2245
Sampling Locations	7136
Analytical Results	632,123

The Air Force Base as an IRP Facility

Based on the information in IRPIMS, the typical Air Force installation has an average of 12 sites. The largest number of sites that exists on an Air Force facility is 132. The average number of monitoring wells installed on an installation is 46, whereas the median number of wells installed per base is 25. The maximum number of wells installed on a particular base exceeds 460. A typical site has an average of 4.5 wells installed with a median of 3 wells. The largest number of wells installed on a given site is 60. The average depth of monitoring wells installed across all Air Force bases is approximately 35 feet.

Sites and Site Types

Information on approximately 2250 sites has been entered into IRPIMS. Air Force IRP sites can be grouped into at least 13 site categories. Figure 5 illustrates the frequency of occurrence of these various site categories. The site types that are found most frequently are: (1) landfills, (2) waste disposal lagoons or waste pits, (3) spill sites, (4) fire training areas and (5) underground storage tanks. By far the most common sites are those that fall into the landfill category.

Sample Location Types

IRPIMS stores information on 14 different sampling location types. Figure 6 illustrates the frequency of occurrence of these sampling types across the entire Air Force IRP program. Monitoring wells are the most

common type of sampling location as indicated by Figure 6. As noted above, information on more than 3500 monitoring wells is available at this time in IRPIMS.
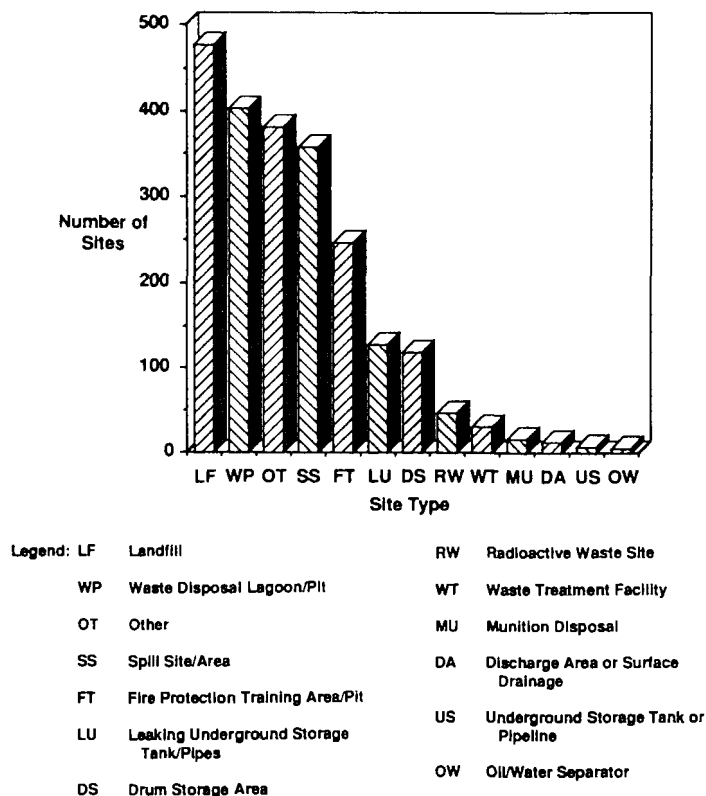
Figure 5
Air Force IRP Program
Frequency of Site Types

Legend:
LF	Landfill	RW	Radioactive Waste Site
WP	Waste Disposal Lagoon/Pit	WT	Waste Treatment Facility
OT	Other	MU	Munition Disposal
SS	Spill Site/Area	DA	Discharge Area or Surface Drainage
FT	Fire Protection Training Area/Pit		
LU	Leaking Underground Storage Tank/Pipes	US	Underground Storage Tank or Pipeline
DS	Drum Storage Area	OW	Oil/Water Separator

Legend:
WL	Well	TK	Tanks & Containers
BH	Borehole	SP	Spring
SL	Surface Location	LH	Leachate
RV	River/Stream	SE	Seep
CH	Channel/Ditch	BR	Barrels
TP	Test Pit	FW	Faucet and Tap
LK	Lake/Pond		
CP	Composite from Several Locations		

Figure 6
Sampling Location Types

Common Organic Compounds Detected in Groundwater

Figure 7 shows a ranked listing of the 10 most common compounds detected in groundwater across the Air Force IRP Program. The constituents are ranked based on a frequency analysis of the total number of sampling locations where organics were detected. Not surprisingly, the constituents that are detected most commonly on Air Force installations are those associated with solvents and fuels which have been released by activities related to airplane maintenance and fuels storage/handling. As Figure 7 indicates, Trichloroethylene (TCE) is certainly the most common contaminant detected. Other constituents such as toluene and benzene also are commonly detected in groundwater. These compounds are found on Air Force installations are typical of those compounds found on other large industrial complexes.

Table 2 shows representative concentration levels for the top 10 compounds. As commonly found in environmental data, the frequency distributions for these compounds are typically skewed towards the higher concentration levels; hence, the mean or average concentrations tend to be much higher than the median levels. This result is common to frequency distributions that vary significantly from a normal distribution. The median is a better measure than the mean of central tendency in the data and thus represents a concentration that one could expect to detect in the field in most instances. The mean concentrations tend to exaggerate representative constituent levels and thus are not recommended for this type of analysis.

Because of the large sample size of data available in IRPIMS, statistically significant estimates of the median and other parameters

(Based on number of detects)
IRPIMS Data Summary
as of August 30, 1990
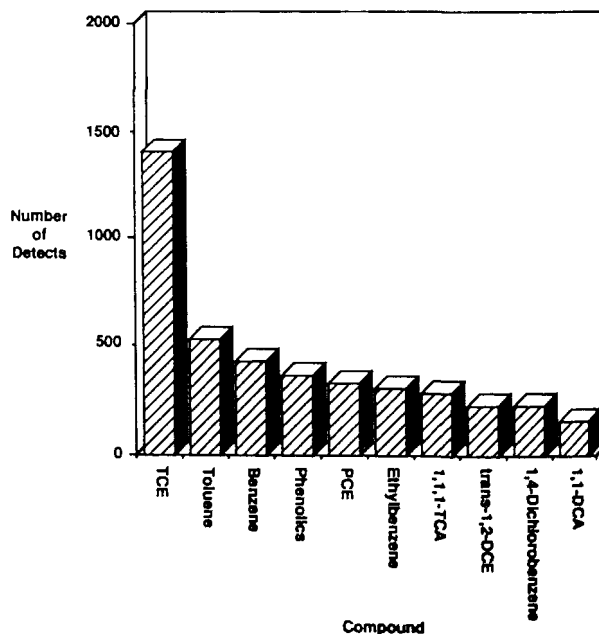
Figure 7
Most Common Organic Compounds
Detected in Groundwater

can be made. It is not likely, therefore, that the median levels for the various constituents will vary significantly even as considerably more data are added to the data base over time.

Table 2
Ranked Listing of Common Organic Compounds Detected in Groundwater

IRPIMS Data Summary
as of August 30, 1990

Compound	Median	Mean	Maximum
TCE	18	1971	610,000
Toluene	2	1780	310,000
Benzene	7	1758	320,000
Phenolics	12	2025	125,000
PCE	4	452	52,000
Ethylbenzene	3	143	3,640
1,1,1-TCA	7	2394	240,000
trans-1,2-DCE	7	509	34,000
1,4-Dichlorobenzene	5	197	18,000
1,1-DCA	5	137	8,800

(Note: All values in µg/L)

Common Organic Compounds Detected at Selected Site Types

When planning sampling protocols (choice of analytical method, etc.) for the common site types, it is of interest to assess the variety of compounds likely to be detected. Figure 8 illustrates the variety of organic compounds detected at selected site types, based on the number of distinct chemical substances encountered during sampling. As one might expect, landfills are the sites that demonstrate the greatest variety in organic constituents detected; nearly 80 different compounds have been detected across the Air Force.

IRPIMS Data Summary
as of August 30, 1990
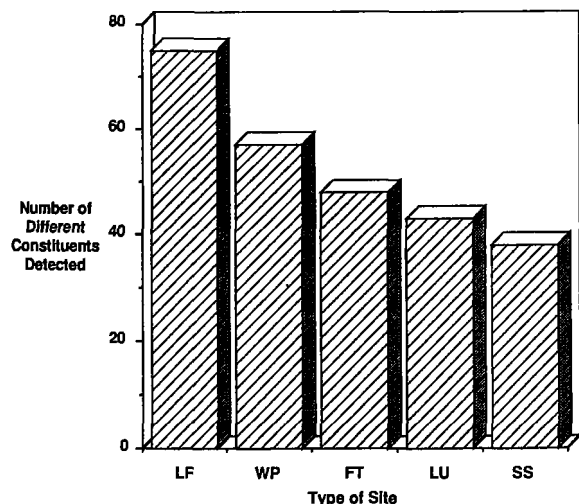
Legend: LF Landfill
        WP Waste Lagoon, Weathering Pit
        FT Fire Training Area
        LU Underground Storage Tank
        SS Spill Site

Figure 8
Variety of Organic Constituents Detected in Groundwater at Selected Site Types

Table 3 lists the top 10 constituents most frequently detected at selected site types. Of these compounds, TCE, toluene, benzene, ethylbenzene, PCE, trans-1,2-dichlorothene and 1,1,1-trichloroethane occur in the respective lists across all of the selected site types. Table 4 illustrates median levels for these constituents as calculated separately for each of the selected site types. One can determine from this table that the median concentrations at underground storage tanks for all constituents, particularly for benzene, are significantly elevated above those levels associated with the other sites. This analysis indicates that leaking underground storage tanks/pipelines tend to pose the greatest environmental threat based simply on the high concentrations likely to be detected.

Table 3
Organic Constituents Most Frequently Detected in Groundwater at Selected Site Types

IRPIMS Data Summary
(Based on number of wells with detections)
as of August 30, 1990

Landfills	Waste Lagoons/ Weathering Pits	Fire Training Areas	Underground Storage Tanks	Spill Sites
Trichloroethylene (TCE)	Toluene	Toluene	Trichloroethylene (TCE)	Trichloroethylene (TCE)
Phenolics	Trichloroethylene (TCE)	Trichloroethylene (TCE)	Benzene	Toluene
Toluene	1,1,1-Trichloroethane	Benzene	Ethylbenzene	Benzene
Benzene	Tetrachloroethylene (PCE)	Ethylbenzene	Toluene	Ethylbenzene
Ethylbenzene	Benzene	trans-1,2-Dichloroethene	trans-1,2-Dichloroethane	Tetrachloroethylene (PCE)
Vinyl Chloride	trans-1,2-Dichloroethene	Tetrachloroethylene (PCE)	1,2-Dichloroethane	xylenes
1,1,1-Trichloroethane	Chlorobenzene	1,1,1-Trichloroethane	Tetrachloroethylene (PCE)	trans-1,2-Dichloroethene
trans-1,2-Dichloroethene	Ethylbenzene	Trichlorofluoromethane	Bromochloromethane	1,1-Dichloroethene
1,1-Dichloroethene	1,4-Dichlorobenzene	1,1,2,2-Tetrachloroethane	xylenes	1,1,1-Trichloroethane
Tetrachloroethylene (PCE)	1,2-Dichloroethane	Vinyl Chloride	1,1,1-Trichloroethane	1,1-Dichloroethane

Table 4
Median Organic Concentrations Found in Groundwater at Selected Site Types

IRPIMS Data Summary
as of August 30, 1990

Compound	Landfills	Waste Lagoons/ Weathering Pits	Spill Sites	Fire Training Areas	Underground Storage Tanks
TCE	3.5	11.4	31.0	17.2	52.5
Toluene	1.2	1.8	4.0	1.9	625.0
Benzene	5.9	1.8	16.5	30.0	1808.0
Ethylbenzene	0.8	2.7	10.5	1.3	23.0
PCE	1.7	2.7	23.0	3.6	109.0
trans-1,2-DCE	4.2	20.0	23.0	6.0	46.0
1,1,1-TCA	3.7	4.0	4.3	1.7	36.1

(Note: All values in µg/L)

CONCLUSIONS

The Human Systems Division developed IRPIMS to support and automate the data management needs of the IRP Program. The system is designed around two principal data bases: (1) a technical information management system and (2) a contract administration management system. Both of these systems share data.

The major design and development phase of the system has largely been accomplished. Large volumes of data are now available for meaningful interpretation and analysis to support IRP decision-makers at various levels within the Air Force.

More than 80% of the data stored in IRPIMS consists of analytical sampling results. Other technical data captured by the system relate to general site location information, lithologic descriptions, well completion information, groundwater level data and the like.

Trichloroethylene (TCE), toluene and benzene are the most commonly detected compounds in groundwater. These compounds are associated with solvents and fuels handling and are common to large industrial complexes. With the large sample size that is available in IRPIMS, it has been possible to estimate representative concentrations of constituents that would commonly be detected in the field across the Air Force program. Occurrences of commonly detected compounds have also been associated and identified with the important site types. Sampling protocols designed for routine site investigations have been derived based on these constituent/site associations.

Beyond the ongoing data loading process, the current focus is to expand and further develop the various technical applications that are possible with IRPIMS. In addition, the system is soon to support the entire Air Force as the central data repository. This development will vastly increase the size of the data base and will pose a significant expansion to the user community. Remote access to the system will be developed to improve the transfer of information to support various Air Force customers.

The current IRPIMS data structure has future applications and is designed to accept other types of data as the RD/RA and the Long Term Monitoring programs respond to new data demands. In addition,

IRPIMS will play an important role in verifying the effectiveness of remediation as various remedial alternatives are implemented and sampling data becomes available for analysis.

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Optimal Regulatory Compliance Strategy for Multisite Investigations Under the Navy Installation Restoration Program at the Naval Air Station (NAS) Pensacola

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ABSTRACT

The Naval Air Station (NAS) Pensacola, Florida, is an active naval flight training and aircraft rework facility located in the northwest Florida panhandle. It is also one of the oldest Naval facilities in the United States. The facility has recently been added to NPL and currently has 37 sites on the Station which require investigations under the Naval Installation Restoration Program (IRP). The sites will be investigated in accordance with conditions and schedules outlined in a Federal Facilities Agreement between the Navy, the U.S. EPA and the State of Florida.

All sites were classified as Solid Waste Management Units in RCRA/HSWA permit for NAS Pensacola. Seventeen of the sites have been identified as requiring RCRA Facility Investigations, and all 37 sites will be investigated under the CERCLA regulations.

Given that all 37 sites need to be addressed under the Navy IRP, an approach has been developed to conduct a multimedia environmental investigation which incorporates the requirements of both RCRA/HSWA and CERCLA regulations. In addition, the 37 sites were combined into 15 groups for maximum efficiency throughout the investigative process. Site groupings were principally based on: (1) similarity of documented or suspected contaminants; and (2) geographic proximity. Some of the sites have documented contamination, whereas other sites are only suspected of or have a low probability of contamination. As a result, a phased approach to conducting the contamination investigations is planned. This phased approach will allow efficient identification of sites where environmental contamination has actually occurred, and also will allow elimination of noncontaminated sites to be eliminated from the program in the most environmentally sound, cost-effective and timely manner possible. Sites identified as being contaminated will be further investigated through the completion of an RI/FS and, ultimately, design and remediation. This overall investigative approach and compliance strategy for NAS Pensacola will ensure the most optimal and streamlined procedure in meeting the objectives of the multiple regulatory requirements of this Naval facility.

INTRODUCTION

In recent years, the United States Naval Air Station (NAS) Pensacola has taken an active role in evaluating past and present hazardous waste practices. As a result, the Navy, under its Installation Restoration Program (IRP), has implemented an investigation and cleanup strategy designed to bring sites identified at NAS Pensacola into conformance with the RCRA, HSWA and CERCLA. The entire facility was added to the NPL in late 1989, providing further impetus for an extensive cleanup effort.

NAS Pensacola is located on 5,874 acres in southwest Escambia County, Florida (Fig. 1). Two major industrial tenant commands are located at NAS Pensacola: the Naval Aviation Depot and the Public Works Center. These industrial facilities support all Naval training activities which operate at the base. This support includes fuel storage and transportation systems and maintenance and repair of aircraft. Throughout the years, these support facilities have generated a variety of materials, the majority of which have been disposed of on the base. These materials include construction debris; municipal solid waste and wastewater treatment plant sludge; and miscellaneous industrial wastes,

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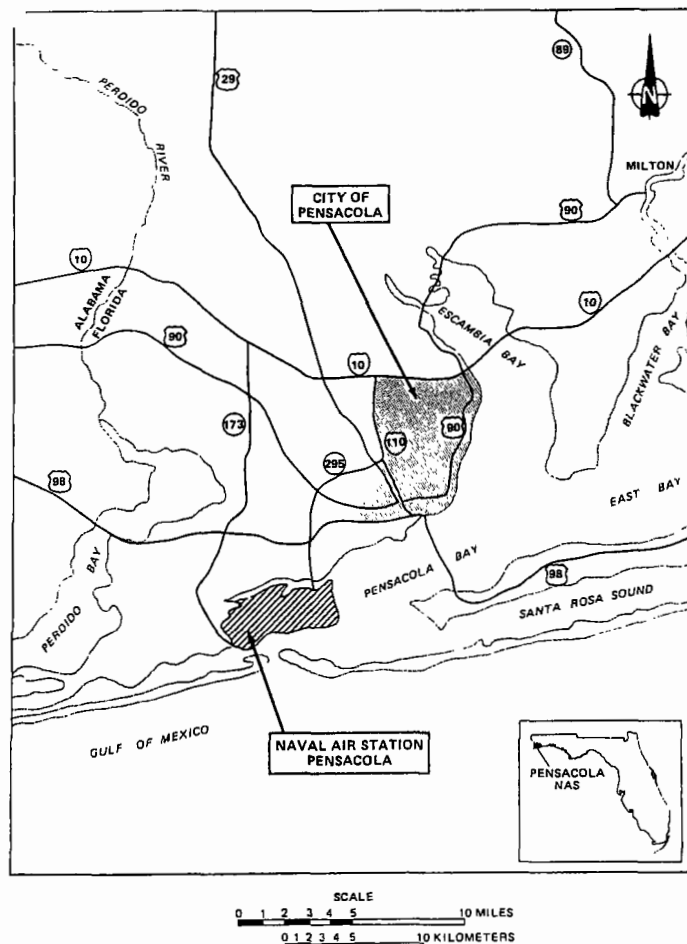
Figure 1
Location of NAS Pensacola

including waste oils, solvents, paints, electroplating liquids and spilled fuels. The 37 potential sites of contamination identified at NAS Pensacola (Fig. 2) are a result of the past generation and disposal practices of these materials.

HISTORY

The NAS Pensacola location has been associated with military activities dating as far back as 1528, when the first European settlement in North America was established at this site.[1] Until the early 19th century, this location served as a fortification point for both the British and the Spanish.

In 1825, a naval yard was constructed by the U.S. Navy at the NAS Pensacola site. Although activity at the yard was in turmoil throughout the remainder of the 19th century and into the early 20th century, the U.S. Navy kept the installation. Subsequently, in 1914, the Navy's first permanent air station was established at this site. Throughout World War I and World War II, this base became the Navy's premier aviation training facility. Along with the training facility, the Navy developed all the required support systems for the various aviation activities which occurred at the site.

In addition to the long time Naval Air Station command at Pensacola, several tenant commands have been established at this base. These tenants include the Naval Education and Training Command, the Navy Public Works Center (PWC) and the Naval Aviation Depot (NADEP). The Education and Training command manages all Naval training activities. The PWC is responsible for all utilities and transportation functions for the Navy's activities in this area. The NADEP serves as a repair and maintenance facility for various Naval aircraft.

ENVIRONMENTAL SETTING

Physiography

NAS Pensacola is located in the Gulf Coastal Lowlands Subdivision of the Coastal Plain Province physiographic division.[2] The 5,800-acre facility is located on a peninsula and is bounded on the east and south by Pensacola Bay and Big Lagoon and on the north by Bayou Grande. The most prominent topographic feature on the peninsula is an escarpment or bluff which parallels the southern and eastern shorelines and on which Fort Barrancas was built. Seaward of the escarpment is a nearly level marine terrace with surface elevations of approximately five feet above mean sea level (MSL). The central part of the peninsula, located landward of the escarpment, is a broad, gently rolling upland area with surface elevations up to 40 feet above MSL.[3,4]

Hydrogeology

There are three principal hydrogeologic units of importance which underlie the NAS Pensacola site. These are, in descending order, the Sand-and-Gravel Aquifer, the Intermediate System and the Floridan Aquifer System.

The Sand-and Gravel Aquifer occurs from land surface to a depth of approximately 300 feet at NAS Pensacola and is composed of a sequence of unconsolidated to poorly indurated clastic deposits.[5,6] The sediments making up this aquifer belong to all or part of the Pliocene to Holocene Series, which, in this area, consist mainly of the Citronelle Formation overlain by a thin cover of marine terrace deposits. In the Pensacola area, the Sand-and-Gravel Aquifer is the primary source of potable drinking water, and groundwater within the aquifer is classified by FDER as G-1 (sole source). Given that the Sand-and-Gravel Aquifer is contiguous with land surface and recharge occurs principally by the direct infiltration of precipitation, the aquifer is particularly susceptible to contamination from surface sources.

The lower limit of the Sand-and-Gravel Aquifer coincides with the top of a regionally extensive and vertically persistent hydrogeologic unit of much lower permeability. This unit is known as the Intermediate System. In the NAS Pensacola area, the Intermediate System is approximately 1,100 feet thick and is composed of the lower portion of the Miocene Coarse Clastics, the Upper Member of the Pensacola
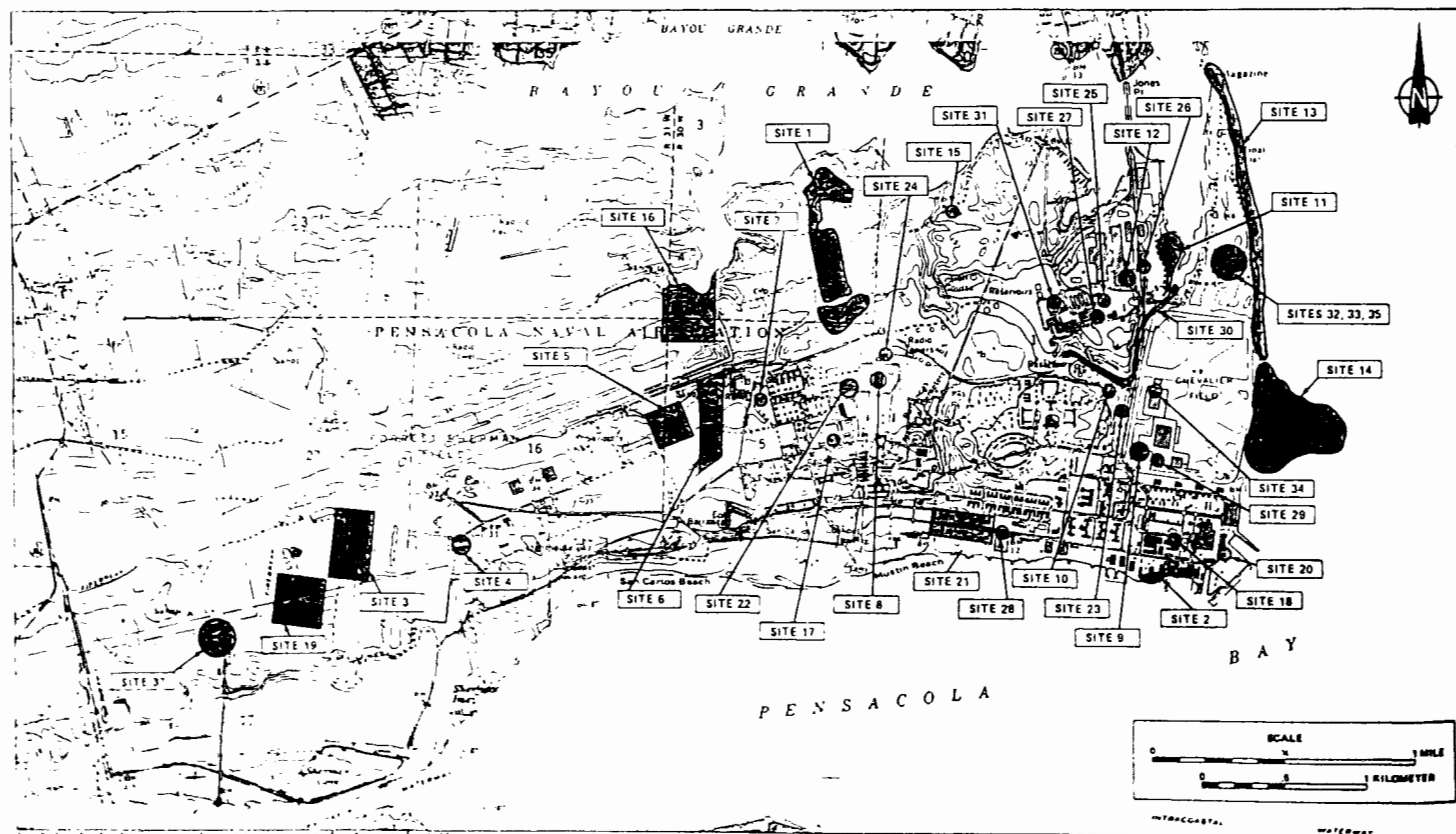
Figure 2
NAS Pensacola Site Locations

Clay, the Escambia Sand Member of the Pensacola Clay and the Lower Member of the Pensacola Clay; all of Miocene Age. In general, the Intermediate System consists of fine-grained sediments and functions as an effective confining unit which retards the exchange of water between the overlying Sand-and-Gravel Aquifer and the underlying Floridan Aquifer System.[5]

Immediately underlying the Intermediate System and occurring at a depth of approximately 1,500 feet below land surface at NAS Pensacola is the Floridan Aquifer System. The Floridan Aquifer in this area is composed of the Middle to Lower Miocene Chickasawhay Limestone and undifferentiated Tampa Stage Limestone. Groundwater within the Floridan Aquifer in this area is highly mineralized and is not used for water supply.[5]

Surface Water

The NAS Pensacola facility is located on a coastal peninsula bounded by Bayou Grande to the north, Pensacola Bay to the south and east and Big Lagoon to the southwest. These surface water bodies have been classified by FDER as Class III (i.e., suitable for recreation and propagation of fish and wildlife). Pensacola Bay and Big Lagoon are partially separated from the Gulf of Mexico by Santa Rosa Island and Perdido Key, both of which are barrier islands.

There are no naturally occurring perennial streams on NAS Pensacola; however, there are approximately 10 naturally occurring intermittent streams and numerous manmade drainage pathways, which include many stormwater outfalls. Discharge is mainly to the south into Pensacola Bay; however, some small intermittent streams discharge into Bayou Grande to the north from Sherman Field and Chevalier Field.[3,4] The southwestern and northern portions of NAS Pensacola contain areas of freshwater wetlands.

The discharge of surface waters into Pensacola Bay, Bayou Grande, and the coastal wetland areas presents the potential for transport of contaminants into these systems. This system could have a significant impact on seagrass and other sensitive plant communities as well as on shell fishing, recreational fishing and swimming in these coastal zones. Discharges, either through the surface water or groundwater, into wetland areas found on-site could also have a significant impact on the biotic communities that are dependent on those habitats.

Biological Resources

The NAS Pensacola facility encompasses approximately 15 terrestrial and aquatic habitats. The majority of the land on the eastern side of the facility is developed for military use or is designated as a historical or cultural resource. However, the NAS Pensacola installation has approximately 3,500 acres in natural or seminatural (plantation) condition, primarily in the western portion of the facility.

A number of threatened and endangered species have been identified in the vicinity of the NAS Pensacola facility.[7] Many rare, threatened and endangered species are associated with the wetland or bog habitats. Any site remediation and, more importantly, any assessment of environmental endangerment must consider the water level requirements of rare and endangered plant species and the foraging activities of birds in the waters surrounding the NAS Pensacola facility, as well as nesting and feeding animals on the facility grounds.

NAVY INSTALLATION RESTORATION PROGRAM

The Navy IRP was established in 1986 to direct the investigation and remediation of uncontrolled hazardous waste disposal sites associated with naval operations. Prior to 1986, these investigation/remediation activities had been managed under the Navy Assessment and Control of Installation Pollutants (NACIP) program.

In accordance with the NCP, the Navy IRP currently is being implemented in full compliance with the statutory requirements of CERCLA and SARA. Furthermore, since CERCLA/SARA specifies the inclusion of all applicable or relevant and appropriate requirements (ARARs), the Navy IRP incorporates compliance with RCRA and the HSWA of 1984, where applicable.

The Navy IRP can be viewed as a five-step investigation and remediation process:

- Site discovery or notification
- Preliminary assessment (PA) and site investigation (SI)
- Establishment of priorities for remedial action (RA)
- Remedial Investigation/Feasibility Study (RI/FS)
- Remedial Design/Remedial Action (RD/RA)

Each of the above steps includes substeps or subdivisions.

In order to supplement the IRP and in an effort to keep interested parties abreast of activities at the NAS Pensacola facility during this investigation, a Technical Review Committee (TRC) was formed. The TRC for this project consists of the U.S. EPA, FDER, an Escambia County official and a representative of private citizens. All documents generated by the Navy for work conducted as part of this investigation are submitted to the TRC for review and comment.

PREVIOUS INVESTIGATIONS

Three major investigation programs have been conducted at NAS Pensacola under the NACIP/Navy IRP programs: Initial Assessment Study (IAS);[1] Verification Study (VS); and Confirmation Study (CS). The IAS was conducted from 1982 to 1983 by the Naval Energy and Environmental Support Activity (NEESA) to identify and assess NAS Pensacola sites that could pose a potential threat to human health or the environment as a result of contamination derived from past naval operations. The VS, conducted in 1984 and the CS, conducted from 1985 to 1986, were carried out by a previous Navy contractor to confirm/refute the presence of contamination at specific sites identified in the IAS.

In addition to the above NACIP/Navy IRP programs, a RCRA Facility Assessment (RFA) has been completed at NAS Pensacola and a RCRA/HSWA permit was issued to the installation by the U.S. EPA on July 27, 1988. Seventeen of the sites were identified on the permit as Solid Waste Management Units (SWMUs) which required RCRA Facility Investigations. A RCRA permit had previously been issued to NAS Pensacola by the Florida Department of Environmental Regulation (FDER) on September 29, 1987.

Table 1 lists the 37 known and potential sites of environmental con-

Table 1
Navy IRP Sites at NAS Pensacola

Site No.	Site Name/Description
1*	Sanitary Landfill
2*	Waterfront Sediments Area
3*	Crash Crew Training Area
4	Army Rubble Disposal Area
5	Borrow Pit
6	Fort Redoubt Rubble Disposal Area
7	Firefighting School Area
8	Rifle Range Disposal Area
9	Navy Yard Disposal Area
10	Commodore's Pond
11*	N. Chevalier Disposal Area
12	Scrap Bins
13	Magazine Point Rubble Disposal Area
14	Dredge Spoil Fill Area
15*	Pesticide Rinsate Disposal Area
16	Brush Disposal Area
17	Transformer Storage Yard
18	PCB Spill Area
19*	Fuel Farm Pipeline Leak Area
20	Pier Pipe Leak Area
21*	Sludge at Fuel Tanks
22	Refueler Repair Shop
23	Chevalier Field Pipe Leak Area
24	DDT Mixing Area
25	Radium Spill Site
26*	Supply Department Outside Storage Area
27*	Radium Dial Shop Sewer
28	Transformer Accident Area
29*	Soil South of Building 3460
30*	Buildings 649 and 755
31*	Soil North of Building 648
32*	IWTP Sludge Drying Beds
33*	Wastewater Treatment Plant (WWTP) Ponds
34*	Solvent Area North of Building 3557
35*	Miscellaneous IWTP SWMUs
36*	Industrial Waste Sewer
37	Sherman Field Fuel Farm

*Listed for further investigation under the 1988 RCRA/HSWA permit.

tamination that have been identified on NAS Pensacola. Site locations are shown in Figure 2.

FEDERAL FACILITIES AGREEMENT

The Federal Facility Agreement (FFA) is an interagency agreement which exists between the Navy, U.S. EPA and FDER. The FFA outlines the conditions and schedules to be followed during the course of the investigations at NAS Pensacola. The general purpose of the FFA is to:

- Ensure that the environmental impacts associated with past and present activities at NAS Pensacola are thoroughly investigated and appropriate CERCLA response/RCRA corrective alternatives are developed and implemented as necessary to protect the public health, welfare and the environment;
- Establish a procedural framework and schedule for developing, implementing and monitoring appropriate response action at NAS Pensacola in accordance with CERCLA/SARA, RCRA, the NCP and U.S. EPA/state-issued guidance and policy relevant to remediation at NAS Pensacola;
- Facilitate cooperation, exchange of information and participation of the Navy, U.S. EPA and FDER in such actions.

INVESTIGATIVE APPROACH

As discussed previously, 17 of the sites are listed on the NAS Pensacola RCRA/HSWA permit as SMWUs, and the investigations of these sites are governed by RCRA requirements. The remaining 20 sites are covered by CERCLA regulations. In an effort to avoid confusion and duplication of effort in this multisite investigation, an integrated approach was developed. This approach complies with the intent and general requirements of both regulatory programs, but is specifically neither. As a result, the investigation terminology has been modified somewhat from the prevailing RFI for sites covered by RCRA and the Remedial Investigation (RI) for sites covered by CERCLA. For simplicity, the investigations of all NAS Pensacola sites will be referred to as Contamination Assessment/Remedial Activities Investigations.

In order to provide for maximum efficiency in the generation of investigation work plans and the implementation of fieldwork for the NAS Pensacola program, the 37 sites have been clustered into 15 groups, as shown in Table 2. Several criteria were established to generate the work plan groups, including: (1) geographic proximity of sites; (2) similarity of contaminant types; (3) similarity of potential investigation methods; and (4) potential scope and complexity of the investigation.

In addition, a phased approach has been developed for performing the NAS Pensacola site investigations. Phase I (Field Screening) is directed toward identifying the principal area(s) and primary contaminants of concern at a site, thereby providing a mechanism for focusing sampling and analytical efforts during subsequent phases of the investigation. The field screening phase will employ a variety of field investigation tasks, including surface geophysics, habitat/biota surveys, soil gas surveys, hydrologic assessments and the collection of surface water, soil, sediment and groundwater samples for laboratory analysis. However, the analysis of these samples will be subject to less rigorous QA/QC requirements, which reflect the "focusing" objective of this phase rather than a formal contaminant quantification objective. Each field screening task will utilize all existing information from preceding tasks, including aerial photograph analysis, to adjust the locations of the various surveys and sampling locations, thereby achieving optimum results.

Phase II (Characterization) is directed toward the formal confirmation and quantification of the full spectrum of site contaminants (if any), thereby allowing determination of whether further investigation is warranted. The primary objectives of the Phase II field investigation are as follows:

- To characterize the nature and magnitude of the full spectrum of potential site contaminants;
- To confirm and validate the contaminant distributions indicated by the Phase I analytical screening results by collecting and analyzing samples under rigorous QA/QC requirements;

Table 2
Work Plan Groups for NAS Pensacola

Work Plan Group	Site No.	Site Name
A	1*	Sanitary Landfill
B	11*	North Chevalier Disposal Area
	12	Scrap Bins
	26*	Supply Department Storage Area
C	2*	Waterfront Sediments Area
	13	Magazine Point Rubble Disposal Area
	14	Dredge Spoil Fill Area
D	15*	Pesticide Rinsate Disposal Area
	24	DDT Mixing Area
E	30*	Buildings 649 and 755
F	9	Navy Yard Disposal Area
	10	Commodore's Pond
	23	Chevalier Field Pipe Leak Area
	29*	Soil South of Building 3460
	34*	Solvent North of Building 3557
G	25	Radium Spill Area
	27*	Radium Dial Shop Sewer
H	8	Rifle Range Disposal Area
	22	Refueler Repair Shop
I	17	Transformer Storage Yard
	18	Polychlorinated Biphenyls (PCBs) Spill Area
	28	Transformer Accident Area
J	3*	Crash Crew Training Area
	19*	Fuel Farm Pipeline Leak Area
	37	Sherman Field Fuel Farm Area
K	7	Firefighting School Area
	20	Pier Pipe Leak Area
	21*	Sludge at Fuel Tanks
L	4	Army Rubble Disposal Area
	5	Borrow Pit
	6	Fort Redoubt Rubble Disposal Area
	16	Brush Disposal Area
M	31*	Soil North of Building 648
N	36*	IWTP Sewer Area
O	32*	IWTP Sludge Drying Beds
	33*	WWTP Ponds
	35*	Miscellaneous IWTP SWMUs

*Listed for further investigation under 1988 RCRA/HSWA permit.

- To support the preliminary identification, screening and evaluation data requirements of potential remedial alternatives.

Phase II characterization will consist of limited soil sampling; biota sampling; the installation, development and sampling of shallow monitoring wells and the sampling of existing wells; a continuation of the hydrologic assessments; and air sampling, if necessary.

The necessity of implementing Phases III and IV (Extent Delineation) will depend on the results of Phases I and II. Phases III and IV, if required, will be directed not only toward fully identifying the horizontal and vertical extents of contamination, but also toward providing the quantitative data base necessary to support the screening and evaluation of potential remedial alternatives.

The main objectives/advantages of this phased approach are as follows:

- Efficient identification of those sites where environmental contamination has actually occurred as a result of past and/or present operations, thereby allowing noncontaminated sites to be eliminated from the program in the most environmentally sound, cost-effective and timely manner possible;
- Focused placement of sampling locations and focused selection of analytical parameters in later phases of the investigation, thereby allowing full characterization of site contamination in the most environmentally sound, cost-effective and timely manner possible;

• Early screening of potential remedial alternatives, which, in turn, allows critical parameters necessary to the evaluation of these alternatives to be incorporated into the analytical program in later phases of the investigation.

All sites at NAS Pensacola will be investigated through Phases I and II. However, it is anticipated that some of the NAS Pensacola sites may not require investigation beyond Phase II. On the other hand, sites which have documented contamination will likely require the additional phases of work and hence will comprise full-scale CERCLA/RCRA RFI/RI/FS-type investigations. As discussed above, however, the investigations for all NAS Pensacola sites will be referred to as Contamination Assessment/Remedial Activities Investigations. The final results of investigations at all sites will be incorporated into a Contamination Assessment Report. Where appropriate, sites will be recommended for No Further Action. The final results of site investigations that require work beyond Phase II will be incorporated into a Remedial Investigation Report which will provide all the information necessary for the development and completion of a Feasibility Study.

Any new sites discovered during the process of investigating known sites will be incorporated into the established approach, depending on regulatory provisions applicable to the site.

Included in the investigative process is the base line risk assessment to characterize current and potential risk to human health and the environment posed by the site. The primary objectives of the base line risk assessment are to identify the contaminants of concern, assess their toxicity and identify the exposure pathways for both the public and the environment. The base line risk assessment provides a preliminary indication of risk before the FS is conducted to identify cleanup alternatives. If little or no threat to human health or the environment from a site is identified, no further action, or only limited action, will be required for cleanup and the FS will be scaled-down appropriately.

As the RFI/RI process is completed, each particular site group will be evaluated promptly for the need of a feasibility study/corrective measures study (FS/CMS) and subsequent remedial design-remedial action/corrective measures implementation (RD-RA/CMI). The strategy for performing these remedial engineering/construction activities at NAS Pensacola will be, in general, similar to that for the fieldwork. Essentially, sites with contaminant similarity and close geographic proximity will be remedially analyzed as a single entity or as a larger group to whatever degree possible.

CONCLUSIONS

NAS Pensacola, Florida, has recently been added to the NPL. This installation has 37 potentially contaminated sites, all of which will be assessed and remediated under an integrated approach which combines the requirements of RCRA and CERCLA. An FFA between the Navy, U.S. EPA and FDER has been developed which details the procedure by which remedial activity will occur at the facility, including the RCRA and CERCLA integration and the responsibilities of each party of concern.

Given that full-scale RI/RFI/FS/CMS investigations may be required for most of the 37 sites, an optimal technical and economic strategy has been implemented to achieve all necessary regulatory requirements.

This optimization strategy prioritizes the sites for investigation as well as groups the 37 sites into 15 more manageable units for the purposes of work plan development, fieldwork implementation and remedial selection and implementation. The strategy also identifies a phased investigative approach to allow noncontaminated sites to be eliminated from the program while providing full characterization of sites where contamination has occurred. This overall approach will provide the maximum great degree of efficiency, with respect to economics and schedule, to such an extensive remedial program.

DISCLAIMER

The views expressed in this paper are those of the authors and not the Department of the Navy.

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Federal Facility Agreement Implementation Oversight at a Superfund Site

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ABSTRACT

Section 120 of SARA provides a mechanism for remediation of federal facilities through federal facilities agreement (FFA). This paper discusses implementation of the FFA for the New Brighton/Arden Hills Superfund site in Ramsey County, Minnesota. The site is owned by the U.S. Army. It covers an area of approximately 25 mi^2, which includes a 4-mi^2 area of the Twin Cities Army Ammunition Plant (TCAAP) and off-TCAAP areas contaminated by the migration of contaminants from TCAAP. The soils and groundwater at the site are contaminated with metals and VOCs. The groundwater contamination emanating from the TCAAP site has threatened water supplies of several communities downgradient of the site that use groundwater as a potable water supply.

This FFA was the first agreement in the country pursuant to Section 120 of SARA. The agreement was intended to ensure that the environmental impacts associated with the TCAAP site are thoroughly investigated and that appropriate steps are taken to protect public health, welfare and the environment. The agreement specifies a shared responsibility for conducting RI/FS at the site. The U.S. Army is responsible for conducting RIs for on-TCAAP areas, the Minnesota Pollution Control Agency (MPCA) is lead agency for conducting RIs for off-TCAAP areas (approximately 25 mi^2) and U.S. EPA is responsible for preparing risk assessments (RA) of on-TCAAP and off-TCAAP areas. Upon completion of the RIs and RAs, the U.S. Army will conduct an FS to identify and evaluate feasible response actions for remediation of contaminated soils and groundwater.

Successful implementation of an agreement of this magnitude and complexity requires innovative management on the part of all participants. Meeting schedules, whether they are the Army's or the U.S. EPA's, is critical to the credibility of the Section 120 process.

This paper highlights the oversight of the RI/FS activities and the resources and approaches needed to meet the rigorous review schedule specified in the FFA. It discusses major features of the FFA, progress made to date, resolutions of disputes among three organizations (U.S. EPA, MPCA and U.S. Army) and schedules and workloads relevant to the implementation of the FFA.

INTRODUCTION

The New Brighton/Arden Hills Superfund site consists of the Twin Cities Army Ammunition Plant (TCAAP), located in Ramsey County, Minnesota and all other areas contaminated by the migration of hazardous substances or contaminants from TCAAP. The U.S. Army owns the TCAAP facility and Federal Cartridge Corporation (FCC) has been operating the facility during most of its existence. TCAAP has been used to manufacture, store and test small arms ammunitions and related materials since 1941. Presently, the plant is inactive, having been on standby status since August 1976. However, two major private companies still use part of the facility for commercial and defense-related operations. These companies are Minnesota Mining and Manufacturing Company and Honeywell, Inc.

Information from past studies indicates that between 1941 and 1981 waste material was disposed of at 14 disposal areas or sites within TCAAP. The U.S. EPA and the Minnesota Pollution Control Agency (MPCA) have determined that there have been releases of hazardous substances, pollutants, or contaminants into the environment. As a result of these releases, the New Brighton/Arden Hills site has been ranked No. 43 on the NPL.

The U.S. Army, U.S. EPA and MPCA entered into a federal facilities agreement (FFA) in 1987 to ensure that the environmental impacts associated with the TCAAP site are thoroughly investigated and that appropriate steps are taken to protect the public health, welfare and the environment. In accordance with the FFA, the U.S. Army initiated remedial activities under the Department of Defense Installation Restoration Program to remove and treat contaminated groundwater at several locations, extract contaminated vapors from soils at two source areas (source areas D and G) and excavate and incinerate PCB-contaminated soils at one source area (source area D) (part of the TCAAP site). Argonne National Laboratory (ANL), a contractor to the U.S. Army, has prepared a remedial investigation (RI) report on the contaminated areas within the boundary of TCAAP. Concurrently, Camp, Dresser & McKee, Inc. (CDM), a contractor to the MPCA, prepared an RI report of off-TCAAP areas to determine the extent of contaminant migration from TCAAP. PRC Environmental Management, Inc. (PRC), oversight contractor to U.S. EPA, performed a risk assessment of the New Brighton/Arden Hills Superfund site.

SITE DESCRIPTION

The New Brighton/Arden Hills Superfund site is located in the northern part of the Minneapolis-St. Paul metropolitan area (Fig. 1). As presently defined, the site covers much of the U.S. Geological Survey's New Brighton, Minnesota, 7.5-minute quadrangle. For historical and administrative reasons, the site is divided into two areas. TCAAP is the source area. As shown in Figure 2, TCAAP includes 14 individual source areas plus the remainder of the installation. The off-TCAAP portion of the site includes portions of several municipalities. The outer boundaries of the site include all areas affected by contamination originating within TCAAP.

Within the New Brighton/Arden Hills study area, groundwater is found in both bedrock and glacial deposit aquifers. There are two major bedrock aquifers in the area—the Prairie du Chein/Jordan Sandstone and the Mt. Simon/Hinckley. There are also four minor bedrock aquifers in the Twin Cities Basin—the Ironton/Galesville, the Reno Member of the Franconia Formation, the St. Peter Sandstone and the

Platteville/Decorah. The St. Peter Sandstone and the Platteville/Decorah units are in direct contact with the overlying glacial deposits in the New Brighton/Arden Hills and Roseville areas, respectively.
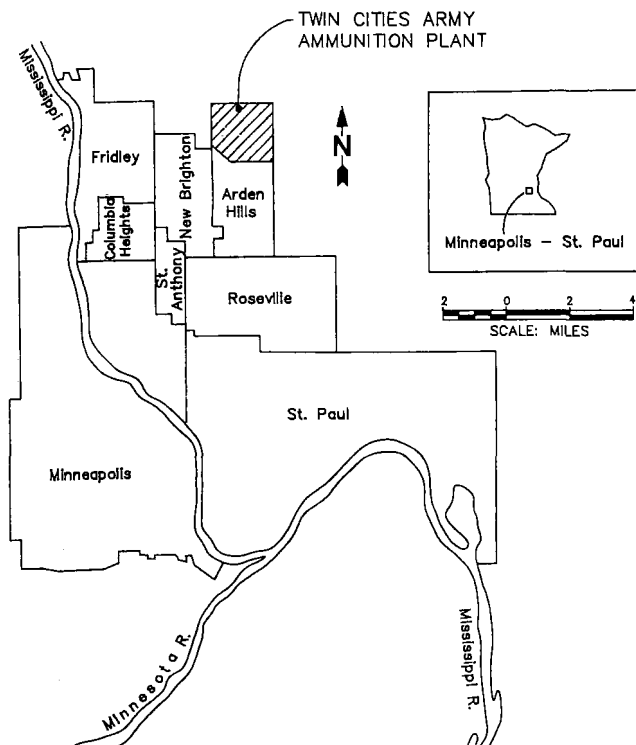
Figure 1
General Location of New Brighton/Arden Hills Superfund Site

LEGEND

KNOWN AREAS OF CONTAMINATION

• MONITORING WELL

— — — SITE BOUNDRY

GROUND-WATER EXPOSURE AREA

(X4) QUADRANT IDENTIFIER

• • • • • QUADRANT IDENTIFIER

— · · · — BOUNDARY OF SURFACE WATER BODY
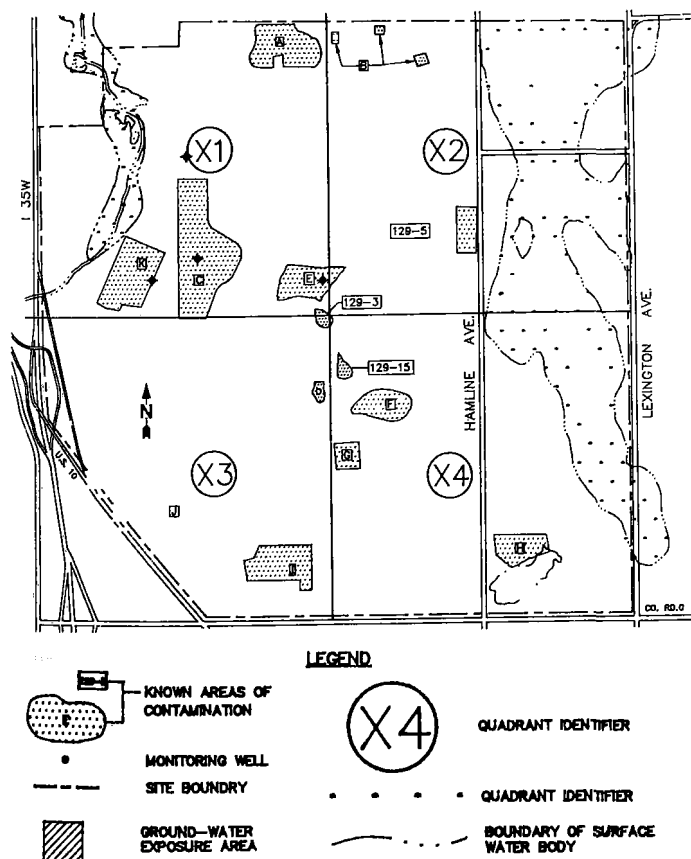
Figure 2
TCAAP Site Map

On top of the irregular bedrock surface, a series of unconsolidated glacial sediments has been deposited. Several of these units are water-bearing and have been affected by the spread of contaminants from TCAAP. In general, there are four aquifer units at the site. Unit 1 is composed of the surficial lacustrine deposits that form the shallow unconfined aquifer. Unit 2 is composed of glacial Twin Cities Till, which acts as an aquitard, preventing hydraulic communication between the surface and the underlying major glacial aquifer. Unit 3 is composed of the Hillside and Arsenal Sands and is the major glacial aquifer in the area. Unit 4 is the uppermost bedrock aquifer beneath the site. It may be hydraulically connected to the overlying Unit 3 aquifer.

SITE BACKGROUND

In 1978, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) performed an assessment of TCAAP, which identified 14 disposal areas at the site. These areas were used for the disposal of waste solvents, acids, caustics, heavy metals and other production wastes. Approximate boundaries of the disposal areas are shown in Figure 2.

Subsequent groundwater sampling and analyses conducted by MPCA and the Minnesota Department of Health (MDH) found VOCs in production wells at TCAAP, the Arden Manor trailer park well in Arden Hills and a number of residential wells in Arden Hills, Shoreview, New Brighton and St. Anthony.

The following events occurred as a result of the identification of VOC-contaminated groundwater:

• The City of New Brighton abandoned several municipal wells and either placed on standby or deepened several others.
• The Village of St. Anthony used U.S. EPA/MPCA funds to decommission one well and connected a portion of the village with Roseville water supplies for an indefinite, but temporary period.
• A number of New Brighton/Arden Hills residents drawing contaminated drinking water were provided municipal water through construction of U.S. EPA/MPCA-funded water main extension.
• Residents of the Arden Manor Trailer Park drawing contaminated drinking water were provided with new wells finished in an aquifer with potable water. The wells were provided by Arden Manor Trailer Park, which was later reimbursed by the Army.
• A New Brighton resident was provided MPCA Superfund money for reimbursement for connection to the New Brighton municipal water supply.

Army reports of investigations and studies at TCAAP (Phases I, II and III) in 1983 and 1984 identified major and minor disposal areas on the facility that were sources of release or threatened release of hazardous substances (mainly VOCs). In their review of these reports, MPCA and the U.S. EPA noted inadequate investigations and studies, the need to address the extent and magnitude of contaminated groundwater and the need to complete an assessment of the disposal areas identified on TCAAP.

In 1984 and 1985, Honeywell submitted (via the Army) investigative reports addressing VOC contamination at Honeywell-leased TCAAP Buildings 103 and 502 (Sites I and K). The reports indicated that the buildings' operations were a source of VOC-contaminated groundwater migrating toward Rice Creek from Building 103 and also to the west or southwest from the Building 502 area. As a result of these findings, Honeywell announced a three-phase off-TCAAP investigation on July 28, 1984, to supplement work being conducted by MPCA to identify off-TCAAP sources of release.

On May 28, 1985, MPCA released the Phase I RI report titled *Phase I Final Report, New Brighton/Arden Hills, Minnesota Multi-Point Source Remedial Investigation*. The report identified four potential source areas of release of VOCs in the study area that had possibly contaminated the area groundwater. The source areas included two areas at TCAAP and two areas adjacent to TCAAP. Phase IA RI activities were initiated in July 1986. The purpose of the Phase IA RI was to further define the nature and extent of groundwater contamination in off-TCAAP areas.

In the spring of 1985, the U.S. EPA initiated an investigation of the force mains off-TCAAP because a number of documented breaks had

occurred in the line in the study area and because VOCs and other hazardous wastes and metals had been detected in the sewer sediments on-TCAAP.

On June 6, 1985, the Army announced a plan to begin addressing groundwater contamination detected on-TCAAP. The plan included a proposed groundwater pump-and-treat system to address TCAAP groundwater contaminated with VOCs. The plan also identified Honeywell as the coordinator of the TCAAP groundwater cleanup effort. In 1986, the Army activated an in situ volatilization system at Sites D and G to remove VOCs from the unsaturated zone.

THE AGREEMENT

To facilitate cleanup of TCAAP, the Army entered into a federal facility agreement (FFA) with the U.S. EPA and the State of Minnesota pursuant to Section 120 of the SARA. The TCAAP FFA, which became effective on December 31, 1987, was the first agreement to be negotiated between the U.S. EPA and any federal agency since the enactment of SARA in 1986. The FFA calls for the on-TCAAP RI to be carried out by the Army, while the off-TCAAP RI is to be done by the state and the U.S. EPA. Following completion of both RIs, the Army will prepare the FS to evaluate alternatives for remediating the entire area of contamination.

Section 120 (e)(2) and (e)(4) of SARA require the U.S. EPA and the head of the responsible federal agency to enter into an interagency agreement at the end of the RI/FS to specify the agreed-upon final remedial action and to expedite its completion. In addition, Section 120 (e)(1) provides that the state and the U.S. EPA administrator will publish timetables and deadlines. The TCAAP agreement is an effort to combine these requirements into an integrated and more efficient document that involves U.S. EPA headquarters and the state, as well as the Army and the U.S. EPA regional office as participants and takes effect before the Army has finished the TCAAP RI/FS process. Thus, this FFA is an agreement "under Section 120" rather than strictly the interagency agreement described in SARA Section 120 (e).

Prior to entering into the FFA, the Army viewed the regulatory agencies, U.S. EPA and MPCA, in an advisory capacity only. Most often, these agencies were notified of the Army's intended actions after these actions were finalized and the agencies' abilities to influence or impact the actions were inhibited.

Purposes of the Agreement

The general purposes of this agreement are to:

- Ensure that the environmental impacts associated with past and present activities at TCAAP are thoroughly investigated and that appropriate remedial actions are taken to protect the public health, welfare and the environment
- Establish a procedural framework and schedule for developing, implementing and monitoring appropriate response actions in accordance with CERCLA/SARA, the National Oil and Hazardous Substances Pollution Contingency Plan, Superfund guidance and policy, RCRA and RCRA guidance and policy
- Ensure cooperation, exchange of information and participation of the parties in such actions

The specific purposes of the agreement are to:

- Identify interim remedial action alternatives appropriate for preventing further migration of contaminated groundwater prior to the implementation of final remedial action(s) for the site
- Establish requirements for the performance of an on-TCAAP RI to determine fully the nature and extent of the threat to the public health, welfare, or the environment caused by the release and threatened release of hazardous substances, pollutants or contaminants at TCAAP and to establish requirements for the performance of an FS for the site to identify, evaluate and select alternatives for the appropriate remedial action(s) to prevent, mitigate or abate the release or threatened release of hazardous substances, pollutants or contaminants at the site in accordance with CERCLA and SARA
- Identify the nature, objective and schedule of response actions to be taken at the site; response actions at the site shall attain that degree

of cleanup of hazardous substances, pollutants or contaminants mandated by CERCLA and SARA

- Implement the selected interim and final remedial action(s)
- Assure compliance with federal and state hazardous waste laws and regulations for matters covered by the agreement

Major Features of the Agreement

The TCAAP FFA contains 11 major features, which are presented below:

- *Point of Contact*: It provided a point of contact to assume responsibility for the Army. This was important to the U.S. EPA because it often could not identify the correct individual to contact regarding issues relevant to TCAAP.
- *Shared Responsibility*: It specified a shared responsibility among the regulatory agencies and the Army for conducting RI/FSs for the site.
- *Reimbursement of Oversight Cost*: It provided means of reimbursement to the U.S. EPA of past and future oversight costs as well as reimbursement of these costs to MPCA and the Minnesota Department of Health.
- *Specific Statement of Work*: It provided a specific statement of work for RI/FS, remedial design (RD) and implementation of remedial actions (RA) at the site.
- *Implementation of Interim Remedial Measures*: It provided for implementing interim remedial actions at the site, a device that the U.S. EPA has used extensively for remediation of contamination at the site (see next section).
- *Integration of RCRA, Section 3004(u) and (v)*: Currently, the U.S. EPA is in the process of delegating RCRA 3004(u) corrective action authority to states. Conforming with the terms of the FFA will satisfy the procedural requirements of Section 3004(u) and (v) and should accomplish the following:
  - Preserve cost-effectiveness as a criterion for selecting remedies
  - Bypass additional, needless and duplicative RCRA requirements, preventing increase of paperwork burden, staff time and administrative costs
  - Provide for unity of program management and more efficient allocation of resources
- *Dispute Resolution Process*: If, after proceeding through a multilayered dispute resolution process, the parties are unable to unanimously agree on the resolution of any given issue, the U.S. EPA administrator will make the final decision, providing a national, rather than a regional, perspective. Without giving written notice to the Secretary of the Army, the U.S. EPA administrator may not delegate this decision-making authority.
- *Exemption from Permits*: This provision precludes the time-consuming permit application process. The Army agrees to abide by all ARARs which such permits would have included.
- *Applicability of Citizens Suits*: While the terms and conditions of the FFA are enforceable by citizen suits brought pursuant to Section 310 of SARA, the actual effects of citizen suits are expected to be ameliorated by the provisions for *Schedule Modifications* and *Extension of Schedules*. The procedures for extending deadlines, if invoked in a timely manner, should revise schedules affected by delays due to circumstances that are beyond the Army's control (i.e., mechanical breakdowns, equipment shortages, harsh or hazardous weather conditions, contractor strikes, etc.), thereby providing the Army with a measure of extra protection from baseless or frivolous complaints.
- *Army to Reimburse the U.S. EPA and the State*: The costs incurred for oversight, investigation, new wells, etc., must be reasonable, consistent with the NCP under CERCLA (including the cost-effectiveness criterion) and subject to Army audit before being reimbursed.
- *Applicability of Penalties*: The U.S. EPA (not the state) may administratively levy fines against the Army for failure to comply with the requirements of the FFA. The fines stipulated in the FFA are lower than the maximum stated in SARA and should be avoidable as long as the Army uses the provisions for schedule modification/extension and dispute resolution. Moreover, if fines are imposed but

are accepted by the courts as constituting "diligent prosecution," citizen suits to enforce the FFA will be effectively precluded.

PROGRESS TO DATE

To date, significant progress has been made for remediation of contaminated soils and groundwater at the site. Some of the response actions were implemented by the U.S. Army before signing the FFA and some were implemented after the agreement. The response or cleanup actions may be divided into four groups: (1) alternative water supplies, (2) unilateral removal authority actions by the U.S. Army, (3) actions with U.S. EPA and state concurrence and (4) other actions initiated by the U.S. EPA and/or the U.S. Army.

Alternative Water Supplies

The alternative water supplies include a number of hookups of individual well owners to city water supplies and construction of interconnecting pipelines between cities. For the city of St. Anthony, an interconnect to the neighboring city of Roseville was made so that St. Paul municipal water supply already used in Roseville could be transported to St. Anthony via Roseville. The State of Minnesota currently has a cooperative agreement with the U.S. EPA to construct a carbon treatment system to treat water from the contaminated St. Anthony wells.

Another alternative water supply is a carbon treatment system for the City of New Brighton. This system was formally operational in June 1990 and was funded by the U.S. Army as part of a litigation settlement. While the U.S. Army signed a ROD for the New Brighton carbon system, the U.S. EPA never concurred with the ROD, but viewed it as an acceptable [to U.S. EPA] means for settling the litigation of the U.S. Army by the City of New Brighton.

Unilateral Actions by the U.S. Army

Unilateral removal actions by the U.S. Army are actions taken by the U.S. Army using its own delegated removal authorities under CERCLA Section 104. Most of these actions were implemented prior to the signing of the FFA. The two most successful actions in this group are the in situ soil vapor extraction (ISV) system for remediation of contaminated soils at Site D and Site G of TCAAP (Fig. 2). These ISV systems were implemented in 1986 and since then, each system has removed approximately 45 tons of VOCs per site. Their operational status is continually reported to the U.S. EPA and the state, with all modifications to the systems mutually agreed to by all three organizations. Other actions in this group are groundwater pump-and-treat systems at sites A, I and K.

The groundwater at Site A is contaminated with VOCs. To remove and treat contaminated groundwater at the site, an interim remedial action was initiated by the Army in 1988. This remedial action consists of a groundwater extraction and treatment system using liquid phase activated carbon. Sites I and K contain VOC-contaminated soils under buildings. Leaks from floor drains and sewer lines are identified as the likely source of contamination. Honeywell, an Army tenant, currently operates these buildings and has performed remedial actions. These actions were implemented in 1988 and include contaminated groundwater extraction and treatment by air stripping. The treated groundwater from Site K is discharged to a sewer under the NPDES permit issued by the state. The treated groundwater from Site I is discharged to the TCAAP groundwater recovery system (TGRS) for further treatment.

Actions with U.S. EPA and State Concurrence

The most significant action under this group includes the TGRS, which includes five source control (SC) wells downgradient of Sites D and G and a boundary groundwater recovery system (BGRS) along the southwest side of TCAAP. The objective of the BGRS was to contain and prevent continued migration of contaminants downgradient of TCAAP. To implement BGRS, the U.S. EPA prepared an ROD in September 1987. The ROD provided the specific criteria for the BGRS. After extensive negotiations among the U.S. EPA, MPCA and the U.S.

Army, the BGRS was implemented in late 1987. This phase of the BGRS included six Unit 3 extraction wells and three air stripping units for treating extracted contaminated groundwater.

A review of a 90-day performance report of the system by the U.S. EPA and MPCA indicated that the BGRS was not in compliance with the remediation criteria (full capture of the contaminated plume) established in the ROD. To comply with these criteria, the BGRS was expanded in 1989 to include six additional wells (two in Unit 3 and four in Unit 4) and one additional air stripping unit. The treated groundwater must meet maximum contaminant levels (MCL) established under the Safe Drinking Water Act before it may be discharged to a gravel pit on-TCAAP. Except for some background metals, all other discharge criteria are met. The capture criteria for the contaminants require the capture of all contaminated groundwater plume migrating off-TCAAP in excess of 10^{-6} cancer risk or a hazard index of one. It is up to the U.S. Army to demonstrate adequate capture to the satisfaction of the U.S. EPA and MPCA.

Other actions under this group include on-TCAAP RI, off-TCAAP RI, risk assessment of on- and off-TCAAP areas, FS, remedial design of appropriate response actions (RD) and implementations of these actions (RA). The on-TCAAP RI is prepared by the U.S. Army, the off-TCAAP RI is prepared by the state, the risk assessment is performed by the U.S. EPA and FS/RD/RA will be conducted by the U.S. Army. In addition, the U.S. Army will prepare annual monitoring reports covering more than 300 groundwater monitoring wells and IRAs. All documents prepared by the U.S. Army are reviewed by the U.S. EPA and the state for consistency and compliance with the requirements of the FFA.

The total mass of contaminants removed since implementation of the above interim remedial actions is presented in Table 1. The groundwater contamination plume for trichloroethene (TCE) in aquifer Units 3 and 4 are presented in Figures 3 and 4.

Table 1
Status of Interim Remedial Actions at TCAAP

IRA	Start Date[1]	Mass Contaminant Removed (lbs.)[2]	
Site A	09/13/88	2.1[3]	by December 1989
Site D	01/29/86	96,300[4]	by December 1989
Site G	02/20/86	90,000[5]	by December 1989
Site I	08/15/86	NA	NA
Site K	08/15/86	NA	NA
BGRS (6 wells)	10/19/87	6,800[6]	by January 1989
Expand BGRS (12 wells)	01/31/89	87,000[7]	by June 1989
SC Wells 2 to 5	01/31/89	25,000[7]	by June 1989

Notes:

1. Interim remedial actions at these sites are ongoing with anticipated completion dates when final remedial actions are implemented.

2. Cumulative mass of organic compounds removed by the dates indicated.

3. Between the start date and December 1989, approximately 2.5 million gallons of ground water have been treated at the site. Information was obtained from monthly operations report, dated January 1, 1990.

4. In the summer of 1989, approximately 1,400 cubic yards of PCB-contaminated soil were treated at the site using an infrared thermal treatment process. Information was obtained from ISV operation reports, dated January 2, 1990.

5. Information was obtained from ISV operation reports, dated January 2, 1990.

6. Estimated VOC removal based on BGRS Annual Monitoring Report, dated May 1989 (4,800 lbs. through October 21, 1988), and projected to be 6,800 lbs. by January 1989.

7. Estimated total VOC removal based on expanded BGRS (12 wells included Site I SC-1) and SC wells 2 to 5 (downgradient of Sites D and G) contaminant concentration data in the first and second quarterly monitoring report for 1989 by Army/Honeywell dated December 5, 1989; and ground-water extraction data in Table 1 of Draft ROD for PGRS by Honeywell dated May 15, 1989.

NA = Information is not available.

Other Actions Initiated by the U.S. EPA and/or the U.S. Army

Several other actions implemented at the site were initiated by either the U.S. EPA or the U.S. Army. Some of these significant actions are presented below:

- Thermal treatment of 1,400 yd^3 of PCB-contaminated soils at Site

D; the U.S. EPA prepared the ROD and risk assessment report
- Water management study to evaluate feasible alternatives for the disposal of treated groundwater anticipated from the future remedial measures; Phase I of this study has been completed and Phase II is currently underway
- Force main RI (Site J) and subsequent cleanup measures
  - Investigation and remediation of 83 aboveground and below ground storage tanks

RESOLUTION OF DISPUTES

The FFA set forth a procedure for resolution of disputes among the three organizations, the U.S. EPA, the state and the U.S Army. The disputes are resolved at the project manager's level. If project managers cannot reach an agreement on any issue within 14 days, then any party may elevates the dispute to the Dispute Resolution Committee (DRC) for resolution. If none of the parties elevate the dispute to the DRC within this 14-day period, the position of the U.S. EPA's project manager is final with respect to resolution of the dispute. The designated members of DRC are the Waste Management Divisional Director of U.S. EPA Region 5, the MPCA Executive Director and the Army's Deputy for Environmental Safety and Occupational Health.

Since the implementation of the FFA at TCAAP, no major disputes have arisen. The primary issues have included schedule of deliverables, hydrogeologic interpretations and technical aspects of the deliverables. These issues have been resolved at a project manager's level in a cooperative manner. The schedule of deliverables has generally been adjusted to ensure that quality of the documents is not sacrificed by the need to meet a deadline. The hydrogeologic interpretations and technical issues have been resolved by calling special meetings, with enough lead time for each party to assemble his/her data and to pre-

sent his/her viewpoint. This process of resolving issues or disputes at project manager and technical levels has resulted in good cooperation among all parties.

SCHEDULES AND WORKLOAD

A schedule of activities for the TCAAP site is shown in Figure 5. As shown in this schedule, several activities are currently underway, including the operation and maintenance of several interim remedial actions. All documents submitted by the U.S. Army, including performance evaluation of the interim remedial actions, are reviewed by the U.S. EPA and state for technical adequacy and consistency with the requirements of the agreement. The review time established in the agreement is 40 calendar days. However, the complex documents, such as on- and off-TCAAP RIs or other similar documents that require longer review time, have been granted mutually agreeable extensions. This is to ensure that quality of the documents is not compromised by the need to meet the rigorous and stringent schedules.

In general, considering the large magnitude and complexity of the site, the number and length of delays have been similar to or better than other Superfund sites in the region. Individual documents sometimes appear to take a long time to finalize (6 months for example), but this is due to resolving any issues on the drafts and then delaying the final issuance while resources are focused on more time-critical projects (e.g., the completion of the design of an IRA).

CONCLUSION

This paper presents highlights of the first federal facilities agreement in the country pursuant to Section 120 of CERCLA/SARA for remediation of soils and groundwater contamination at the New Brighton/Arden Hills Superfund site in Ramsey County, Minnesota. It discusses the

Figure 3
TCE Groundwater Contamination Plume in Unit 3

Figure 4
TCE Groundwater Contamination Plume in Unit 4

Figure 5
Schedule of Activities for TCAAP Site

experiences gained and progress made through the implementation of the agreement at this very large and complex site.

The agreement requires that all documents submitted by the U.S. Army be reviewed by the U.S. EPA and the state for technical consistency within 40 calendar days. There are several activities concurrently being conducted at the site. To perform consistency tests within the specified schedule is and has been a challenge for the three organizations and their contractors. To meet this challenge and ensure high quality work has required innovative management procedures and prompt allocation of resources on the part of all participants. The spirit of cooperation shown by all participants in resolving technical and schedule-related issues has been crucial in successfully implementing the agreement.

Field Detection Kits for TNT and RDX in Soil

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ABSTRACT

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and the Naval Weapons Center, China Lake, jointly developed an indicator tube in the mid-1980s for the detection of TNT in Army Ammunition Plant effluents. The tubes were later adapted for use in field detection of TNT in groundwater and soil. These tubes have been used extensively by the Army to assist in locating explosives-contaminated areas and in placing monitoring wells.

Recently, the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and USATHAMA have developed a simpler, faster and more quantitative method for TNT determination in soil. Soils are extracted with acetone and quantitation is based on production of the highly colored Jackson-Meisenheimer anions with strong base. Measurement is obtained with a field-portable spectrophotometer at 540 nm.

A similar method has also been developed for RDX. The soils are extracted with acetone and the extracts are passed through a disposable, strong anion exchange resin to remove any nitrate and nitrite present. RDX is then reacted with zinc and acetic acid to produce nitrite, and the nitrite concentration is measured using the two-step Griess reaction. Measurement is also obtained colorimetrically at 540 nm.

INTRODUCTION

One of the most serious environmental problems facing the U.S. Army today is the presence of soil contaminated with munitions residues at military installations throughout the United States. TNT and RDX are the two explosives most commonly observed in munitions-contaminated soils because of their widespread use and their long-term stability in the environment. Further, because of their mobility in the soil profile, TNT and RDX pose an immediate problem for groundwater contamination.

Field screening methods can be rapid, inexpensive tools for locating explosives-contaminated surface soils. They can be useful in initial site surveys to locate zones of high contamination and select samples for more in-depth laboratory analysis. They also can be used during site cleanup to accurately locate the clean soil/contaminated soil interface.

Background of TNT Test

As early as 1891, Janovsky[1] observed that colored reaction products were formed when polynitroaromatic compounds reacted with alkali such as potassium hydroxide. Meisenheimer[2] and Jackson and Earle[3] independently proposed a quinoidal structure to explain this phenomenon. Equation 1 shows the production of the Jackson-Meisenheimer anion from 2,4,6-trinitrotoluene (TNT). In general, Jackson-Meisenheimer anions for dinitroaromatics are blue to purple

in color, while those from trinitroaromatics are red.[4]

$$ (1) $$
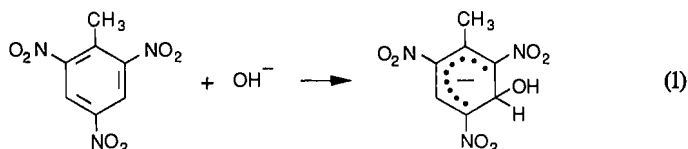
When sulfite ion is present along with hydroxide, addition of sulfite to the aromatic ring also can occur.[5] This anion is more stable than the anion formed from hydroxide alone,[6] with stabilities extended from approximately 30 minutes for the hydroxide complex[7] to at least six hours.[6]

When the base-catalyzed reaction takes place in a ketone solution such as acetone (Janowsky reaction), addition of the carbanion (Equation 2) can also result.[8]

$$ (2) $$
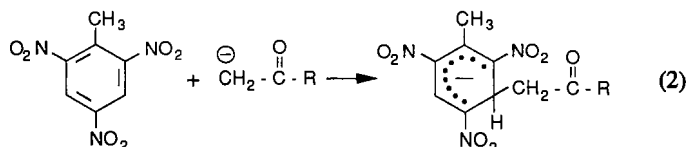
These reactions have been used analytically for a number of applications. Yinon and Zitrin[9] show examples of their use for forensic detection of TNT in post-blast debris. Heller et al.[10] used the reaction of strong base with TNT as the basis of a field kit for detection of low levels of TNT in water. The use of this kit was later extended to estimation of TNT in soil extracts.[11] A discussion of their procedure, its method of detection, and an assessment of its utility are presented elsewhere.[12] In general, the kit provides a field method to detect the presence of TNT in soil, but is less useful for estimating concentration.

Background of RDX Test

Colorimetric chemical methods for RDX have been developed for forensic application.[9] These procedures generally rely on sequential reactions where RDX is first converted to nitrous acid using the Franchimont reaction (Equation 3). The nitrous acid is used to nitrosate an aniline derivative such as sulfanilic acid (Equation 4) and the resulting diazo cation couples to a naphthylamine (Equation 5) to form a highly colored azo dye (Griess Reaction). Several other pairs of reagents may be used to produce azo dyes.[13] A reagent containing procaine and N,N-dimethyl-naphthylamine is used for the test described in this paper. Wyant[14] tested several reagents and found this combination to be best in terms of detection capability and shelf life. The authors are not aware

of a field method for RDX in soil based on this reaction sequence.

$$\text{RDX} + \text{Zn} \xrightarrow{\text{Acetic Acid}} 3\,HNO_2 \qquad (3)$$

Franchimont Reaction (1897)

$$HNO_2 + \text{(aniline)} \rightarrow \text{(diazonium)} \qquad (4)$$

$$\text{(diazonium)} + \text{(naphthylamine)} \rightarrow \text{Azo Dye} \qquad (5)$$

Griess Reaction (1864)   Azo Dye
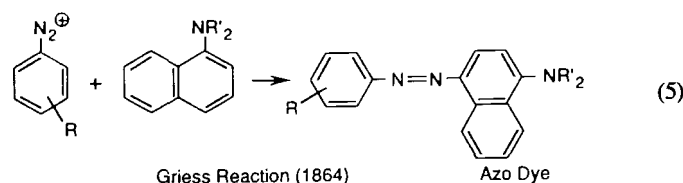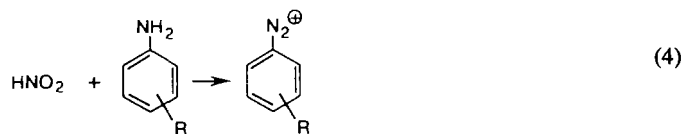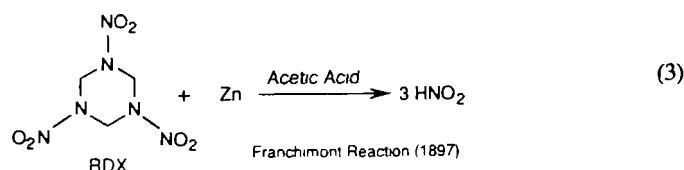
OBJECTIVE

The objective of the research described here is to develop simple, rapid field methods to estimate TNT and RDX concentrations in soil. The chemicals and equipment needed should be usable under field conditions by analysts with only minimal chemical expertise. The method should not require electrical power so that measurements can be made at the site of potential pollution. It should be rapid enough to allow decision-makers on-site to utilize the results to make judgments regarding the need to take additional samples for laboratory analyses or, under a cleanup scenario, continue or halt soil excavation.

EXPERIMENTAL

Analytical Standards

Analytical standards for 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were prepared from Standard Analytical Reference Material (SARM) obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. The SARMs were dried to constant weight in a vacuum desiccator in the dark, and standards were prepared in HPLC grade acetone.

Soils

Soils used for laboratory extraction studies included field-contaminated and uncontaminated soils from a number of present and former military installations in 10 different states. Interference tests utilized a commercial potting soil obtained locally that was rich in humus and uncontaminated soils from a variety of military installations.

Soil Extraction

Soils were extracted by manually shaking a 20-g sample for 3 minutes with 100 mL of acetone and filtering the extracts with Millex-SR disposable syringe filters.

Removal of Nitrate and Nitrite

Nitrate and nitrite ions were removed from acetone soil extracts by passing 10 mL of the extract through a disposable strong anion exchanger (Supelco, Alumina-SAX) at 5 mL/min.[22]

Generation of Jackson-Meisenheimer Anions for TNT Test

A pellet of potassium hydroxide (KOH) and approximately 0.2 g of sodium sulfite were added to 20 to 25 mL of acetone soil extracts. Samples were manually shaken for 3 minutes, then filtered through a Millex-SR filter unit into a cuvette. Absorbance was read at 540 nm.

Production of Azo Dye from RDX

Acetone soil extracts were passed through an Alumina-A strong anion

exchange cartridge at 5 mL/min to remove any nitrate and nitrite which could be present. A 5-mL aliquot was acidified with 0.5 mL glacial acetic acid and reacted with 0.3 g of zinc dust in the barrel of a syringe fitted with a disposable filter unit. This solution was rapidly filtered into a vial containing 17 mL of a Griess color developing solution. The color developing solution was prepared by dissolving 0.35 g each of procaine and N,N-dimethylnaphthylamine in 100 mL of 1/1 glacial acetic acid-water. Prior to use, this solution was further diluted 5/12 v/v with water.

Spectrophotometers

Spectrophotometers were used to measure absorbance at various wavelengths in the visible region of the spectrum. A Coleman Junior II (Model 6/20) was used for laboratory tests and either a Hach DR/2 or DR/2000 was used in the field.

DEVELOPMENT OF TNT METHOD

Absorbance Spectra of Analyte Anions in Acetone

A 2.1-mg/L solution of TNT was prepared in 95% acetone—5% water and Jackson-Meisenheimer anions generated as described above. The absorbance spectrum was obtained from 400 to 600 nm (Fig. 1). Two λ_{max} were observed, at 462 and 540 nm, the molar absorptivities being 2.70×10^4 and 1.77×10^4 L/cm · mole, respectively. This solution was visually red.

A number of other nitroaromatics, nitramines, nitrate esters and polynitrophenols were tested under similar conditions and the visible spectrum of their anions obtained (Table 1). Clearly, several other
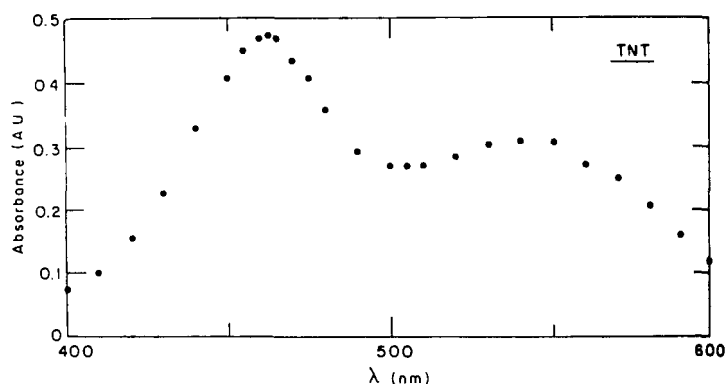
Figure 1
Visible Absorbance Spectrum of TNT Anion in Acetone

Table 1
Colors and λ_{max} Obtained for Acetone Solutions
of These Compounds Treated with KOH and Sodium Sulfite

Compound	Color observed This study	Color observed Bost and Nicholson (4)	λ_{max} (400-600 nm) (nm)
Nitrobenzene	None	None	---
o-nitrotoluene	None	None	---
m-nitrotoluene	None	None	---
p-nitrotoluene	None	None	---
1,3-dinitrobenzene	Purple	Purplish-blue	570
2,4-dinitrotoluene	Blue	Blue	570
2,6-dinitrotoluene	Pinkish purple	----	550
1,3,5-trinitrobenzene	Red	Red	460 , 560
Tetryl	Orange	---	460 , 550
2-Amino-DNT	Pale yellow	---	400
4-Amino-DNT	None	---	---
Nitroglycerine	None	---	---
PETN	None	---	---
RDX	None	---	---
HMX	None	---	---
Picric Acid		Reddish-orange	420
2,4-dinitrophenol		Yellowish-orange	430
TNT	Red	Red	462 , 540

polynitroaromatics and polynitrophenols also give colored anions under these conditions that would be very difficult to distinguish from TNT. During site cleanup activities, however, the ability to detect tetryl or TNB as well as TNT may be quite useful.

Effects of Variable Concentrations of Water in Acetone Extracts

Extraction of moist field soils with acetone will result in extracts containing variable concentrations of water. A test was conducted to assess the effect of variable water concentrations on the absorbance of TNT anions in acetone.

A series of 1.9-mg/L solutions of TNT in acetone was prepared with water contents ranging from 0 to 53% by weight. Jackson-Meisenheimer anions were generated and absorbances obtained at 540 nm (Table 2).

Table 2
Effect of Various Water Contents on the Absorbance of TNT Anions in Acetone

Concentration of water in acetone (% by weight)	Corresponding* soil moisture content (% of wet weight)	Absorbance (540 nm) for 1.9 mg/L TNT solution (AU)
0.0	0.0	0.076
3.0	12.2	0.183
5.9	24.8	0.181
8.9	38.7	0.158
11.7	52.5	0.140
17.4	83.4	0.136
28.2	**	0.054
53.4	**	0.014

* Corresponding soil moisture contents on a wet weight of soil basis if 20 g of soil is extracted with 100 mL of acetone.

** Exceeds possible water present in 20 g of wet soil.

The results indicate that absorbance is dependent on the amount of water present in the acetone. At intermediate concentrations of water in acetone (1 to 17%), however, similar absorbances (+/− 15%) are obtained. If a 20-g sample of wet soil is extracted with 100 mL of acetone, the 1 to 17% range of water in acetone would correspond to soil moisture contents ranging from 5 to 83% (on a wet weight of soil basis). This range of moisture content should include the large majority of surface soils from potentially contaminated sites.

Reagent Contact Time

Experiments were conducted to determine if reagent (KOH, Na_2SO_3) contact time had an effect on measured absorbance.[19] Contact time was varied from 1 to 18 minutes, after which solutions were filtered and absorbances measured. All experiments were conducted at laboratory temperatures (22° +/− 2°C).

Maximum absorbance was obtained by 3 minutes in all cases. Exposure to the reagents for longer periods resulted in reduced absorbance at 540 nm. Thus, a 3-minute reaction time was selected.

Field tests at Eagle River Flats, Alaska, indicated that at lower reaction temperatures, 3 minutes was not sufficient for full color development. An experiment to relate proper reaction time to ambient temperature is planned. Under field conditions, a standard solution can be used to select the time appropriate for a specific circumstance.

Experiments were conducted to determine the stability of the color after filtering.[15] The results indicate that color in filtered solutions is stable for at least 2 hours.

Instrument Calibration

Experiments were conducted to determine whether this procedure results in linear calibration curves.[15] Using least-squares regression analysis at the 95% confidence level and lack-of-fit testing, linearity and zero intercept were established for the concentration range 0.5 to

50 $\mu g/g$ (absorbances less than 0.9 AU). Thus for daily calibration a replicated single point standard is sufficient.

Background Absorbance of Blank Soils

Experiments with a variety of blank soils indicated that the color of acetone extracts will vary from colorless to yellow. An example of the visible absorbance spectrum of a commercial potting soil before and after addition of the reagents is shown in Figure 2. The initial absorbance of the soil extract was considerably greater between 400 and 500 nm than between 500 and 600 nm. After the extract was allowed to react with KOH and Na_2SO_3, the absorbance approximately doubled over the entire range of wavelengths, with rather large absorbances toward 400 nm.
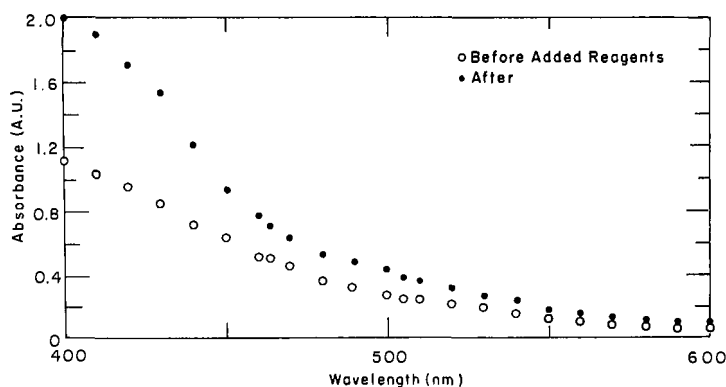
Figure 2
Visible Absorbance Spectrum of Acetone Extract
of High-Humus Potting Soil, Before and After Addition
of KOH and Na_2SO_3

The results of this test indicate that a blank absorbance measurement must be made on acetone soil extracts prior to addition of KOH and Na_2SO_3 to account for background absorbance of humic materials that could be present in the extracts. To determine if the factor-of-two increase in absorbance for the potting soil extract is typical of other soils, extracts from a series of blank soils from eight different military sites were tested. The ratio of the absorbance at 540 nm after reagent addition to that before reagent addition ranged from 1.1 to 3.5 with a mean value of 2.1 (Table 3). Thus, to correct for background absorbance, the initial blank reading should be doubled and subtracted from the absorbance reading obtained after addition of the reagents.

Extraction Efficiency of Field Procedure

For a field method to provide accurate estimates of TNT concentration in the soil, the extraction step must be rapid. Previous extraction

Table 3
Absorbance Measurements for Acetone Extracts of Blank Soils, Before and After Addition of KOH and Na_2SO_3

Sample location	Absorbance (540 nm) Before	After	Ratio after/before
USATHAMA Standard Soil	0.002	0.007	3.5
Keystone Ordnance Works	0.001	0.003	3.0
Lake Ontario Ordnance Works	0.003	0.005	1.7
Susquehanna Ordnance Depot	0.003	0.004	1.3
Raritan Arsenal	0.005	0.015	3.0
Hawthorne Army Ammunition Plant	0.000	0.002	--
Hastings East Industrial Park	0.019	0.030	1.6
Fort Hancock	0.005	0.006	1.2
Weldon Springs Training Area	0.123	0.140	1.1

$\bar{x}$ = 2.1

studies indicated that long extraction times were required when acetonitrile or methanol were used as the extraction solvent.[16]

In order to determine how rapidly acetone will extract TNT from soil, 16 field-contaminated soil samples from nine different sites were extracted with acetone using 3 minutes of manual shaking. An aliquot of the extract was removed and the remaining soil/acetone slurries were placed in an ultrasonic bath for 18 hours. Both sets of extracts (3 minutes and 18 hours) were analyzed by RP-HPLC as described elsewhere;[15,17] the results are presented in Table 4. The average recovery after 3 minutes of manual shaking with acetone was 96.1% of that obtained with the more exhaustive procedure, indicating that acetone is an excellent extraction solvent with respect to its extraction kinetics.

Table 4
Comparison of Extraction Efficiency of Field Procedure and Standard Laboratory Procedure (TNT)

Sample Origin	TNT concentration (µg/g)		Recovery by
	Field extraction procedure*	Laboratory extraction procedure**	field extraction method†
Vigo Chemical Plant	11.7	13.4	87.3%
Hawthorne AAP	4.53	4.75	95.4%
Nebraska Ordnance Works	0.065	0.071	91.5%
Nebraska Ordnance Works	340	349	97.4%
Hastings East Industrial Park	67.6	68.8	98.3%
Weldon Springs Training Area	0.96	1.26	76.2%
Sangamon Ordnance Plant	21.5	23.2	92.8%
Weldon Springs Training Area	163	176	92.6%
Hawthorne AAP	5.79	5.65	102.5%
Nebraska Ordnance Works	63.5	67.9	93.5%
Raritan Arsenal	71.7	80.6	89.0%
Nebraska Ordnance Works	0.39	0.32	121.9%
Lexington-Bluegrass Depot	5.90	7.11	83.0%
Chickasaw Ordnance Works	0.21	0.16	131.3%
Hawthorne AAP	0.79	0.90	87.8%
Weldon Springs Training Area	0.075	0.077	97.4%
		$\bar{x}$ = 96.1	
		s = 13.6	

* 20 g soil shaken with acetone for 3 minutes.
** 20 g soil extracted with acetone for 18 hours in sonic bath.
† Relative to laboratory extraction method.

Comparison of TNT Concentration Estimates for Soil Extracts

The extracts obtained after manually shaking the soil with acetone, as described above, were also analyzed by a colorimetric procedure utilizing the Jackson-Meisenheimer anions. A 20-mL sample of the extract was placed in a scintillation vial, KOH and sodium sulfite were added and the vials were shaken manually for 3 minutes. The vials were allowed to stand for 5 minutes and the solution filtered into a clean cuvette. The initial absorbance, before the reagents were added, was doubled and subtracted from the absorbance obtained after reagent addition, and the resulting difference was used to estimate TNT con-

Table 5
Comparison of Colorimetric and RP-HPLC Analysis of Soil Extracts for TNT

Sample origin	TNT concentration (µg/g)		TNB concentration* (µg/g)
	Colorimetric method	RP-HPLC method	RP-HPLC method
Vigo Chemical Plant	13.5	11.7	<d
Hawthorne AAP	5.49	4.53	<d
Nebraska Ordnance Works	2.39	0.065	2.72
Nebraska Ordnance Works	592	340	157
Hastings East Industrial Park	85.3	67.6	2.7
Weldon Springs Training Area	4.02	0.96	0.3
Sangamon Ordnance Plant	32.7	21.5	0.68
Weldon Springs Training Area	145	163	19.3
Hawthorne AAP	8.67	5.79	3.2
Nebraska Ordnance Works	146	63.5	74.1
Raritan Arsenal	85.3	71.7	<d
Nebraska Ordnance Works	0.38	0.39	<d
Lexington-Bluegrass Depot	15.0	5.90	<d
Chickasaw Ordnance Works	<d	0.21	<d
Hawthorne AAP (sh)	1.20	0.79	<d
Weldon Springs Training Area	0.33	0.075	<d

* Obtained from a separate subsample using acetonitrile extraction, as described in Jenkins et al. (17).

centration. TNT estimates for the 16 field-contaminated soils are given in Table 5. For comparison, the results of analysis of the extracts for TNT by the standard RP-HPLC procedure[17] also are presented, along with the estimates of TNB concentration obtained from a separate subsample extracted with acetonitrile. TNB could not be reliably determined in acetone extracts due to its instability in acetone.

The colorimetric results were correlated with both the TNT estimate by HPLC and the sum of TNT and TNB. The correlation with TNT alone resulted in a slope of 0.59 and an R^2 of 0.943. The correlation with TNT plus TNB resulted in a slope of 0.86 and an R^2 of 0.985 (Fig. 3). A paired t-test indicated that the concentration estimates for TNT from the colorimetric method and the sum of TNT and TNB by the HPLC procedure were not different at any level of significance. Thus it appears that the colorimetric results are best represented as the sum of TNT plus TNB. The slope of 0.86 indicates that, in general, the colorimetric procedure gives a slightly greater estimate for TNT than can be accounted for by TNT and TNB (Fig. 3). One interpretation of these results is that other TNT degradation products such as trinitrobenzoic acid, trinitrobenzyl alcohol, and trinitrobenzaldehyde,[18] which are not identifiable by RP-HPLC analysis of the extracts, form colored Jackson-Meisenheimer anions.

$$Y = 2.614 + 0.858 [x]$$
$$R^2 = 0.985$$
$$N = 16$$
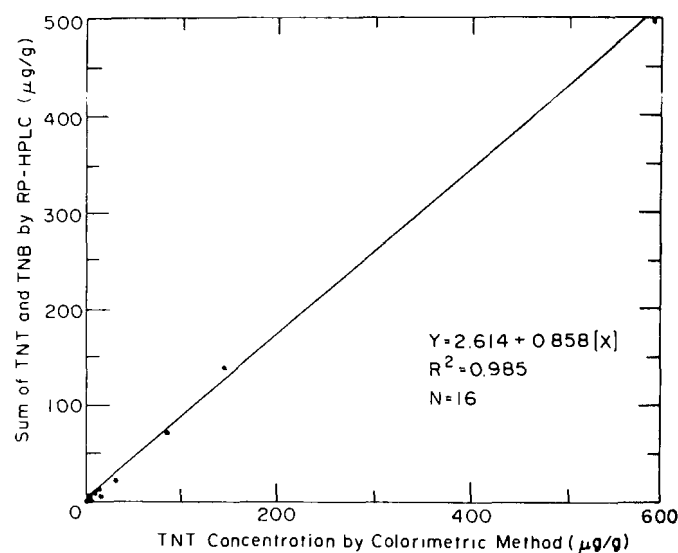
Figure 3
Correlation of Concentration Estimate Using Colorimetric Method for TNT Versus the Sum of TNT and TNB from RP-HPLC Analyses

Estimation of Detection Capability

The reporting limit for this procedure was established using the method of Hubaux and Vos[19] as described in USATHAMA.[20] The calculated certified reporting limit was 0.72 µg/g. A lower CRL would be obtained, however, if lower spike levels were included in the test.[21]

Field Testing

The method was given an initial field test at Umatilla Army Depot, Umatilla, Oregon. Since TNT concentrations were expected to be very high, a smaller subsample of soil was used and the extracts were diluted before reacting with KOH and Na_2SO_3.[15] This field test was conducted before the importance of reagent contact time was understood. Contact times of 10 minutes were used here.

The remainder of each soil/sediment sample was returned to the laboratory and analyzed for TNT using the standard laboratory procedure.[17] The results are included in Table 6 for comparison.

Except for sample 8a, the results of laboratory analysis are higher than those obtained using the field method. Correlation analysis of the field and laboratory results was conducted. Sample 8a was not included in the correlation analysis since very different behavior was observed

Table 6
Comparison of Results of Field Samples from Umatilla Depot Using Field and Laboratory Methods

	TNT concentration (μg/g) *	
Sample	Field method	RP-HPLC lab method
1b	1060	2250
2a	3560	7430
3b	704	1180
3a	3180	4030
4a	4490	8520
5a	2530	3990
6a	84	131
8a	102000 †	38600 †
9a	6610	7690
11a	716	1300
12a	109	183

Both laboratory and field method results are reported on a dry weight of soil basis to allow direct comparison.

Results for this sample were very different than observed for others and, because of very high values, the results were not included in correlation analysis.

for this sample and the TNT concentration was an order of magnitude higher than for any of the other samples. The correlation for the remaining 10 samples was excellent, with an R2 value of 0.865 which was significant at the 99% confidence level. The slope of the best fit relationship was 0.627, indicating the field procedure, on the average, gave results only about 63% as high as the laboratory results.

Two factors may have contributed to the low results for the field method. First, an excessively long reagent contact time prior to filtration was used. Thus, the absorbance would have been reduced relative to its maximum value. Second, the TNT concentrations in the Umatilla soil were much higher than those in the other field-contaminated soils tested, and the percentage extracted in the short extraction time used by the field method could have been reduced compared to the 18-hour extraction with acetonitrile used in the laboratory procedure. Nevertheless, the field results were encouraging for a first test.

An additional field test was conducted at Eagle River Flats, Alaska. All soils except one were determined to be free of TNT and other nitroaromatics by the field procedure, and these results were verified by the standard laboratory method.[17] One yellowish extract developed
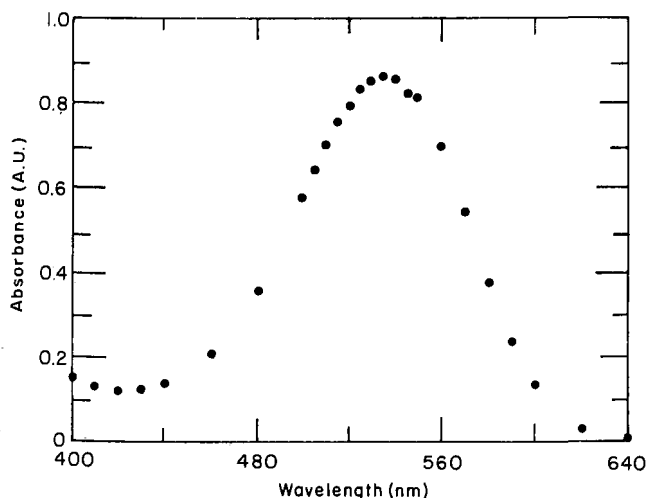
Figure 4
Visible Absorbance Spectrum of the Azo Dye Produced from RDX

a greenish color upon reaction with KOH and Na_2SO_3 and was found to contain 2,4-DNT at about 30 μg/g. Reaction with 2,4-DNT standards produces a bluish color which, when combined with the yellowish background, results in the observed greenish color. This color faded rather quickly, however, unlike color produced by TNT.

DEVELOPMENT OF RDX METHOD

Absorbance Spectra for Azo Dye Produced from RDX

A 4.0-mg/L solution of RDX was prepared in 97% acetone-3% water and the azo dye produced as described above. This solution had a bright pink color. The absorbance spectrum shows a λ_{max} at 535 nm (Fig. 4), and the molar absorptivity is 1.67 x 10^4 L/cm · mole. The same azo dye also is produced when HMX, NG, NC or PETN are treated under similar conditions.

Effects of Variable Concentrations of Water in Acetone Extracts

In the field, soil extracts will be obtained by manually shaking 20 g of soil with 100 mL of acetone. Since the soil will be moist in most cases, water will be a component of the soil extracts. An experiment was performed to see how variable amounts of water affect the production of the azo dye.

To simulate the extracts obtained from soils with moisture contents ranging from 5 to 100% (wet weight basis), 10-mL aliquots of a solution containing 2.3 mg/L of RDX were mixed with either 0.1, 0.2, 0.3, 0.5, 1.0 or 2.0 mL of water. The azo dye was produced as described previously. Absorbance was found to vary with the amount of water present (Table 7), with maximum absorbance for the case simulating a soil with a moisture content of 25% (wet weight basis).

Table 7
Effects of Various Water Contents on the Absorbance Obtained from RDX Tests

Volume (mL) water added to 10 mL acetone	Corresponding soil moisture content (% of wet weight)*	Absorbance (540 nm) for 2.3-mg/L RDX solution	
0.1	5.0	0.150	
0.2	10	0.3	0.3
0.5	25	0.425	
1.0	50	0.421	
2.0	100	0.399	

*Corresponds to soil moisture content if 20 g of wet soil is extracted with 100 mL of acetone.

Reagent Contact Time

Development of the azo dye from RDX is a two-step procedure. First, the RDX is reacted with zinc dust and acetic acid to produce nitrous acid. The nitrous acid then reacts with a Griess color reagent to produce the azo dye.

The amount of time the RDX is allowed to react with the zinc dust and acetic acid is critical.[22] Initial experiments with RDX dissolved in acetone indicated that a 10-minute contact time was required to reduce RDX. However, if a small amount of water was present in the acetone, as will be the case with soil extracts, the reaction kinetics were much faster. Contact times exceeding 30 seconds resulted in less nitrous acid production, presumably because the nitrous acid was further reduced to ammonia. Once the nitrous acid is produced, the solution must be filtered to remove the zinc dust. Because of the fast kinetics, this filtration is conveniently performed by reducing the RDX in the barrel of a syringe fitted with a disposable filter unit as described previously. Once the filtered solution is added to the color developing solution, full color development takes approximately 15 minutes (Fig. 5). The color is stable for several hours.

Background Absorbance from Blank Soils

The acetone extracts from soils high in humic material will be yellow. However, once the acetone extract is acidified and mixed with the color reagent, the humic material precipitates and may be removed by filtration. Experiments[22] with a wide variety of blank soils showed that background was negligible in all cases.
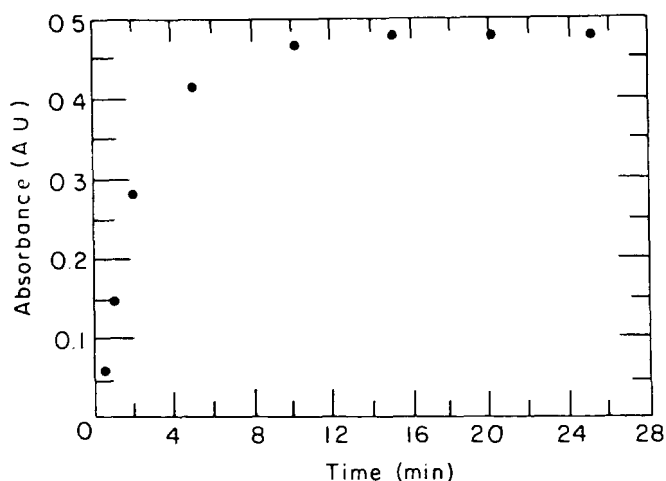
Figure 5
Kinetics of Color Development for Griess Reaction

Extraction Efficiency of Field Procedure

The field method described previously for TNT was used for RDX and compared to the standard laboratory procedure (Table 8). For the seven soils tested, the average recovery obtained by manual shaking with acetone was 98.4% of that obtained by the sonic bath procedure.

Table 8
Comparison of Extraction Efficiency of Field Procedure and Standard Laboratory Procedure

| | RDX concentration (µg/g) | | Recovery by |
| | Field extraction | Lab extraction | field extraction |
Sample origin	method *	method**	method(%)†
Hawthorne AAP	1.97	2.01	99.0
Nebraska Ordnance Plant	13.6	14.1	98.3
Hawthorne AAP	3.32	2.96	105
Lexington Bluegrass	9.10	9.37	98.5
Nebraska Ordnance Plant	60.2	65.9	95.5
Nebraska Ordnance Plant	1073	1080	99.7
Nebraska Ordnance Plant	9001	10,445	92.6
		X =	98.4
		S =	3.8

* 20 g soil shaken with acetone for 3 minutes.
** 20 g soil extracted with acetone for 18 hours in sonic bath.
† Relative to laboratory procedure.

Comparison of RDX Concentration Estimates for Soil Extracts

Eleven field-contaminated soils were used to compare the RDX concentrations estimated by the field method with those obtained by RP-HPLC analysis.[17] The results using the field method were correlated with those obtained by the HPLC method for both RDX alone and the sum of RDX and HMX (Table 9). The correlation for RDX resulted in a slope of 1.1 and an R^2 of 0.986 (Fig. 6). The correlation with RDX plus HMX resulted in a slope of 1.2 and an R^2 of 0.990. Paired t-tests indicated that the estimates of RDX concentration obtained by the field procedure were not significantly different from those obtained by the HPLC procedure for RDX alone or for the sum of RDX and HMX.

Effect of the Presence of TNT in Soil Extracts

For the RDX field method, the presence of RDX is indicated by the development of a pink color. As shown in Table 9, some other colors were produced from extracts of field-contaminated soils. Red was produced in those soils containing very high concentrations of RDX (i.e., greater than 1 mg/g). Orange was produced in those soils containing high concentrations (i.e., greater than 50 µg/g) of TNT or

Table 9
Comparison of Colorimetric and RP-HPLC Analysis of Soil Extracts for RDX

| | RDX concentration (µg/g) | | | |
| | Field colorimetric | | HMX concentration (µg/g) | Color |
Sample origin	method	RP-HPLC method	RP-HPLC method	obtained
Nebraska Ordnance Plant	1058	1247	115	Red
Hawthorne AAP	233	127	56.0	Orange
Raritan Arsenal	10.5	4.38	t	Brownish-yellow
Nebraska Ordnance Plant	2.66	3.65	t	Pink
Nebraska Ordnance Plant	1104	1143	105	Red
Nebraska Ordnance Plant	10.0	19.0	3.45	Pink-orange
Hawthorne AAP	5.52	2.6	<d	Pink
Nebraska Ordnance Plant	129	104	12.0	Orange
Nebraska Ordnance Plant	15.6	13.6	2.28	Pink
Nebraska Ordnance Plant	20.5	59.9	13.0	Orange
Nebraska Ordnance Plant	1.74	<d	<d	Faint pink
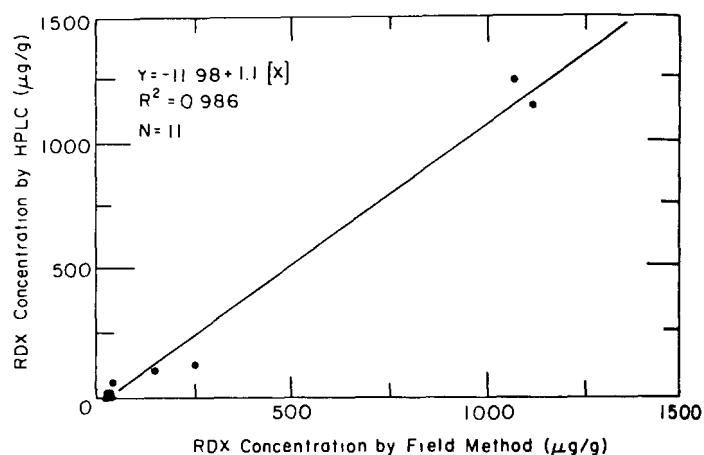
Figure 6
Correlation of Concentration Estimates Using Colorimetric Method for RDX Versus the Sum of RDX and HMX by RP-HPLC Analyses
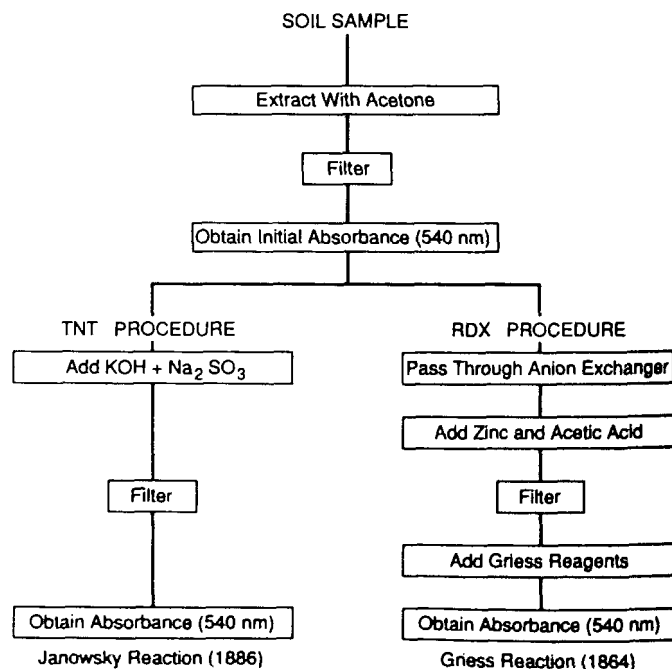
Figure 7
Flow Chart for Field Methods for TNT and RDX

TNB, as determined by RP-HPLC. While standards of TNT or TNB alone do not produce a color, standards containing RDX and TNT result in the same orange observed in some soil extracts. Nitroaromatic compounds, such as TNT and TNB, may be reduced to aminoaromatic compounds in the presence of zinc and acid. We speculate that these reduction products can be nitrosated by the nitrous acid produced from RDX and, like sulfanilic acid or procaine, couple to the naphthylamine in the color-developing reagent, producing another azo dye. Thus, in the field, development of a pink to red color indicates that RDX is the principal contaminant, while development of an orange color is evidence for both TNT and RDX together.

One soil extract developed a brownish-yellow color. As determined by RP-HPLC, this soil was also contaminated with TNT (>745 μg/g), 2,4-DNT (42.7 μg/g) and 2-amino-4,6-DNT (37.1 μg/g). A standard containing these analytes at concentrations similar to the soil extract resulted in a yellow color.

Estimation of Detection Capability

The reporting limit of RDX concentration using this field procedure was estimated using the method of Hubaux and Vos[19] as described in USATHAMA.[20] The calculated certified reporting limit was 1.4 μg/g.

Field Testing

This method was field tested at Eagle River Flats, Alaska. Of the 40 soils tested, no soil produced a positive result for RDX. All soils were also analyzed by RP-HPLC and no evidence of RDX was found. The method was found to be usable under field conditions, but certain precautions have to be taken. The color- developing reagent will turn pink if not protected from sunlight. Glacial acetic acid must be kept from freezing to allow volumetric addition; it has a melting point of 16.6°C. Lastly, high humidity will cause the zinc dust to clump; therefore, it should not be placed into the syringe barrel until immediately before use.

CONCLUSION

A flow chart of the two field procedures is given in Figure 7. For these field methods, soils are extracted by manually shaking a 20-g portion of soil with 100 mL of acetone for 3 minutes. A 25-mL aliquot is removed for the TNT test and filtered through a Millex SR disposable filter assembly and the initial absorbance obtained at 540 nm. One pellet of KOH and approximately 0.1 to 0.5 g of Na$_2$SO$_3$ are added and the extracts are manually shaken for 3 minutes. The solutions are immediately filtered through another Millex SR filter and the absorbance at 540 nm is measured again. Absorbance was found to follow the Beer-Lambert Law through the absorbance of 0.91 AU.

For the RDX test, approximately 10 mL of the acetone soil extract are filtered through a Millex SR disposable filter unit and then passed through an Alumina-A anion exchange cartridge. This procedure is necessary to remove nitrate and nitrite that would otherwise give a false positive result for RDX. Next, the plunger of a 10-mL syringe is removed and a filter unit is fitted to the syringe tip. A measuring spoon is used to add 0.3 g of zinc dust to the syringe barrel. A 5-mL aliquot of the filtered soil extract is acidified with 0.5 mL glacial acetic acid, swirled to mix and poured into the barrel of the syringe. After approximately 15 seconds, the plunger is fitted to the syringe and depressed. The solution is filtered into 17 mL of a Griess color-developing reagent and, after 15 minutes, the absorbance is read at 540 nm. If the solution is cloudy due to precipitation of humic material, the solution is filtered prior to measuring absorbance.

TNT and RDX concentrations were estimated using these field methods for a number of field-contaminated soils, and the results were compared with those from the standard laboratory procedure. Excellent linear correlations were obtained in both cases.

Field tests of these procedures were conducted and the methods were found to be quite usable under field conditions.

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Three-Dimensional Groundwater Quality Modeling in Support of Risk Assessment at the Louisiana Army Ammunition Plant

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ABSTRACT

Regional, three-dimensional, groundwater flow and solute-transport models were constructed at the Louisiana Army Ammunition Plant (LAAP). This work was performed in support of a Feasibility Study/Risk Assessment primarily focused on the problems of nitroaromatic contamination of the shallow groundwater at the site.

LAAP is located in the northwest portion of the State of Louisiana on lands situated in Bossier and Webster parishes, 22 miles east of Shreveport. Previous investigations have revealed groundwater problems from several sources: (1) wastewater (pink water) leaching pits, (2) unlined ponds containing metals manufacturing wastes, (3) abandoned landfills, (4) explosive loading areas and (5) burning ground areas.

One of the primary waste products of an ammunitions plant is pink water, the common name for wastewater contaminated with explosives such as 2,4,6-TNT or RDX. Pink water was dumped in various lagoons across the site for nearly forty years. Some of the explosive compounds and their by-products are toxic. The objective of this modeling study was to predict the future concentrations of these toxic compounds and their location in groundwater as part of the feasibility study risk assessment.

MODFLOW, a numerical model published by the U.S. Geological Survey, was used to simulate the regional groundwater flow at the site. The flow system was represented as three aquifers. The top aquifer was an unconfined aquifer in the upper Pleistocene section. The second aquifer included the lower Pleistocene and the upper Eocene Sparta Sand. The third aquifer comprised the Paleocene/Eocene Wilcox-Carrizo aquifer.

The output from MODFLOW was used as input to a translation program, PREMOD3D, to convert potentiometric heads to three-dimensional velocity vectors, which are in turn used as input to RAND3D, the solute-transport program.

RAND3D is a three-dimensional solute transport model based on the random walk algorithm. Several significant improvements were made to the model for this study. The program allows the user to simulate the movement of contamination and includes the effects of advection, dispersion, retardation and decay. The temporal progression of the plume is graphically displayed on the computer screen during the simulation at a scale selected by the user. RAND3D simulated the fate of the contamination at each of the six sites.

INTRODUCTION

The objective of the study was to define the regional flow system and the fate of the groundwater contamination at six areas within the Louisiana Army Ammunition Plant (LAAP) in support of the feasibility study/risk assessment being performed. The Louisiana Army Ammunition Plant is a government-owned and contractor-operated facility in northwestern Louisiana where munitions are loaded and packed. The plant was constructed in 1942 and has been in continuous operation since. Munition loading and waste disposal operations have contaminated groundwater at this site in a number of specific locales: Area P, Burning Ground No. 8, Burning Ground No. 5, Landfill No. 3, the Oily Waste Landfarm and the M-4 Lagoon. Figure 1 shows the locations of these areas and the general location of LAAP.
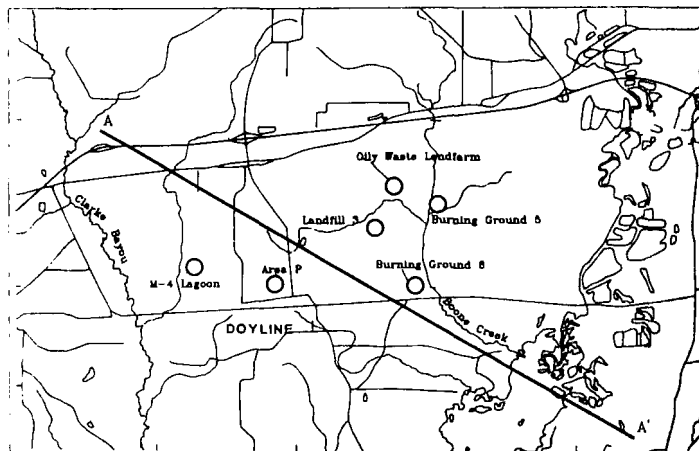
Figure 1
LAAP Study Sites

The area of greatest concern is Area P. Pink water, the common name for water containing dissolved nitroaromatic compounds, was dumped into unlined lagoons at Area P for nearly forty years. Previous investigations have yielded conflicting information on the size of the plumes and the direction of contaminant movement. Contamination has been found off-site and in what were thought to be up-gradient monitoring wells. Some of the more pressing questions included:

* Where is the contamination going? Previous studies suggest a west-southwest movement off the site toward the municipal well field of Doyline.
* Are any of the three municipal well fields located within a 3-mile radius of Area P going to be affected and when?
* Is the LAAP well field itself drawing the contamination into deeper horizons?
* What will be the effect on the contaminant plumes if the LAAP is decommissioned and on-site pumping stops?

A regional, steady-state three-dimensional groundwater flow model was developed and calibrated to both steady-state and transient conditions. This flow model was used as input to a random walk solute transport model.

GEOLOGY

The flow system at the LAAP was represented by three aquifers (Fig. 2) At the surface there are Pleistocene terrace deposits composed of alternating beds of mixed sands, silts and clays typical of Mississippi Coastal Plain sediments. For purposes of hydrogeologic modeling, the Pleistocene interval was divided into two aquifers. The aquifer boundaries were defined by the water table surface on the top and a semicontinuous clay layer on the bottom, and it is known as the Upper Terrace. This clay was used as the boundary between the top and the middle aquifer. However, the Upper Terrace is not continuous and pinches out in the southeast section of the model area.
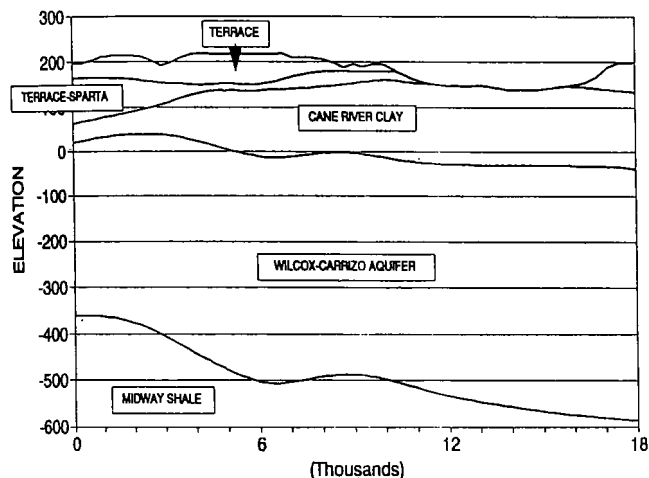
Figure 2
Regional Geographical Section

Constant head nodes were used at the edges of all layers to simulate the continuation of the aquifers. The constant heads were based on historic water levels, topography and adjustments made during calibration where data were sparse.

The middle aquifer is comprised of the lower Pleistocene terraces and the Eocene Sparta sand below. The hydrogeologic characteristics of the lower Pleistocene are similar to the Sparta and the two units were combined into one aquifer known as the Lower Terrace/Sparta. The Sparta lies unconformably below the Pleistocene terraces and consists of nonmarine massive sands, silty sands and silty shales, with occasional lignite and lignitic shales.

Below the Sparta is the Cane River Formation, the middle member of the Eocene Claiborne Group. It consists primarily of marine clay with abundant foraminifera, but also contains some silt and shale. The Cane River, where present, forms the confining layer between the second and third aquifers.

The deep aquifer, though it is called the Wilcox-Carrizo, is actually composed of mostly Wilcox Group at the LAAP site. The Wilcox group sediments consist mainly of nonmarine, white to grey, thin-bedded, micaceous sands and sandy shales with numerous thin lignites which lie on the Midway Group. The group is from upper Paleocene to lower Eocene in age. Regionally, the sequence varies in thickness from 350 to 1000 feet; however, thicknesses at LAAP only reach 550 feet.

The Midway Group was formed during the stand of the early Tertiary Sea and consists of the basal uniform marine black shale 500 to 600 feet thick. The clays are described as dense and are considered to be an effective lower confining layer to the aquifer system.

FLOW MODEL

The USGS MODFLOW model was used to simulate the regional groundwater flow at the arsenal. The groundwater flow system was set up as a three-layer model. The first layer was the Upper Terrace in the unconfined top Pleistocene terrace interval. The second layer was made up of the Lower Terrace/Sparta in the confined aquifer made up of the bottom Pleistocene terrace interval plus the Sparta sand that lies beneath. The bottom aquifer was the Wilcox-Carrizo located between the Cane River Formation and Midway confining beds. The Cane River Formation was modeled as a confining layer.

A 54-column by 30-row model grid was developed (Fig. 3) to simulate an area large enough to permit accurate simulation of well-field pumping on the LAAP and local municipalities; the grid also is spaced close enough for contamination simulation. The minimum grid spacing was 900 feet. The model was calibrated at steady-state using the monitoring well level data for all three aquifers. The average difference between the model and actual data was 0.06 feet and the root-mean-square difference was 4.76 feet (73 wells in the Upper Terrace and Lower Terrace/Sparta aquifers). The calibrated water levels for the three layers are shown in Figures 4 to 6.
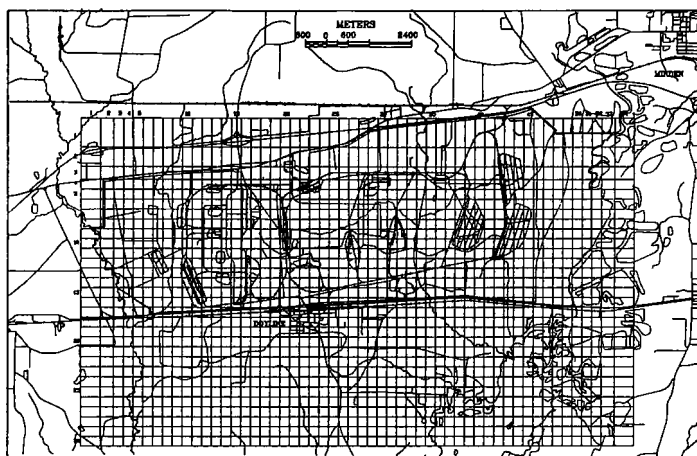
Figure 3
Model Grid
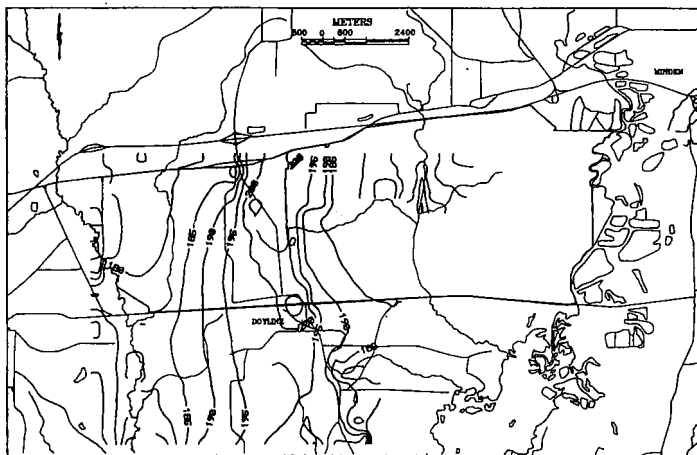
Figure 4
Calibrated Water Levels Upper Terrace Aquifer

SOLUTE TRANSPORT

Solute transport was simulated at each site separately, as differentiated from the regional flow model. The program PREMOD3D calculated the groundwater velocities at each contamination site based on the calibrated water levels. The three-dimensional random walk

model RAND3D utilized these velocities to simulate the solute transport at the six sites.

The explosive compounds simulated were the compounds found in the greatest concentrations and presented the greatest potential risks based on their toxicity. The most common contaminant was RDX, but other pollutants such as TNT, DNT and TNB also were simulated. Initial conditions of the pollutants were taken from previous remedial investigations. Figure 7 shows the initial RDX plume at Area P for the Upper Terrace aquifer and Figure 8 shows the initial RDX plume for the Lower Terrace/Sparta aquifer.
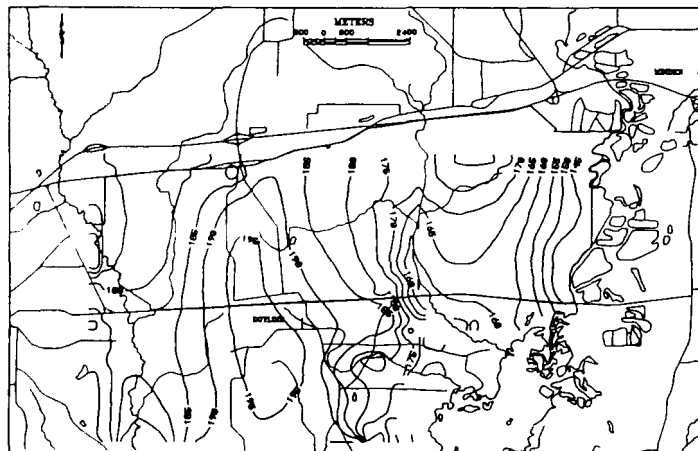
Figure 5
Calibrated Water Levels Lower Terrace/Sparta Aquifer
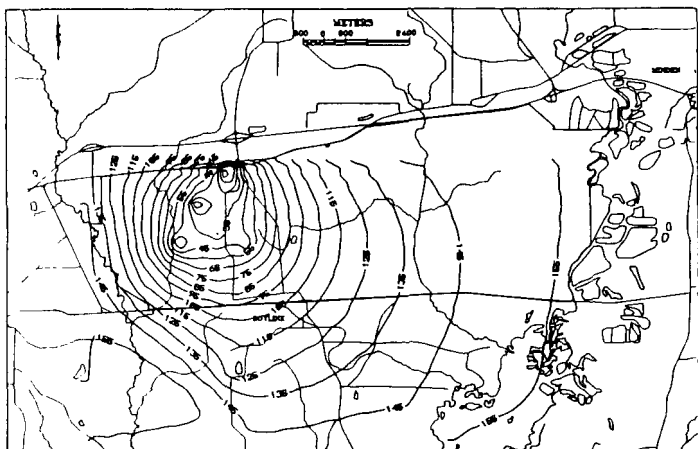
Figure 6
Calibrated Water Levels Wilcox-Carrizo Aquifer

The RAND3D model simulated solute transport for a total of 100 years at time steps of five years. Figures 9 and 10 show the RDX plumes after 50 years for the Upper Terrace and Lower Terrace/Sparta aquifers, respectively. Figure 11 shows the corresponding screen graphics displays of plan view and cross-sectional view generated by the RAND3D program for the simulation of 50 years. Figures 12 to 14 show the results after 100 years of simulation. Note that at this point RDX is shown seeping into Boone Creek via the Lower Terrace/Sparta aquifer.

Similar simulations were undertaken at the other five sites. Like Area P, four other sites, Burning Grounds No. 5 and 8, Landfill No. 3 and the Oily Waste Landfarm, showed contamination seepage into Boone Creek during the 100 year transport simulation. The M-4 Lagoon in comparison had contamination seepage into Clarke Bayou.

Figure 7
Area P Initial RDX Plume (ppb)
Upper Terrace Aquifer

Figure 8
Area P Initial RDX Plume (ppb)
Lower Terrace Aquifer

Figure 9
Area P RDX Plume after 50 Yrs
Upper Terrace Aquifer

Figure 10
Area P RDX Plume after 50 Yrs
Lower Terrace Aquifer

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Figure 11
Area P RDX Plume after 50 Yrs
RAND3D Screen Display

Sensitivity analyses were performed because of the uncertainty in the input parameters. The sensitivity of assumptions regarding adsorption, dispersivity, porosity, recharge at Area P and plant closure of the LAAP was tested.

CONCLUSION

A successful flow model of the LAAP groundwater was created with three layers: the Upper Terrace aquifer, consisting of Pleistocene alluvial terraces; the Lower Terrace/Sparta aquifer, consisting of Pleistocene

alluvial terraces and the Eocene Sparta member of the Claiborne Group; and the Wilcox-Carrizo aquifer, consisting of the Eocene Carrizo Sand and Wilcox Group. The Lower Terrace/Sparta aquifer and the Wilcox-Carrizo aquifer are hydraulically separated by the Eocene Cane River Formation, a thick marine clay.

Figure 12
Area P RDX Plume after 100 Yrs
Upper Terrace Aquifer

Figure 13
Area P RDX Plume after 100 Yrs
Lower Terrace Aquifer

The groundwater flow in the shallow aquifers (Upper Terrace and Lower Terrace/Sparta) at LAAP is dominated by the surface topography and surface water system. The direction of groundwater flow is generally towards the streams which bisect the LAAP. Boone Creek is the major groundwater discharge area with five of the six sites showing contamination seepage into this stream.

The Cane River Formation is a clay layer underlying the Upper Terrace and Lower Terrace/Sparta aquifers under most of the LAAP (and all of the area known to be contaminated). It effectively stops contamination in the shallow aquifers from migrating to the Wilcox-Carrizo aquifer which is the source of drinking water for the LAAP and other nearby towns. This conclusion is supported by the results of the intensive water level monitoring program.

Area P was the major disposal area for pink water at the LAAP. It is the area most heavily contaminated with explosive compounds. RDX, TNT and total DNT were simulated for this site. The simulation results

indicate the existing groundwater contamination at Area P will travel east through the Lower Terrace/Sparta aquifer to Boone Creek, which is in the opposite direction of Doyline community. After 100 years, 2% of the existing (1989 RDX concentrations in groundwater) RDX enters Boone Creek or its tributaries. After 100 years, 3% of the existing (1989 TNT concentrations in groundwater) TNT enters Boone Creek or its tributaries. After 100 years, 12% of the existing total DNT (1989 2,4 and 2,6 DNT concentrations in groundwater) reaches Boone Creek or its tributaries. Under the model setup assumptions, no explosive contamination from Area P crosses the LAAP boundaries.

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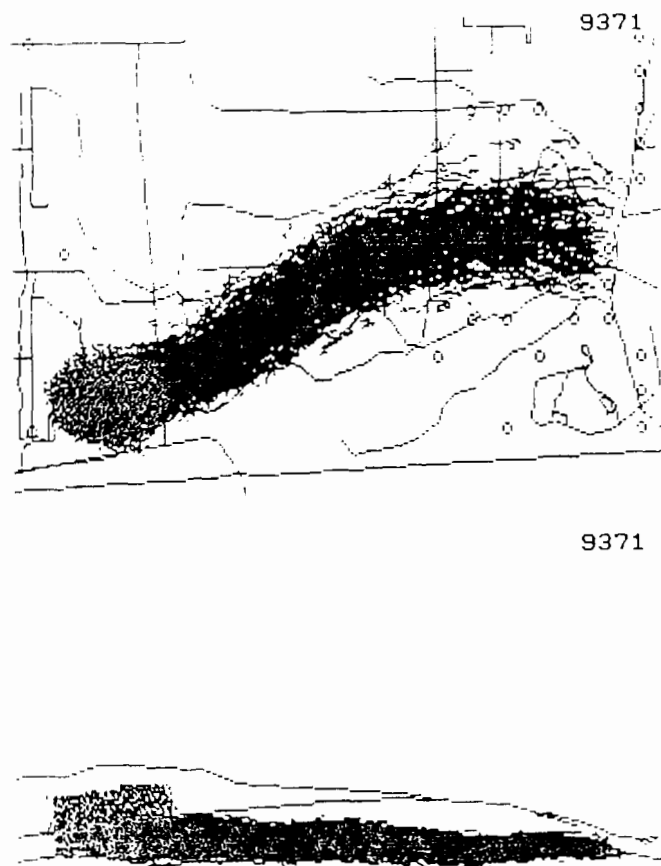
Figure 14
Area P RDX Plume after 100 Yrs
RAND3D Screen Display

Burning Ground 5 (BG5) is an area used for the disposal (burning) of explosives. Open burning was practiced before 1986. RDX, TNT and total DNT were simulated for this site. This site is adjacent to Boone Creek and a tributary. The simulation results indicate the existing groundwater contamination at BG5 will travel to the adjacent streams with most of the RDX, TNT and DNT contamination reaching surface water within twenty-five years.

Burning Ground 8 (BG8) was an area used for the disposal (burning) of explosives and as a sanitary landfill. There were also pink water lagoons at this site. RDX, TNT and TNB were simulated for this site. The simulation results indicate the existing groundwater contamination at BG8 will travel east to Boone Creek through the Lower Terrace/Sparta aquifer. After 100 years, approximately 80% of the existing RDX, TNT and DNT contamination enters Boone Creek.

Landfill 3 (LF3) was the site of pink water lagoons and later a landfill for construction debris. RDX was simulated at this site. The simulation results indicate the existing groundwater contamination will travel west to Boone Creek through the Upper Terrace and Lower Terrace Sparta aquifers. After 100 years, 98% of the existing RDX enters Boone Creek or its tributaries.

The Oily Waste Landfarm (OWL) is an area where oily wastes and chlorinated solvents were disposed of by landfarming. TCE has been detected in groundwater at this site in small concentrations. A theoretical slug source of contamination representing a conservative pollutant was simulated. After 50 years, 99% of the contamination has entered Boone Creek and its tributaries.

The M-4 Lagoon was used for the retention of wastewater from an electroplating operation until 1964. No groundwater contamination was detected by monitoring wells at this site. A theoretical release of a conservative pollutant was simulated at this site. The pollutant travels west to Clarke Bayou and after 100 years, 98% of the contamination enters Clarke Bayou.

The largest uncertainty in the above predictions is the travel time of contaminant movement. The source of this uncertainty is the lack of knowledge regarding the adsorption of the explosive chemicals onto the aquifer sediments. Adsorption retards the movement of the chemicals. Sensitivity analysis was performed to quantify the magnitude of the uncertainty. The following table shows the impact of different adsorption assumptions on the speed of contaminant travel. Data in Table 1 report the number of years when 50% of the initial contamination seeps from the aquifer into surface water.

Table 1
Retardation Sensitivity - Years for 50% Removal

Site	Contaminant	Retardation Base Case	Assumption None	High
Area P	RDX	>100(98%)	48	>100(100%)
	TNT	>100(97%)	50	>100(100%)
	DNT	>100(88%)	48	>100(100%)
BG5	RDX	7	5	60
	TNT	7	4	37
	DNT	6	3	30
BG8	RDX	11	5	>100(55%)
	TNT	5	3	13
	TNB	7	4	21
LF3	RDX	24	7	99
OWL		23	23	>100(64%)
M-4 Lagoon		60	60	>100(100%)

In the above table, where the time to 50% removal from the aquifers is greater than 100 years, the percentage of the initial contamination remaining in the aquifers after 100 years is in parentheses.

Dispersion is another source of uncertainty in the model predictions. Higher dispersion causes the initial plumes to spread out more, thus lowering concentrations. The mean travel path of the plume is not changed.

Another source of uncertainty in the model is effective porosity. Porosity increases travel times for larger porosities. Thus the impact is similar to that of adsorption. Porosity varies over a much smaller range than adsorption (retardation), however, so it is a much less sensitive parameter.

The impact on contaminant transport of shutting off the LAAP water supply wells was simulated. Shutting off the water supply wells caused water levels in the Wilcox-Carrizo aquifer to recover. The recovery was virtually complete within five years. There were no changes in the water table and potentiometric surface of the Upper Terrace and Lower Terrace/Sparta aquifers; thus, the shut-down of the water supply wells will have negligible impact on the predictions of contamination fate and transport.

The impact of leakage from the Area P lagoons on groundwater flow was simulated. The steady-state groundwater flow rerun was performed with a significant mound in the water table at the Area P lagoons. This mound in the water table changed groundwater velocities slightly. The contamination in Area P spread out radially from its initial position and after 100 years, the plume was distributed over a wider area to the north, west and south than it was with the calibrated steady-state flow model. The fate of almost all of the contamination, however, was still Boone Creek and its tributaries. A very small amount (< 1%) traveled south and west in the Lower Terrace/Sparta aquifer at Area P.

Arsenic-Contaminated Groundwater Treatment Pilot Study

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ABSTRACT

Groundwater treatment for the removal of contaminants may be needed at a number of U.S. Army installations, including Army depots. Treatability testing of potentially applicable technologies may be needed to facilitate design and operation of treatment systems. The study described here is a treatability test for the removal of arsenic from groundwater. The goal of the study was to evaluate the effectiveness of ion exchange (IE), granular activated carbon (GAC) and activated alumina (AA) for the removal of arsenic from groundwater.

Laboratory IE, GAC and AA isotherms were conducted to select the two best performing carbon and resin types and the operating pH for the carbon and alumina media for further testing. Pilot-scale continuous flow column tests were conducted at Sharpe Army Depot in Lathrop, California, using the two carbons (Calgon Filtrasorb 400 and Hydrodarco 3000) and the two resins (Amberlite IRA 402 and Ionac A-641) selected during the isotherm studies. Alcoa F-1 AA was also used during the pilot-scale continuous flow column tests. The carbon and AA were tested at an adjusted pH of 4.0 and the resin was tested at natural pH. A pilot-scale, conventional packed column air stripper was used to remove volatile organics (primarily trichloroethene) from the groundwater prior to treatment by the pilot-scale columns. The data from the laboratory and pilot study were analyzed and a report was prepared to present the results and conclusions. The study concluded that arsenic can be removed to the U.S. EPA MCL for arsenic of 50 ug/L and that AA provided significantly longer runs (as measured by bed volumes of water treated) than either GAC or IE resins.

INTRODUCTION

Groundwater treatment for the removal of contaminants may be needed at a number of U.S. Army installations, including Army depots. Treatability testing of potentially applicable technologies may be needed to facilitate design and operation of treatment systems. Sharpe Army Depot (SHAD), located in Lathrop, California, presently has a groundwater treatment system for the removal of trichloroethylene (TCE). The groundwater also contains arsenic, possibly of natural origin, and there may be a need to remove the arsenic prior to discharge.

The goal of this study was to examine, via pilot-scale testing, the possibility of arsenic removal from SHAD groundwater by ion exchange (IE), granular activated carbon (GAC) and activated alumina (AA) processes.

BACKGROUND

Arsenic (As) can occur in four oxidation states in water (+5, +3, 0 and -3), but generally is found in the trivalent and pentavalent states. At low pH, pentavalent arsenic (As (5)) exists primarily as H_3AsO_4. Between pH 3.0 and approximately pH 6.5, the predominant form is $H_2AsO_4^-$, while from pH 6.5 through pH 12.5, $HasO_4^{-2}$ predominates. Above pH 12.5, Aso_4^{-3} is the predominant species. At all pH values below approximately pH 9, trivalent arsenic (As (3)) exists primarily as the undissociated weak acid H_3AsO_3. The distribution between As (3) and As (5) species is determined by the redox condition of the water, with As (3) being stable under reducing conditions and As (5) under oxidizing conditions.[1] Thus, depending upon both pH and redox potential, various arsenic species may be present.

Among the various treatment methods for arsenic removal, including complexation with polyvalent metal species, coprecipitation with a metal hydroxide, coagulation, lime softening, adsorption on activated carbon, AA and IE, the literature suggests that the use of AA is the most promising treatment alternative for treatment of low levels of arsenic in groundwater. Much of the available literature on the AA treatment method involves the use of AA for the removal of arsenic from drinking water.

The pH (as well as other anionic species) of feedwater, arsenic concentration, sulfate concentration, chloride concentration and fluoride concentration play a major role in determining the AA capacity for arsenic removal.[2] The presence of other anions, such as sulfate and fluoride, reduced the amount of arsenic removed by as much as 80%. Substantial removals of As (5) by AA reportedly have occurred within a pH range of 4 to 7.[3]

AA has an equilibrium capacity for As (5) up to 10 times greater than that for As (3). This capacity is because at a pH of below 9, As (3) is present in a unionized form as H_3AsO_3.[4] Oxidation of As (3) to As (5) is necessary to achieve effective arsenic removal. Chlorine has been successfully used to accomplish this oxidation.[5] Results from pilot tests on AA systems indicated that with an empty bed contact time (EBCT) of 7.5 minutes, pH adjustment to 6.0 and oxidation of As (3) to As (5), up to approximately 16,000 bed volumes could be processed prior to reaching a maximum contaminant level (MCL) of 50 ug/L in the treated water, with a raw water As (5) concentration of approximately 100 ug/L.[6]

When the adsorptive capacity of the AA is reached, it can be regenerated with a 4 to 5% sodium hydroxide (NaOH) solution. The general procedure for regeneration, which has been successfully used in pilot tests, includes upflow treatment followed by downflow treatment with NaOH, raw water rinse and neutralization with sulfuric acid. The regeneration of an AA system would generate a concentrated waste containing elevated levels of arsenic that may require disposal in an approved hazardous waste landfill. It has been reported in the literature[6] that the volume of the waste products generated during the regeneration of the AA system would be approximately 0.1% of the production of the system (quantity of treated water).

Limited information is available in the literature on activated carbon

treatment of arsenic-contaminated water and wastewater. In one study involving arsenic removal from a potable water supply using activated carbon adsorption, 70% removal of As (5) was achieved with a raw water arsenic concentration of 200 ug/L.[7] Another study indicated that the optimum pH for adsorption of As (5) on activated carbon is 4.0.[3] A recent study in which activated carbon was used for treating a synthetic solution of arsenic (prepared by dissolving As_2O_3 in distilled water) indicated a GAC adsorption capacity of 2.5 lbs As (5) per 100 lbs of carbon.[8] Batch adsorption experiments to evaluate GAC for arsenic removal from the groundwater at SHAD indicated an ultimate capacity for arsenic at an influent concentration of 734 ug/L, 0.05 lb As (5) per 100 lbs carbon.[9] This result is significantly lower than the GAC adsorption capacity reported in the previously mentioned study. The difference could have been due to the different sources of water with different chemical compositions used in the studies.

The IE process for arsenic removal involves the use of a strong-base anion resin that allows the exchange of chloride ions attached to the resin with negatively charged arsenate ions ($H_2AsO_4^-$) in the raw water. When the adsorptive capacity of the resin is reached, the resin must be regenerated using a concentrated sodium chloride (NaCl) solution that replaces the $H_2AsO_4^-$ with chloride ions.

The results of pilot-plant testing of ion exchange treatment for removal of arsenic from drinking water at the Fallon, Nevada, Naval Air Station indicated that with a 5 minute EBCT, approximately 300 bed volumes could be processed before reaching the MCL of 50 ug/L in the treated water with a raw water arsenic concentration of approximately of 100 ug/L.[10] The results further indicated that the efficiency of treatment using a strong-base anion exchange resin is dependent on the quantity of other anions in the water, particularly sulfate, which are preferentially removed before arsenic. Successful treatment of wastewater containing arsenate and arsenite with a strong-base resin, at pH values ranging from 4 to 13, is reported in the literature.[7]

In an experimental study using the IE process, soluble As (5) at a concentration of 500 ug/L was completely removed from storm run-off water.[11] An EBCT of 3.6 minutes, hydraulic loading of 4.2 gpm/ft^{2} and bed depth of 2 ft were employed in the 1-in. diameter column used in the study.

One potential benefit of using a strong-base ion exchange resin over AA occurs during regeneration, where sodium chloride could be used instead of caustic soda followed by an acid neutralization. The initial cost of the resin probably will be higher than AA, but the lower cost of NaCl and its easier handling may make an IE process less expensive in the long run.[4]

Precipitation of alkalinity (i.e., calcium carbonate) in the IE vessel is a possible complication with an IE system.[6] This process would require the additional expense of removing the cations with a softener (cation exchanger) prior to arsenic removal.

MATERIALS AND METHODS

All tests performed during this project employed groundwater from wells at SHAD as the test water. Wells MW-403A, 407A and 431A were used for the isotherm studies, and well MW-440A was used for the pilot-scale tests. Contaminant concentrations in these wells varied during the test period. Table 1 presents the analytical data obtained from initial sampling of wells 403A, 407A and 431A.

Isotherm Laboratory Tests

Isotherm tests were performed for selected IE resins, activated carbon types and a single AA at Roy F. Weston, Inc.'s (WESTON's) Environmental Technology Laboratory (ETL) in Lionville, Pennsylvania. Groundwater was collected at SHAD and shipped to ETL for testing.

Since treatment for arsenic removal at SHAD would likely be implemented following removal of TCE in the existing air stripper, the contaminated groundwater from SHAD was pretreated for TCE removal by batch aeration using spargers. For isotherms to be conducted at other than natural pH,[12] the pH of the groundwater was adjusted to the desired value using sulfuric acid. Isotherm tests were then conducted on the pretreated groundwater samples.

Table 1
SHAD Pilot Study Groundwater Characteristics
(December 22, 1989)

Parameter	Well 403A	Well 407A	Well 431A
Volatile Organics			
Trichloroethene, μg/l	5 u	34	5 u
Metals			
Arsenic, total, μg/l	143	214	11.7
Cadmium, total, μg/l	10.0 u	10.0 u	10.0 u
Cobalt, total, μg/l	50.0 u	50.0 u	50.0 u
Chromium, total, μg/l	18.0	10.0 u	10.0
Copper, total, μg/l[a]	8.1	6.8	15.1
Iron, total, μg/l	7,070	4,020	18,000
Lead, total, μg/l[a]	9.6	16.8	15.9
Selenium, total, μg/l	6.3	9.5	5.0 u
Zinc, total, μg/l	172	71.2	196
Inorganics			
Ammonia nitrogen, mg/l	0.10 u	0.10 u	0.10 u
Nitrate/nitrite as nitrogen, mg/l[b]	17.7	23.5	43.1
Sulfate, mg/l	125 u	125 u	125 u
Phosphate as phosphorous, mg/l[c]	1.6	2.3	0.67 u
Other Parameters			
Temperature, °F	53.5	56.0	56
Conductivity, μmhos	1,479	1,250	756
pH	7.47	8.26	7.90

[a]Laboratory control standards for copper and lead were outside the control limits of 80-120%.
[b]Measured as nitrite nitrogen after reduction of nitrate; MCAWW Method 353.1.
[c]Samples analyzed beyond regulated holding time.

Note: u = Compound was analyzed but not detected. The associated numerical value is the sample detection limit.

Seven 250-mL aliquots were used for each isotherm. Tests were conducted in polyethylene bottles. Preweighed quantities of adsorbent media were added to the groundwater aliquots to provide the required dosages. The bottles were sealed to preclude liquid and vapor losses during agitation. Samples were agitated at room temperature on a rotating laboratory shaker for a period of 24 hours. Each isotherm test included one blank, containing no adsorbent medium.

Following agitation, each sample (including the blank) was filtered through a Whatman 0.45 micron GF/F filter into a clean filter flask to remove the contaminant-laden adsorption medium. Each filtrate sample was then analyzed for total arsenic concentration.

From these data, the equilibrium concentration of arsenic in the solution (Ce) and the arsenic loading on the adsorbent medium (qe) were calculated. These data were plotted on log-log paper in accordance with the Freundlich equation for adsorption:

$$q_e = X/M = KC_e^{1/n} \tag{1}$$

where,

q_e = Adsorbent loading.
X = C_o-C_e the amount of arsenic adsorbed for a given volume of solution.
M = Weight of adsorbent added.
C_o = Initial amount of arsenic.
C_e = Amount of arsenic remaining in solution.
K and $1/n$ are empirical constants.

The results of these tests were used to select media to be testing in the pilot-plant study phase of the project.

Pilot-Plant Studies

The objective of pilot-plant studies was to evaluate potential operating characteristics of selected adsorbent types under actual operating conditions, with respect to such parameters as adsorbent bed depth, hydraulic loading rate and EBCT. Pilot-scale testing of the media selected from the isotherm data was conducted at SHAD using a skid-mounted transportable activated carbon column pilot plant designed and built for USATHAMA. The system can be used to evaluate treatment using GAC, IE or AA technologies. The plant consists of three skids and accessory tankage. One skid consists of the motor control center, feed

pumps and utility pumps. Each of the other two skids contains four plexiglas columns which hold the adsorption medium to be tested. This pilot plant was designed to provide a high degree of operating flexibility, using variable bed depths and wastewater flow arrangements. Additional tanks and pumps are provided to allow for groundwater retention, pH adjustment and flow control as necessary.

An air stripper 8 in. in diameter by 23 ft high with 15 ft of packing, designed for a water flow rate of 5 gpm, was used to remove TCE in the groundwater prior to treatment for arsenic.

In addition to the treatment units described above, the following additional tankage was added to the GAC/IE/AA pilot treatment system:

• Two 3,000-gal influent holding tanks to receive and hold groundwater from the selected well

• One 2,000-gal equalization tank between the air stripper and the GAC/IE/AA unit. When required by the Test Plan,[12] pH adjustment was carried out in this tank

• Two 3,000-gal effluent holding tanks to retain the treatment effluent to be discharged after testing

Figure 1 shows the schematic configuration of the combined air stripping/GAC/IE/AA pilot system that was used in this study. As shown, there were three GAC/IE/AA treatment trains. These three trains were operated in parallel to allow for study under three different experimental conditions at the same time.

In order to evaluate the need for an arsenite oxidation step during the pilot study, portions of samples from candidate wells were subjected to arsenic speciation analysis. These specialized analytical services were provided by the Benedict Research Laboratory of the Academy of Natural Sciences.

ANALYTICAL METHODS

Samples were analyzed for total arsenic at WESTON's Stockton, California, laboratory by USATHAMA-certified Method SD01. Samples were analyzed for TCE at WESTON's Lionville, Pennsylvania, and Stockton, California, laboratories by U.S. EPA Method 8010.

EXPERIMENTAL RESULTS AND DISCUSSION

Isotherm Testing

A single round of isotherm testing was conducted for the purpose of examining equilibrium adsorption characteristics of the various adsorption media and to select media for use in pilot testing. Preliminary selection of media types for isotherm testing was based upon literature and vendor information.

The isotherm tests performed during this study indicated that each of the major media types (IE resin, GAC and AA) may be capable of treating arsenic-bearing groundwater at SHAD to less than 50 ug/L. The lowest required dosages (weight of adsorbent per volume of contaminated water) and highest qe values for equilibrium adsorption were observed with Alcoa Type F1 AA. In general, the selected IE resins appeared to perform better than activated carbon when compared on the basis of adsorbent dosages, with GAC achieving equilibrium arsenic concentrations less than 50 ug/L only at high carbon dosages. Table 2 summarizes the results of isotherm testing in terms of the media selected for pilot-scale evaluation.

Arsenic Speciation

Arsenic speciation in the potential pilot study supply wells was evaluated in order to determine the need for an oxidation step during the
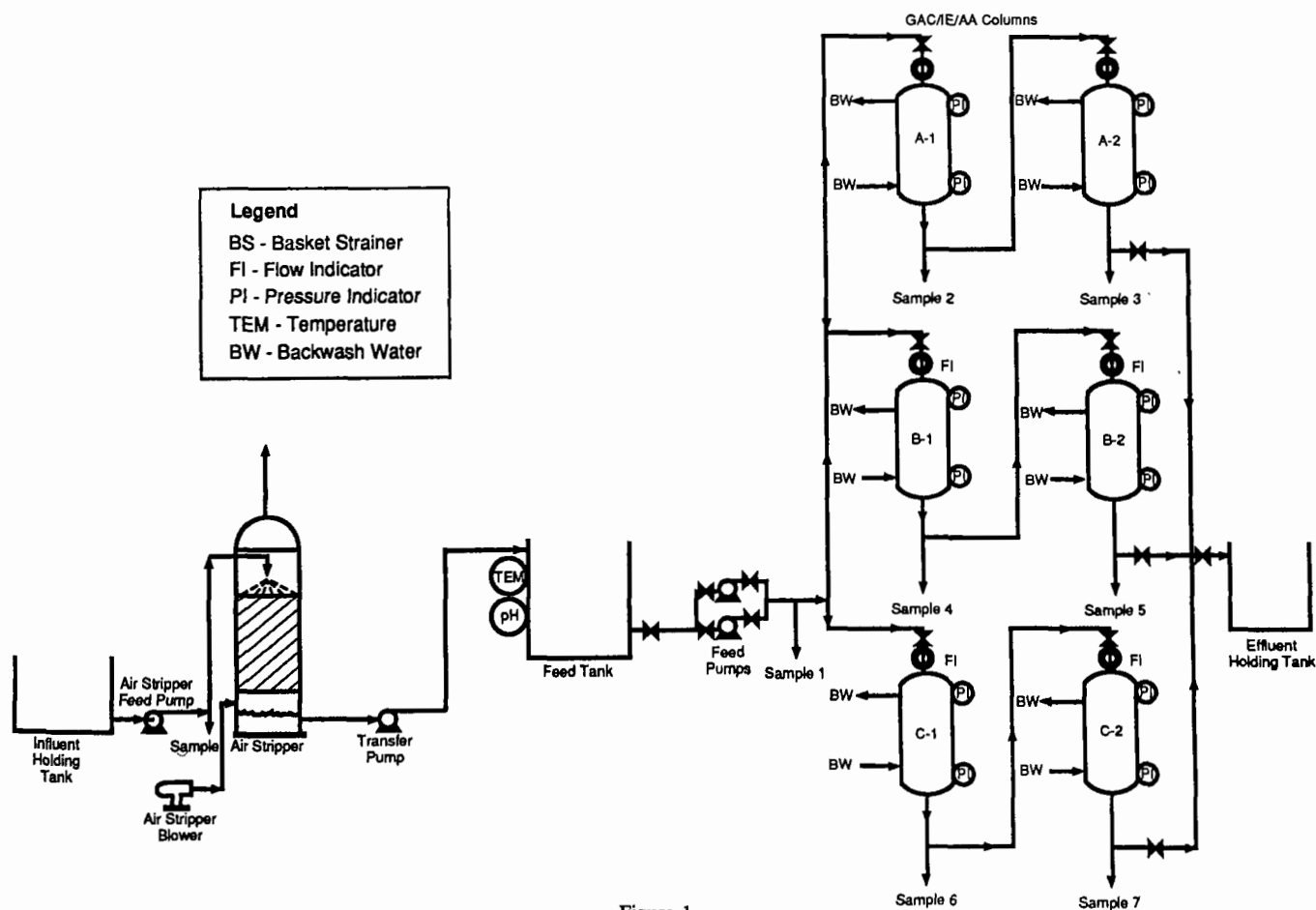
Figure 1
Pilot Treatment Unit Configuration

pilot study. If the groundwater at SHAD contained predominantly As^{+5}, a pre-oxidation step using chlorine as the oxidant was planned.

Sampling for the initial characterization of arsenic speciation in MW403A, 407A and 431A took place on February 28, 1990. Additional sampling, from MW440A and at the actual pilot plant influent, took place on May 23, 1990, during the pilot-plant phase of the study. Arsenic speciation data from these samples are presented in Table 3. These data demonstrate that arsenic in the sampled wells existed almost entirely ($\geq 99.5\%$) as the oxidized As^{+5} form.

The finding that the arsenic to be treated existed in the oxidized form obviated the need for a chlorine oxidation step in the pilot study. Since As^{+3} concentrations were all well below the MCL of 50 μg/L, effective removal of the pre-existing As^{+5} would likely permit attainment of the discharge standard. The incremental increase in bed life (before breakthrough at 50 μg/L total arsenic) that might be achieved by oxidation of the low levels of As^{+3} likely would be slight.

Table 2
Summary of Media Selection

Adsorbent	Adsorbents Screened in Isotherms	Adsorbents Selected for Pilot Testing
Ion Exchange Resin Amberlite	Rohm and Haas Amberlite IRA-402	Rohm and Haas IRA-402
	Rohm and Haas Amberlite IRA-900 Sybron Ionac A-641 Sybron Ionac ASB-1	Sybron Ionac A-641
Activated Carbon	Calgon Filtrasorb 200 Calgon Filtrasorb 300 Calgon Filtrasorb 400 Hydrodarco 3000 Hydrodarco 4000	Calgon Filtrasorb 400 Hydrodarco 3000
Activated Alumina	Alcoa Type F-1, 28-48 Mesh	Alcoa Type F-1, 28-48 Mesh

Therefore, based upon the results of the initial arsenic speciation analysis, as confirmed in subsequent resampling during the pilot-study phase, chlorine oxidation of the influent groundwater was not employed in this study.

Pilot-Scale Testing

The overall objective of the pilot scale test program was to evaluate the potential performance of the selected media under continuous flow conditions simulating those likely to be employed in a full-scale treatment system. Specific objectives pertinent to this effort included:

- To determine the effectiveness of the medium in removing arsenic to the MCL (50 ug/L) under continuous flow conditions
- To determine the adsorption capacities of the medium
- To select the best performing medium

- To evaluate potential operating conditions for a treatment system, including hydraulic loading rate and EBCT

These objectives were addressed in a test program conducted at SHAD using USATHAMA's skid-mounted transportable pilot system described earlier. The overall duration of the pilot test program (not including mobilization and demobilization) was approximately 17 weeks. The test program encompassed a total of seven experimental runs. Table 4 presents a summary of the test program.

Each adsorbent bed rested upon a 1-ft thick base consisting of a layer of stone sandwiched between two layers of borosilicate glass wool, specified as being free from heavy metals, fluorine and alumina. Adsorption media were prepared as water slurries, allowed to soak overnight and then be added to the columns to provide a settled bed depth of 4 ft. The column was sealed, leak tested and backwashed prior to commencing each test run. Once begun, each test ran continuously until breakthrough with the exception of brief shutdowns for necessary repairs. Breakthrough was defined as the MCL of 50 μg/L.

Each column was backwashed as needed during the run to remove accumulated solids at the head of the column which interfered with flow and contributed to excessive head loss across the column. In general, columns were backwashed when the head loss across the column exceeded 5 psi, as indicated by the pressure gauges mounted on the inlet and outlet of each column. During backwashing, the adsorbent bed was also generally broken up, minimizing plugging or channeling of flow through the bed. The duration of the backwashing operation was approximately 15 minutes.

This study evaluated the potential treatment of arsenic-contaminated groundwater by three different technologies: IE, GAC adsorption and AA. While the specific mechanism of arsenic removal may vary, the implementation of each of these technologies is similar, each likely employing a series of fixed bed down flow treatment columns (although other configurations are possible) with varying degrees of pretreatment and/or post treatment. Therefore, the performance of the different media can be compared in part on the basis of the quantity of contaminated water, normally expressed in terms of bed volumes, which can be treated prior to breakthrough.

Table 5 summarizes the results of pilot tests conducted in this study in terms of the quantity (bed volumes) of contaminated groundwater treated under various operating conditions prior to breakthrough in the primary column effluent, with breakthrough being defined as effluent arsenic concentrations equal to or exceeding the Safe Drinking Water Act MCL of 50 μg/L.

DISCUSSION

These data indicate that both IE resins and AA can provide treatment of SHAD groundwater to levels below the MCL. The longest bed lives were achieved with AA at reduced pH, relatively low hydraulic loading rates and contact times on the order of 9.8 to 14.7 min. Bed

Table 3
SHAD Pilot Study
Groundwater Arsenic Speciation Data

Parameter	MW 403A 28 February 1990	MW 407A 28 February 1990	MW 431A 28 February 1990	MW 440A 23 May 1990	Pilot Plant Influent 23 May 1990
Arsenite, (As^{+3}), μg/L	0.64	0.77	0.03	0.91	0.84
Arsenate, (As^{+5}), μg/L	133	240	7.47	224	193
Total Arsenic (Std. Dev.), μg/L	133 ($\pm$ 4.6)	241 ($\pm$ 25.1)	7.50 ($\pm$ 0.34)	225	194

Table 4
Summary of Pilot Test Runs

Test	Adsorbent (primary column)	Train	Flow rate (gpm)	Hydraulic loading (gpm/ft^2)	Bed Depth (ft)	EBCT[a] (min)	Influent pH	Dates (all 1990)	Notes
1a	IRA 402	a	0.2	2	4	14.7	natural[b]	19-26 March	
1b	IRA 402	b	0.3	3	4	9.8	natural	19-24 March	
1c	IRA 402	c	0.7	7	4	4.2	natural	19-23 March	
2a	A-641	a	0.2	2	4	14.7	natural	29 March - 3 April	
2b	A-641	b	0.3	3	4	9.8	natural	29 March 2 April	
2c	A-641	c	0.7	7	4	4.2	natural	29 March - 1 April	
3a	Hydrodarco 3000	a	0.7	7	4	4.2	±4	28 April 29 April	
3b	Hydrodarco 3000	b	0.2	2	4	14.7	±4	28 April 29 April	
3c	Hydrodarco 3000	c	0.3	3	4	9.8	±4	28 April 29 April	
4a	Filtrasorb 400	a	0.3	3	4	9.8	±4	1 May	
4b	Filtrasorb 400	b	0.7	7	4	4.2	±4	1 May	
4c	Filtrasorb 400	c	0.2	2	4	14.7	±4	1 May	
5a	Alcoa F-1	a	0.2	2	4	14.7	4-6	5 May - 17 June	
5b	Alcoa F-1	b	0.3	3	4	9.8	4-6	5 May 30 May	
5c	Alcoa F-1	c	0.7	7	4	4.2	4-6	5 May 13 May	
6a	Filtrasorb 400	c	0.2	2	4	14.7	natural	9 June	distilled H$_2$O slurry
6b	Filtrasorb 400	c	0.1	1	4	29.	natural	10 June 11 June	distilled H$_2$O slurry
7a	Alcoa F1	a	0.2	2	4	14.7	natural	21 June - 28 June	with TCE spike
7c	Alcoa F1	c	0.3	3	4	9.8	natural	21 June - 27 June	with TCE spike
7c	Alcoa F1	a	0.3	3	4	9.8	natural	3 July 13 July	with no TCE spike

[a]EBCT = Empty bed contact time.
[b]pH of influent generally ranged between pH 8 and pH 9.

Table 5
Summary of Pilot Test Results

Test	Medium	Hydraulic Loading Rate (gpm/ft^2)	EBCT (min)	Influent[a] Arsenic (µg/L)	Influent pH	Bed Volumes of Water[b] Treated (Approximate)
1a	IRA402	2	14.7	227.8	Natural[c]	450
1b	IRA402	3	9.8	227.1	Natural	375
1c	IRA402	7	4.2	200.5	Natural	1,510
2a	A-641	2	14.7	238.7	Natural	285
2b	A-641	3	9.8	252.8	Natural	250
2c	A-641	7	4.2	225	Natural	210
3a	Hydrodarco 3000	7	4.2	--	±4	--
3b	Hydrodarco 3000	2	14.7	--	±4	--
3c	Hydrodarco 3000	3	9.8	--	±4	--
4a	Filtrasorb 400	3	9.8	--	±4	--
4b	Filtrasorb 400	7	4.2	--	±4	--
4c	Filtrasorb 400	2	14.7	--	±4	--
5a	Alcoa F-1	2	14.7	196.1	4-6	3,700
5b	Alcoa F-1	3	9.8	212.7	4-6	3,475
5c	Alcoa F-1	7	4.2	257.8	4-6	2,100
6a	Filtrasorb 400	2	14.7	--	Natural	--
6b	Filtrasorb 400	1	29.4	--	Natural	--
7a	Alcoa F-1	2	14.7	181.6	Natural	500
7b	Alcoa F-1	3	9.8	179.9	Natural	525
7c	Alcoa F-1	3	9.8	202.9	Natural	850

[a]Weighted average concentration.
[b]Volumes treated prior to breakthrough effluent arsenic concentration $\geq$50 µg/L.
[c]pH of influent generally ranged between pH 8 and pH 9.

lives on the order of 3,000 or more bed volumes of water treated appear to be achievable in a single activated alumina column operating under these conditions. Figure 2 is a plot of the arsenic breakthrough curve for AA Run 5A. By contrast, ion exchange bed lives on the order of 200 to 500 bed volumes of water might be obtained.
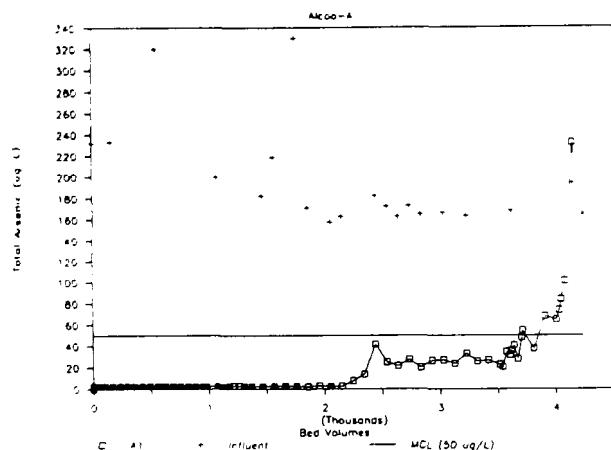
Figure 2
Plot of the Arsenic Breakthrough Curve for AA Run 5A

Granular activated carbon does not appear capable of meeting the arsenic treatment requirements under the conditions used in this study, as shown in Table 5.

Definite selection between the two treatment technologies exhibiting satisfactory performance in this study would depend upon analysis of the relative treatments costs and the operating advantages/disadvantages associated with each technology. This comparative analysis would consider the capital equipment requirements as dictated by such factors as hydraulic loading and contact time, pre and posttreatment requirements, regeneration requirements and the attrition rate and replacement costs of the media. For example, although AA exhibited the longest bed lives in this study, the data indicate that a pH adjustment step is required and that relatively low hydraulic loading rates and long contact times (corresponding to relatively large adsorption units) are required. By contrast, IE data suggest relatively little dependence on loading rate and contact time over the ranges evaluated; thus relatively smaller adsorbers operating at higher loadings may prove suitable.

Table 6
Regeneration Requirements

Ion Exchange

Example: IRA-402:

1. NaCl, 5-10% solution, : 4 lb. salt/ft³ resin, at 0.25
    1.0 gpm/ft³

2. Rinse with water.

Source: Amberlite IRA-402 Technical Literature

Activated Alumina

1   Regeneration, NaOH, 1% solution, 4 bed volumes.
2   Rinse with water, 8 bed volumes minimum.
3   Acid rinse, 0.05 N H₂SO₄, 1 bed volume minimum.
4   Final rinse, water, 1 bed volume.

Source: References 11, 12, and 13

Regeneration of media was not addressed in this study. Since the adsorption capacities of regenerated media may differ in some respects from these of virgin media, this aspect should be addressed prior to

design of a treatment system. Based upon previous research and manufacturer's recommendations (summarized in Table 6), regeneration of either IE resins or AA is a relatively straightforward operation requiring conventional reagents, and attrition of the media during regeneration can be controlled.

With respect to media replacement, it should be noted that the IE resins recommended by vendors for use in this study were relatively expensive as compared to, for example, conventional softening resins. The recommended resins cost approximately \$230/ft³. By contrast, the cost for the AA is relatively low, at approximately \$71/ft³ (\$1.65/lb).

CONCLUSIONS

The following conclusions are drawn from the data obtained in this study:

• Strong base anion exchange resins (specifically Rohm and Haas IRA 402 and Sybron Ionac A-641) and AA (specifically Alcoa Type F-1, 24 to 48 mesh) are capable of treating arsenic-contaminated groundwater from well MW-440A at SHAD to effluent concentrations below the Safe Drinking Water Act MCL of 50 μg/L (as total arsenic). The granular activated carbons tested were not capable of effective arsenic treatment under the conditions evaluated in this study.

• Of the successful media, AA provided the longest bed lives (in terms of bed volumes of water treated prior to breakthrough at the MCL level).

• The use of AA requires a pH reduction step. Hydraulic loading rates of 2 to 3 gpm/ft² and EBCTs of 9.8 to 14.7 minutes provided the longest bed lives.

• IE resins exhibited less dependence on hydraulic loading rate or EBCT than did activated alumina. However, bed life at all loading rates was lower than with AA.[13]

• Analytical data from wells MW-403A, MW-407A, MW-431A and MW-440 indicate that pentavalent arsenic (As^{+5}) is the predominant arsenic species present in SHAD groundwater and that trivalent arsenic (As^{+3}) is present only in small amounts. In fact, removal of As^{+5} alone would be sufficient to achieve the SDWA MCL for total arsenic of 50 μg/L. As a result, no oxidative pretreatment step was required or employed in this study and, as long as this situation prevails, oxidative pretreatment should not be required in a full-scale system.

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Selecting State-of-the-Art Incinerators for Complex Aqueous Wastes: The Rocky Mountain Arsenal Basin F Liquids Treatment Action

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ABSTRACT

The Rocky Mountain Arsenal (RMA) in Adams County, Colorado, has been identified as a priority site on the Superfund National Priority List. The Program Manager's Office of RMA announced in early 1990 their intention to implement installation of a state-of-the-art incineration plant to treat the most complex and controversial waste stream on the site.

Established in 1942, the Arsenal served as an Army manufacturing center for chemical agents such as mustard gas, white phosphorus, napalm and GB nerve agent. Parts of the site were also leased to Shell Oil Company which manufactured pesticides and other agricultural chemicals at this location between 1952 and 1982.

To support these activities, the Army operated a 93-acre surface impoundment called Basin F for collection and evaporation of chemical wastewaters. As a result of the wide variety of wastes received and concentrated at Basin F, and early treatment attempts, its contents became a unique chemical cocktail. By the time that a formal interim response action for remediation was initiated in 1985, the Basin composition consisted of a multiphase fluid and sludge including supersaturated levels of inorganic salts; 30% or more organics such as pesticides, military agent byproducts, degradation products and solvents; high levels of ammonia compounds and bound nitrogen; and percent levels of copper, arsenic and other metals.

Selection of a remedial alternative involved 12 years of characterization studies and 11 years of treatability testing programs encompassing the universe of containment, encapsulation, stabilization, component separation, thermal, electrical, chemical and biological degradation technologies. The program resulted in the selection of a state-of-the-art down-fired liquid incinerator for destruction of aqueous organic contaminants in metallic salt matrices.

The treatability demonstration and technical justification for selecting the T-Thermal submerged quench incinerator for this application are the subject of this paper.

INTRODUCTION

The Rocky Mountain Arsenal (RMA) was established in 1942 on rural property located in Adams County, Colorado, 10 miles from downtown Denver. The Arsenal production facilities have been used for the manufacture of materials such as mustard gas, white phosphorous, nerve agents and napalm; filling of munitions with agents and incendiary materials; and the destruction or "demilitarization" of chemical weapons.

Between 1952 and 1982, a series of private firms ending with Shell Chemical Company (now Shell Oil Company) manufactured agricultural chemicals, primarily pesticides, at the Arsenal.

During the 1980s an extensive battery of characterization studies, conceptual process studies and treatability tests were conducted to develop potential remedial alternatives for the Basin F contents which had been tentatively linked to groundwater contamination downgradient of the Basin. Also during this period, the 8.5 million gallons of liquid contents were removed from the Basin and placed in above ground storage. In late 1988, Woodward-Clyde Consultants began a concentrated effort to evaluate and interpret the prior studies, and identify and justify a preferred alternative for destruction of the former Basin contents. This selection of a preferred alternative has since been published and approved by the Army, Shell Oil and all the responsible regulatory authorities.

BACKGROUND

In 1956, Basin F, a 243-million gallon evaporation pond was constructed in a natural depression by lining it with an approximately 1/2-inch catalytically blown asphalt surface, covered by a 1-foot protective layer of earth. This Basin was the last in a series of linked surface basins used for the evaporation of wastewaters from the Army and industrial chemical activities at the site. From August 1957 until its use was discontinued in early 1982, Basin F was the only evaporation pond at the Arsenal containing a liner. Wastewaters entered the former Basin F for more than 20 years, directly or indirectly, from three different manufacturing sources: the Army North Plants, the Army South Plants and Shell South Plants.

Army North Plants

The North Plants complex operated from 1953 to 1984 for the manufacture, munitions filling and later demilitarization of GB nerve agent. During the period between 1953 and 1973 the plant produced bulk GB agent and loaded GB into munitions. During that period the plant also filled munitions with agents produced elsewhere, such as VX-nerve agent, and manufactured other devices such as microgravel mines and button bombs. From 1973 to 1984 the North Plants served as a "demilitarization" (demil) facility for destruction of GB agent; VX agent, Adamsite phosgene bombs and DDT-contaminated equipment.

Wastewaters from these manufacturing and demil operations were discharged indirectly to both Basin A and Basin F. Waters were caustic neutralized in a disposal sump and then pumped to these Basins for evaporation.

Army South Plants

The South Plants operated from 1942 through 1969, producing Lewisite, mustard gas and incendiary mixes, and filling munitions with incendiary materials and phosgene. During World War II, the plant produced Lewisite (a blister agent) and sulfur mustard. Phosgene was not manufactured, but was purchased from private industry and used to fill bombs in the plant. The South Plants also produced or used

napalm gel, cluster bomb incendiary mixtures, button bomb pyrotechnic mixtures, white phosphorous and hydrazine preparation for missile fuels.

The plant was used for destruction of bulk mustard from 1971 to 1974. Wastes from the Army processes and demilitarization were managed in a variety of ways including incineration, neutralization and evaporation in surface impoundments, including Basin F.

Shell South Plants

After WWII, portions of the South Plants area were leased to private chemical manufacturers. The most significant lessees included Julius Hyman and Co. and Shell Chemical Company, which manufactured Chlordane, Aldrin, Dieldrin, Endrin, Vapona, Nemagon and other organochlorine and organophosphorus pesticides and nematocides between 1947 and 1982. Some wastewaters from these processes were discharged to the evaporation basin system and ultimately to Basin F.

Other Sources and Factors

Other factors contributed to the creation of the unique mixture of components in the Basin as well. The most significant factor involved early attempts at remediation of the contents. In the late 1950s it became obvious that Basin F was not large enough to handle all the wastewaters generated on-site. The U.S. Army Chemical Corps considered deep well disposal, and in 1960 the Corps of Engineers attempted to modify Basin F for the purpose of pretreatment prior to disposal. A chemical addition area was constructed at the Basin, and 100 tons of ammonium phosphate were added to the Basin contents in an attempt to simulate microbial activity and liquify some of the solids. Although injection wells were drilled and injection was attempted in the early 1960s, the pretreatment was never successful and ultimately the injection attempts were abandoned. However, the presence of the additional 200,000 pounds of ammonium salts had a significant long-term affect on the behavior of the liquids.

The final contributor to the Basin's properties was the very action for which the Basin was designed. Years of warm-weather evaporation at high altitude contributed to the creation of a supersaturated body of liquid by the time characterization and remediation studies began in 1978. The residuals from the evaporation were so concentrated, in fact, that during repeated Corps of Engineers attempts to sample the Basin in the 1980s the sample devices acted as seeds for precipitation and caused instantaneous crystallization.

THE TECHNICAL PROBLEM

As a result of the processes and actions described above, Basin F liquids evolved into a mixture unique among chemical wastewaters. The Basin F contents are generally an aqueous mixture consisting of approximately one-third water, one-third organics and one-third dissolved solids, primarily salts and metals.

Table 1 lists some of the organic components identified in Basin F, primarily agent byproducts and pesticides and their intermediates and byproducts. Most individual organic species reported have been identified as present at concentrations from 1 to 1000 ppb, with the exception of two pesticides and three pesticide byproducts present at concentrations from 2000 to 100,000 ppb. However, no single organic component is a significant contributor to the liquid's properties.

The liquid's properties appear to be driven by the high concentrations of inorganic salts and metals. Table 2 shows the levels of selected inorganic components. Table 3 describes some properties of the liquid including those particularly affected by inorganic constituent levels such as conductivity and density. In general, Basin F can be described as:

- Supersaturated with salts (30 to 35%)
- Unusually high in ammonia (5%)
- Contaminated with environmentally significant levels of nerve agent byproducts, pesticide-related compounds and arsenic
- Prone to off-gassing
- Highly corrosive

While the above items represent significant engineering handling and treatment problems, three beneficial properties of the liquid are that it is not: (1) radioactive, (2) flammable or (3) explosive.

Table 1
Selected Organic Chemical Components Detected in Basin F Liquids During Characterization Studies 1978 to 1988

Component	Source
Aldrin	insecticide
Isodrin	insecticide intermediate
Dieldrin	insecticide decomposition product
Endrin	insecticide
Dithiane	mustard gas decomposition product
pp DDE	pesticide
pp DDT	pesticide
CPMSO	pesticide decomposition product
CPMSO₂	pesticide by-product
Hexachlorocyclopentadiene	pesticide intermediate
Atrazine	herbicide
Malathion	organophosphorus pesticide
Parathion	organophosphorus pesticide
Supona	organophosphorus pesticide
Vapona	organophosphorus pesticide
DIMP	nerve agent by-product
DMMP	nerve agent by-product

Table 2
Selected Inorganic Components Detected in Basin F Liquids During Characterization Studies 1978 to 1988

	Values Reported (ppm)
Ammonia	up to 61,000
Urea	up to 143,000
Potassium	up to 2,900
Sodium	up to 65,000
Chloride	up to 159,000
Fluoride	170
total phosphorus	up to 16,200
Copper	up to 5,860
Arsenic	8

Table 3
Selected Physical/Chemical Properties of Basin F Liquids

Parameter	Units	Value
Specific gravity		1.24
Viscosity 25°C	cp	5.0
Viscosity 2°C	cp	2.3
Conductivity	μmhos/cm	110,000
COD	ppm	up to 230,000
Total Organic Halide	ppm	up to 570,000
pH	-	5.8 to 7.2

THE ADMINISTRATIVE PROBLEM

Two administrative agreements which govern the RMA remedial activities were signed in February 1989 by Shell Oil Company, the Army and Federal Agencies responsible for oversight of the cleanup. The Federal Facility Agreement (FFA) and the Settlement Agreement (SA) define the mechanisms for selection of remedial actions and the technical and financial responsibilities for each party. The FFA also defines how the Interim Response Actions (IRAs) will be carried out. The Basin F Action was identified as an IRA. The signed agreements required that the liquids, which by this time had been removed from the Basin and stored in three above ground tanks and a lined surface pond, would be permanently destroyed within 5 years of the date they were placed in the tanks. The 5-year period was based on the assumed design life

of the tanks and implies that the liquids have to be destroyed by mid-1993. This deadline complicated an already tough engineering problem by requiring that a selected alternative must involve equipment that was already proven for corrosive service on aqueous organic brines and immediately commercially available.

THE APPROACH

Characterization and treatment studies for remedial alternatives for the liquid were conducted by multiple organizations from 1978 to December 1989. The technologies considered and tested during this period spanned the entire spectrum of currently available treatment approaches and included:

- Thermal destruction
- Electrical destruction
- Non-combustion thermal oxidation
- Chemical biological photolytic oxidation
- Separation and component recovery
- Stabilization and immobilization

More than 40 different conventional and innovative technologies were addressed. The technologies addressed included some as commonplace as mechanical filtration and some as new and developmental as supercritical water oxidation. More than a dozen different bench-scale and pilot-scale test programs were conducted. Based on the governing Federal Facilities Agreement, any technologies which were to be retained from the foregoing studies for detailed evaluation needed to meet the following criteria:

- The technology and equipment had to be suitable for the complex properties of Basin F liquids.
- It had to be generally capable of meeting Applicable or Relevant and Appropriate Requirements (ARARs).
- It must have been successfully demonstrated on actual Basin F liquids.
- It had to be commercially available at full scale within the 5-year time frame.

As a result, six technologies were retained for a detailed alternatives evaluation conducted by Woodward-Clyde Consultants during 1988 and 1989. They were:

- Electrical Melter Furnace (EMF)
- Solidification
- Submerged Quench Incineration (SQI)
- Wet Air Oxidation (WAO)
- Wet Air Oxidation with Powdered Activated Carbon Biotreatment (PACT)
- Off-site commercial incinerator

The detailed evaluation consisted of two major components - a risk evaluation and an engineering evaluation using quantitative scoring and sensitivity studies to rank alternatives in the context of the CERCLA evaluation criteria.

Risk assessments considered short- and long-term risks from both the operations and the materials transport (feed chemicals and residual products) for each proposed alternative. In general, the transportation risk from export of untreated liquids outweighed the risks arising from on-site treatment.

The engineering evaluation involved a numerical scoring of each alternative per each of seven of the nine standard CERCLA criteria. Two criteria, community acceptance and State acceptance, were not utilized in the ranking study because they were evaluated explicitly through a multistep community involvement program conducted after the study. The ranking study, based on multiattribute utility theory, used a variation in weights on the CERCLA criteria to study the singular effects of individual criteria and to model various viewpoints. This process resulted in the identification of on-site submerged quench incineration as the technically preferred alternative. In general, however, despite the extensive decision methods utilized, it was basically the properties of the Basin F liquids that caused each of the other alternatives to be ranked low or be ruled out altogether. That is, each other alternative had a potential "fatal flaw" with respect to the liquid properties that could ultimately render it unsuitable.

Electric Melter Furnace

The electric melter furnace is a high temperature furnace used for the production of glass from liquid or solid feeds with the addition of silicates; no flame is present in the combustion chamber. Initially, this equipment which is designed to handle fluids with high solids and high metals content seemed like a strong candidate for a one-step process to destroy Basin F's organics and stabilize its metals. But Basin F's two other key components, salts and ammonia, posed significant potential problems for this process.

The equipment is designed to run with a single-phase melt flowing continuously along the bottom of the thermal chamber. Basin F, with or without addition of glass formers, would create a two-phase melt with salts lying above, and interfering with the purging of, the metals stream. More importantly, at the high temperatures of this process (2500°F), the ammonia nitrogen in Basin F was expected to form NO_x compounds at rates that could not meet Denver air standards even after selective catalytic reduction, thermal $DeNO_x$ or other NO_x treatment steps.

Solidification

This process may have been suitable if Basin F's metallic aqueous brine contained no organics or ammonia. While solidification of contaminated soils and sludges is frequently a straightforward one- or two-step process, the process needed for material with Basin F's composition would have been extraordinarily complex. First, due to the high content of ammonia and the normally high pH of many solidification additives, numerous ammonia sequestering additives were needed to prevent escape of large quantities of gas. Second, many of the organic components were not only not amenable to stabilization themselves, but also interfered with the inorganic matrix formation that was to bind metals and inorganic ions. In total, this approach would have required so much chemical addition it would have increased the treated volume to a minimum of 3 to 5 times the untreated waste volume.

Wet Air Oxidation

This process represented a possible way to achieve primary destruction of organic components without the high temperatures common to incineration processes that tend to create NO_x emissions. High pressure oxidation reactors have been utilized industrially on a variety of rich and lean aqueous organic mixtures. However, Basin F's composition posed serious technical problems in the design of such equipment. The manufacturers had difficulty identifying materials of construction for high pressure, small diameter, high velocity reactor tubes in corrosive and abrasive service which could be guaranteed to survive for the life of the project.

Wet Air Oxidation with PACT

This approach was considered as a potential means of enhancing WAO's overall destruction efficiency by utilizing microorganisms in a polishing step on the WAO product. However, even though the WAO effluent would have smaller, less toxic organic molecules than the Basin F feed that may be suitable for biodegradation, the effluent still would contain two other Basin F components - ammonia and copper. While microorganisms utilize ammonia nitrogen as a nutrient, the copper serves as a relatively potent biocide and must be removed. The flow sheet incorporating removal of copper-ammonium salts between WAO and PACT became so complicated as to render the overall process potentially impossible to startup and bring to steady-state.

Off-site Incineration

Most commercial incinerators, whether liquid injection type or kiln type with liquid afterburners are capable of accepting waste with some level of "ash content," that is, noncombustible inorganics. However, despite a nationwide survey and several acceptance test trials, no commercial installation could be identified that would guarantee acceptance of Basin F once they understood its chemical composition. Two properties caused the most concern: (1) the "ash content," due to the supersaturation of salts, was much higher than they felt they could pump, purge from their equipment and stabilize with their product ash;

and (2) the ammonia content relative to the low Btu content was likely to drive their operation above acceptable NO_x emission levels.

THE SOLUTION - SUBMERGED QUENCH INCINERATION

The first and foremost requirement of the incinerator is the complete destruction of the highly sensitive organics. However, the presence of approximately 1,500 pounds per hour of salts and heavy metals dictated an incinerator from which those materials could be continuously removed. The high concentration of bound nitrogen and chlorides also require that the incinerator be of a controlled atmosphere type to limit NO_x and other secondary pollution problems. The submerged quench fits all of those parameters.

The incinerator chamber of the SQI is a vertical cylinder instead of horizontal as is common for most other incinerator designs. The burner and waste injectors are located at the top of the chamber and are downfired. This orientation allows the salts which are molten liquids at typical incineration temperature to flow down the chamber walls carrying any other inorganic metals with them. The outlet of the incinerator chamber is the submerged quench system. The submerged quench is a unique design which not only cools the gases, but also provides for excellent mass transfer, lowering the demands on the downstream pollution control system to neutralize acids and remove particulates. The hot corrosive gases and molten salts enter the quench via a downcomer. The downcomer is a metal tube which extends into the quench water bath. The bottom of the downcomer is open, allowing the salts to drop into the quench tank solution and redissolve. The quench solution for the system is a concentrated salt solution to which caustic is added to react with the acid gases.

The gases exit the downcomer through holes in its side. These holes are 24 inches below the solution level in the quench tank and are designed with enough pressure drop to provide a jet sparging effect of the gases into the water. As the gases exit the holes, they rise as millions of small bubbles providing extended surface area for heat and mass transfer. In the quench tank, almost all of the acid gases are neutralized and more than 99% of the particulates including heavy metals above 2 microns are removed from the gases before they enter the downstream pollution control equipment.

The destruction efficiency of the highly sensitive organics present in the waste has to meet U.S. EPA incinerator standards. However, the presence of the other inorganic compounds containing large concentrations of carbon monoxide, chloride and nitrogen required an incinerator system in which the atmosphere could be controlled and in which the destruction could be achieved at temperatures at which those compounds would not create secondary air pollution problems.

The SQI combustion is carried out at approximately 1900°F and 3.5% O_2, with a 2 second retention time. These parameters were derived through pilot plant tests at the existing pilot facility at Conshohocken, Pennsylvania, which were conducted both prior to and during the design. At that set of parameters the destruction of organics exceeds 99.99%, and the CO is less than 100 ppm corrected to 7% O_2. The low oxygen concentrations ensured that the chlorine present forms as HCl versus free Cl_2, therefore improving its scrubbing efficiency. The SQI accomplishes all of this because of the high turbulence in the chamber providing excellent mixing of the vaporized waste, combustion air and hot burner combustion products which initiates the waste oxidation reactions. The high turbulence is derived from the Vortex burner and optimized design of the chamber, waste injectors and secondary combustion air nozzles.

The SQI system represents the state-of-the-art for handling this type of waste today as well as it did almost 20 years ago when it was first utilized. Therefore, not only can it be considered innovative, but it also has been proven in over 125 installed systems around the world. The operating experiences from those systems have resulted in improvements to this system which will increase its reliability and safety.

CONCLUSIONS

Basin F Liquid is a unique chemical mixture that poses a significant treatment engineering problem due to its physical and chemical properties including:

- Supersaturation of salts
- High concentration of complex organics
- Corrosivity
- Tendency to ammonia off-gassing
- Tendency to precipitate salts

As a result, the selected alternative for permanent remediation of this liquid required use of equipment that could not only destroy the organic components, but could also simultaneously:

- Withstand the corrosive activity of the dissolved solids
- Continually purge itself to prevent accumulation of salts
- Process high rates of ammonium nitrogen throughput

The singular piece of equipment that was able to meet both the CERCLA criteria and the demands of treating this problematic liquid was the submerged quench incinerator.

Abandoned Well Closure Program
at a Hazardous Waste Facility
Rocky Mountain Arsenal Denver, Colorado

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ABSTRACT

At the Rocky Mountain Arsenal in Denver, Colorado, more than 1500 wells have been installed into various aquifers during the past 50 years. This concern over the integrity of these wells prompted the identification, examination and closure of wells which could contribute to aquifer cross-contamination.

The well closure program at Rocky Mountain Arsenal was conducted using a three-phase approach. Phase 1 involved a records search and compilation of available data on wells; Phase 2 was a two-tiered field search for the wells, involving data review, visual inspection, geophysical survey and land survey; and Phase 3 involved the actual well closure.

Of 493 wells identified and approved for closure at Rocky Mountain Arsenal, 352 have been located and closed. The various materials used in the construction of these wells included polyvinylchloride (PVC), steel of varying grades, concrete and brick. Wells ranged in size from two inches to six feet in diameter and were completed to depths up to 780 feet. Drilling methods employed in the closure of the wells included auger, rotary, reverse circulation with cable tool or air hammer operations. Casings and obstructions were removed or drilled out during the closure operations. Conventional and unconventional "fishing" tools were used to remove casing. If casing could not be removed, then the casing was perforated. After the casing was removed or perforated, the sand zones and contacts within each of the wells were sealed following Colorado regulations on well closure/abandonment. The materials used to seal the wells included a grout mixture, bentonite, pea gravel and commercial concrete.

INTRODUCTION

The Rocky Mountain Arsenal (RMA) occupies more than 17,000 acres (27 mi^2) northeast of Denver, Colorado (Fig. 1). The Arsenal was established in 1942 and has been used for the manufacture of chemical and incendiary munitions as well as the demilitarization of chemical munitions. Additionally, RMA lessees manufactured pesticides and herbicides from 1947 to 1982. RMA is currently an active Superfund site undergoing remediation. Part of the remediation involves the closure of unused or abandoned wells to prevent the vertical migration of contaminants through these wells.

More than 1,500 wells have been identified at RMA, with as many as 250 of these water wells historically used for irrigation, stock watering and domestic use. Most of these wells were constructed prior to the establishment of RMA in 1942 and are hand-dug, ranging from 24 to 60 inches in diameter with completion depths up to 100 feet and are constructed of brick or concrete. Since the establishment of RMA, hundreds of monitoring wells have been installed on the property. The concern over the potential for contaminant migration through unused or abandoned wells prompted the Program Manager for RMA to develop

a task to locate, examine and close wells that could contribute to cross-aquifer contamination. Two hundred eighty-eight of these monitoring wells had either poor construction or no potential future use and were therefore targeted for closure. These wells varied from 2 to 10 inches in diameter and ranged in depth from 6 feet to 250 feet. This initial list was expanded to include 493 wells, of which 352 wells have been
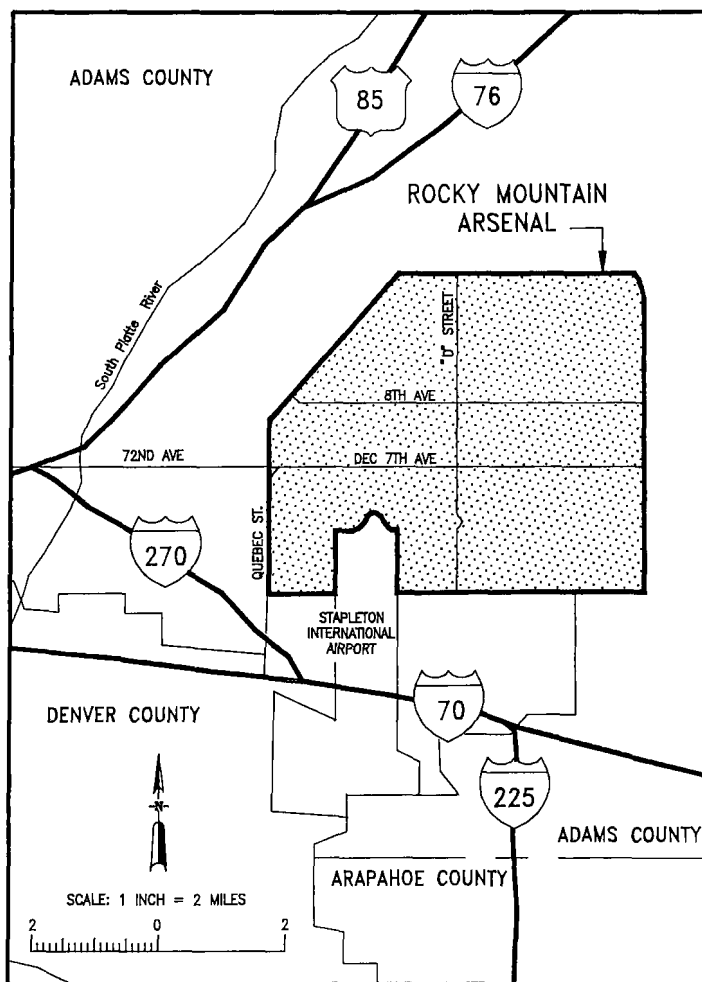
Figure 1
Rocky Mountain Arsenal—Site Location

located and closed.

The scope of work for the RMA well closure program included: compilation of a well inventory and closure list, field location of wells, cleaning and closure of all located wells and documentation of closure activities.

WELL INVENTORY AND CLOSURE LIST DEVELOPMENT

The compilation of a well inventory and preparation of a data base provided a means for evaluating and documenting historical well closure information. Information sources utilized for the well inventory and database included: existing databases, hard copy historical records and field data collected during well search and closure activities.

Well closure was evaluated on:

- Past, current and future use of the well
- Evaluation of well construction details
- Subjective evaluation of reported well construction
- Proximity or location to active/known contaminant plumes
- Quality of groundwater (if known)

After completing the evaluation, a list of wells targeted for closure was compiled.

WELL CLOSURE PLAN

Upon approval of the well closure list, well characteristics were evaluated and appropriate well closure techniques determined. These decisions were based on the Well Closure Plan which included the following:

- Well closure specifications—in compliance with all Applicable or Relevant and Appropriate Requirements (ARARs)
- Procedures for well cleaning and data collection—in compliance with Federal and State ARARs
- Compilation of topographic and elevation survey data
- Procedures for related support activities (i.e., waste management)
- Procedures for field drilling techniques
- Procedures for data management and Quality Assurance (QA)

FIELD LOCATION OF WELLS

All wells identified for potential closure were subjected to a two-tiered search. The first level field search involved a historical data review followed by a detailed visual inspection of the reported well location followed by a detailed sweep of the suspected area with a hand-held magnetic gradiometer. Any wells found visually during the first level field search were surveyed and assessed for their physical characteristics and current condition. Wells not visually located during the first level field search were subjected to a second level field search. If necessary, a detailed geophysical survey using a magnetometer was conducted in the suspected area to further define the areas to be excavated. If no geophysical anomalies were detected, no further search efforts were conducted and the search was canceled. If an anomaly was identified, then a visual field check was performed and recommendations were made for a more detailed geophysical survey or an excavation to determine the source of the anomaly.

Geophysical Survey

During the closure program, 90 suspected well locations were subjected to gradiometer/magnetometer surveys. Approximately 35% of the wellheads were located. Survey grids used at the site were 300 feet on a side with 25-foot spacings. Additional fill-in surveys were conducted on 10-foot grid spacings over smaller areas to locate the source of any detected anomaly.

A SAGA Geophysics GSM-19 gradiometer/magnetometer was used to conduct the surveys. The SAGA GSM-19 permitted simultaneous measurement of vertical magnetic gradient and total field readings using a dual sensor arrangement.[1]

Data obtained in the field were stored in the SAGA GSM-19 computer. These data were downloaded to a PC computer. A contouring program was used to create contour maps of the total magnetic field and vertical magnetic gradient. These contour maps allowed a means to evaluate anomalies and anomaly signatures.

Well Inspection and Cleaning

Well closure and cleaning procedures are dependent on the actual amount of debris or obstructions within wells and the type, construction, diameter and depth of each well. For this reason, the accurate collection and field verification of well condition and construction details are of critical importance. Well cleaning was conducted prior to closure to verify that well depth information were accurate, ensuring effective closure techniques were selected. Figure 2 illustrates recommended steps involved in the well inspection and cleaning process. Well construction data generated during the field investigation was checked against existing records to verify or reconstruct well construction details. In some cases, it was necessary to remove debris or redrill a well to clear obstructions prior to closure/cleaning.
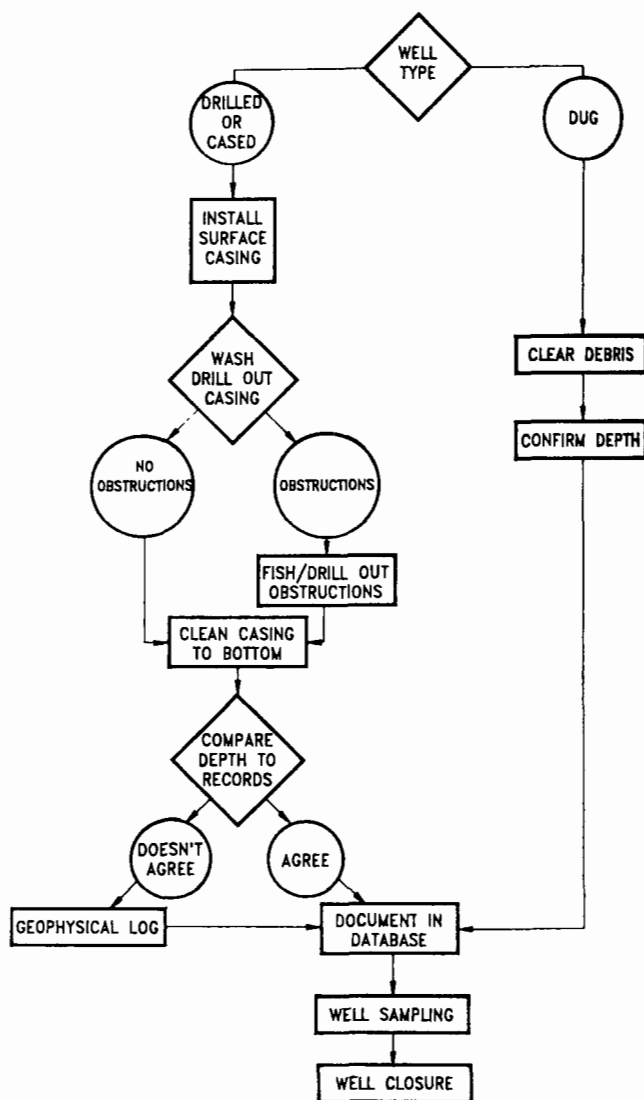
Figure 2
Well Inspection and Cleaning

Geophysical Logging Techniques

Borehole geophysical logging methods were utilized in wells deeper than 200 feet to define downhole characteristics such as casing and screen condition and location, hole condition and stratigraphy. Geophysical logging included casing collar locator (CCL), neutron and gamma logging. The information compiled from caliper logs, CCL logs, gamma logs and neutron logs helped in confirmation or identification of well construction and stratigraphy. The stratigraphy of the borehole was particularly important in the determination of zones to be perforated

to properly seal the well bore.

Caliper logging (three-arm tool) was conducted to determine the diameter of the well or well bore and to identify washout zones, locate swelling clay zones and detect holes in the casing material. The CCL log was conducted to help determine the condition of the hole, casing and screen.

Gamma logging consists of a measurement of naturally occurring radiation emitted from materials encountered in and adjacent to the borehole.[2] The gamma log helped define the stratigraphy of the hole and was run in association with a neutron log. Neutron logs employ a neutron source with either a gamma-ray detector or neutron detector. Combining the data gathered from the neutron log with the gamma log helped to identify the stratigraphy and lithology of the well bore. This process located permeable, sandy zones or contacts important in determining the best zones for casing perforation.

WELL CLOSURE DRILLING TECHNIQUES

The variety of wells encountered at RMA include PVC, steel, brick and concrete, ranging from 2 inches to 72 inches in diameter, with reported depths of up to 1,000 feet (Fig. 3). Due to the wide range of well construction, various conventional drilling techniques were used for well closure (Fig. 4). Closure ideally included the removal of well casing, screen and all well construction materials. Since wells were assessed on a case-by-case basis for closure, a variety of modifications from conventional methods were employed during well closure. Conventional drilling techniques included: auger, direct rotary, reverse rotary, hammer and modified use of cable tools.

Auger Drilling Method

Continuous-flight hollow-stem augers (HSA) cut a borehole using excavation methods and carry cuttings up the hole along the flights (Fig. 5). Hollow-stem augers were used to overdrill PVC (and some steel casing) 2 to 6 inches in diameter and up to 180 feet deep. The CME-75 and CME-750 auger rigs were selected for the work at RMA due to capability of the rig.

PVC wells, 2 inches to 6 inches in diameter, were measured with tape or drill rod to verify depth within 10[4] of the historical record. If

WELL TYPE	CONSTRUCTION MATERIAL	SIZE RANGE	DEPTH RANGE
Domestic	Concrete Brick, Steel	24" 72"	20 ft. – 90 ft.
Domestic	Steel Stovepipe	3" – 20"	20 ft. – 1000 ft.
Monitoring	Steel PVC	3" – 10"	6 ft. – 260 ft.
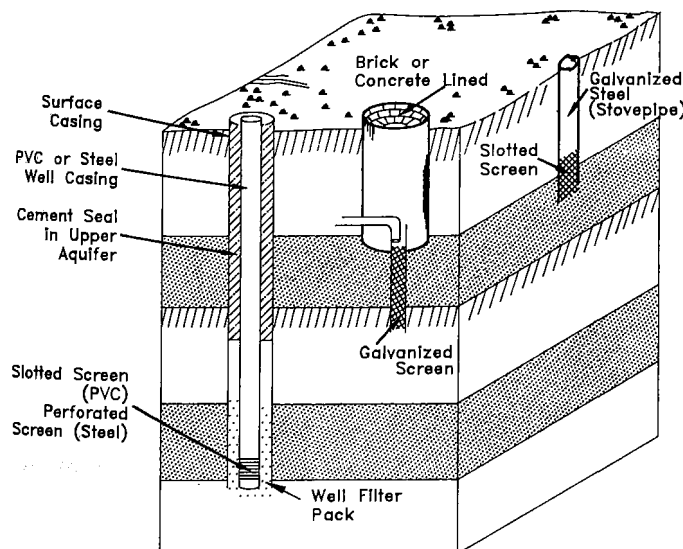
Figure 3
Wells Encounter at Rocky Mountain Arsenal

WELL DEPTH	WELL DIAMETER	CONSTRUCTION MATERIAL	RECOMMENDED METHOD
6' – 150'	2" – 6"	PVC, GALVANIZED	HOLLOW STEM AUGER PERCUSSION HAMMER
50' – 200'	6" – 24"	PVC, GALVANIZED, BRICK	MUD ROTARY REVERSE CIRCULATION
20' 100'	24" – 60"	GALVANIZED, BRICK	REVERSE CIRCULATION ORANGE PEEL BUCKET
150' – 1000'	3" – 5"	GALVANIZED	MUD ROTARY

Figure 4
Well Closure Techniques
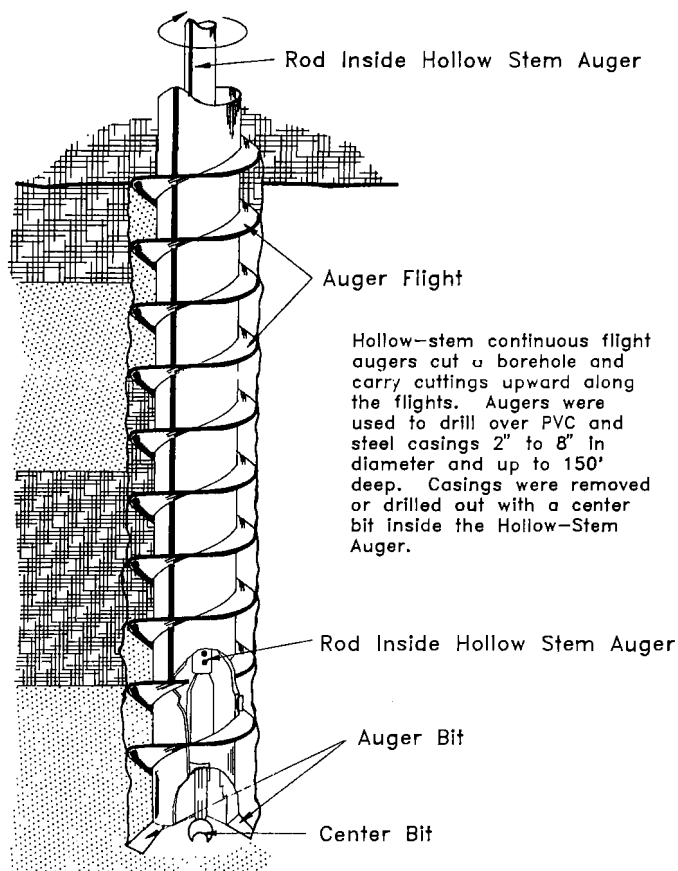
Figure 5
Hollow Stem Auger Drilling

the well was open, a center rod was inserted to help the HSA stay centered on the well during overdrilling. If the hole was closed by grout, the drilling speed was reduced and cuttings were observed for indications of drilling across the well. If problems of staying on the well occurred, the center bit was inserted in the HSA and the well casing was removed by drilling.

Drilling methods chosen for PVC wells with a diameter greater than 8 inches were considered on a case-by-case basis. Some were drilled out with a center bit. In other cases, rotary drilling was used to remove well debris. The auger rig and/or a rotary rig were used in some of these cases.

Steel, galvanized, or "stovepipe" wells generally ranged from 5 to 8 inches in diameter. Rotary drilling methods (with the auger rig) were used to clean these wells of sediment and obstructions. Verification of recorded depth was conducted by drilling through the bottom of the well into the formation below. Due to the size ranges of these types of wells, methods of overdrilling and pulling casing were determined on a case-by-case basis.

ROTARY DRILL METHOD
Drilling fluid is pumped down through
the drill pipe to the bit, to lubricate
and cool the bit, and jet material
from the bottom of the hole.
The fluid is then displaced upward
in the annular space between the
drill rod and casing or borehole wall,
carrying cuttings in suspension. At the
surface the drilling fluid is channeled
into a mud pit where cuttings
settle out before fluid recirculates.

Rotary drilling was used to
close wells exceeding 200'.
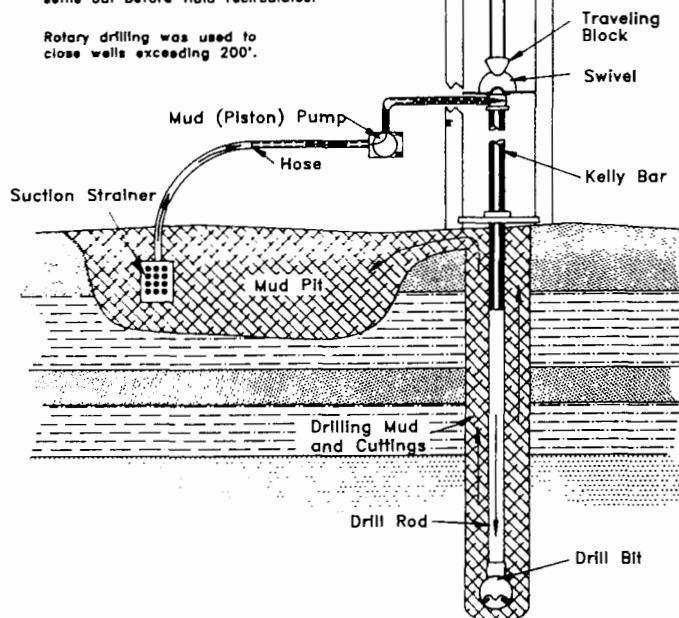
Figure 6
Rotary Drilling Method

Once a well was successfully overdrilled to remove construction materials, attempts were made to pull the casing by: sand locking, plugging off the lead auger or using fishing tools. If PVC casing could not be retrieved, the hole was redrilled with a center bit in the HSA. Cuttings were observed to verify that the well was drilled out. Generally, there were no problems in pulling the steel well casing in the shallow holes.

Some problems that occurred with the auger method included:

- Wells not installed straight generally required the well to be drilled with a center rod in place, making it difficult to determine that the well construction materials were removed.
- Wells not installed straight may have been drilled across during over-drilling, possibly pushing casing to the side wall of the closure boring.
- Difficulty was encountered in pulling the larger diameter steel casing.
- Crooked steel wells and twisted well casing caused augers to wedge in the hole.

Direct Rotary Drilling Method

Direct rotary drilling was used to circulate material out of a well to clean the well of obstructions. In direct rotary drilling, the drill string (Kelly, drill pipe, collar and bit) advances by rotation that breaks the formation or accumulated sediments. As the bit is rotated, drilling fluid is pumped down through the drill pipe to the bit to lubricate and cool the bit and to jet material from the bottom of the hole to the surface. The fluid is displaced upward in the annular space, between the drill rod and well casing or borehole wall, carrying cuttings in suspension to the surface.[3] At the surface, the drilling fluid is channeled to a mud pit where cuttings settle out before fluid recirculates down the hole. Figure 6 contains a summary of the direct rotary drilling method. Mud pits were generally excavated at the site; however, portable mud pits were used on occasion. The bit generally used to clean the hole was a roller bit or tricone bit.

Direct rotary drilling was used to clean out wells up to 1,000 feet deep, ranging from 3 inches to 16 inches in diameter, including some

Table 1
Fishing Tools, Operation and Application

Fishing Tool		Operation and Application
Taper tap		Internally engages larger, heavy objects such as drill pipe or well casing. Tool is constructed with flutes or threads from a small end and tapered to a larger diameter end that is rotated until it internally engages.
Die collar (box tap)		Externally engages over the top of drill pipe, well casing, or pump rod by rotation. The inside of the collar is threaded; guides can be used to engage over the top of an object.
Releasing spear		Internally catches drill pipe or well casing on rotation. A grapple above the nose of the spear grabs onto the fish.
Overshot	Circulating	Slips over the top of the fish and expands on circulation. Used to retrieve twisted-off drill pipe or pump rods.
	Releasing	Release or engage on rotation over the top of the fish. Used to retrieve twisted-off drill pipe or pump rods.
Junk mill		Bit with tungsten carbide on the grinding surface to chew (chip) up an object (fish). Material is circulated or a basket is used to catch the material from the fish.
Wireline grab		Harpoon-type spear with jagged edges to engage snarled/twisted wireline.
Magnet		Magnetic tools with a controlled permanent magnetic field, used to pick up small objects (usually irregular shaped).
Impression block		Lead-filled cylinder used to make an impression of the top of the fish to determine size and shape.

* From Wilson Downhole Services Fishing Seminar [5]

shallow holes closed by the auger rig. After a hole was cleaned out, total depth verification/determination was conducted by drilling through the bottom of the well into the formation. Wells greater than 200 feet deep were then subjected to borehole geophysical logging as described earlier. Logs were then assessed to verify reported well construction and stratigraphy and to aid in determining the proper sealing method for final closure. Wells deeper than 200 feet generally required perforation of the well casing to achieve proper sealing.

Colorado state regulations[4] require that a minimum of 50 feet of casing into the formation below the alluvium be removed. To help in the removal of the casing, washover pipe was used to overdrill the casing to a selected depth below the formation contact. As the washover pipe was rotated and advanced, cuttings from the boring were circulated out of the hole as previously described. After the depth was achieved, attempts were made to "fish" casing out of the hole using conventional petroleum industry fishing tools. Fishing tools were also used to remove any solid obstructions encountered in the well during well cleaning activities. The fishing tool was attached to the drill string, lowered to the obstruction and rotated until the tool was firmly engaged. Table 1 summarizes the fishing tools and operation used during the Closure Program.[5]

Problems encountered with the direct rotary drilling method included:

- Crooked wells created problems of tools or drill pipe stuck in hole
- Site accessibility was difficult because of rig and equipment size
- Large volume of water used for circulation created mud pits that required recontouring and reseeding of the site

Reverse Circulation Rotary Drilling Method

Reverse circulation rotary drilling was used to remove accumulated sediment and debris from wells that were constructed of concrete, brick and, occasionally, steel or stovepipe. The wells closed with this method ranged from 16 inches to 72 inches in diameter to depths of 150 feet. Some wells had cased or screened extensions below the concrete or brick casing.

The reverse circulation rig utilizes large capacity centrifugal or jet pumps to aid in the removal of cuttings from the borehole. Drill pipe (threaded or flanged) is larger in diameter than direct rotary drill pipe to accommodate drill cutting removal and to drill larger diameter holes up to 72 inches. The drill string is rotated from a Kelly table instead of a Kelly pipe (bar) due to the higher torque required to rotate the larger and heavier drill string. The formation or accumulated sediment are cut by drag bits or reamer bits.

In reverse circulation rotary drilling, the flow is reversed from the direct rotary method (Fig. 7). The drilling fluid and suspended cuttings move upward inside the drill pipe (string) by a centrifugal pump and are discharged into the mud pit. Cuttings are allowed to settle out in the mud pit prior to the drilling fluid returning to the borehole by gravity flow. The fluid flows down the annular space, between the drill pipe and well casing or borehole wall, to the bottom of the hole, picks up

REVERSE CIRCULATION ROTARY DRILLING
The drilling fluid/water flows from the mud pit down the borehole outside the drillrods. Fluid is then pulled through the bit into the drillrod carrying cuttings. Fluid is pulled upward, flowing through the swivel and mud pump and into the mud pit, where the cuttings settle out.

Reverse Rotary Drilling was utilized to close larger diameter holes 24" – 72").

Figure 7
Reverse Circulation Drilling Method

cuttings and re-enters the drill pipe through ports in the bit carrying cuttings in suspension back up through the drill pipe. Cobbles or boulders that cannot pass through the drill pipe are removed with an orange-peel bucket.

The orange-peel bucket was used to excavate accumulated sediment and/or debris in the wells. The heavy metal bucket, fitted with four leaves that form a steel jaw, opens outward from the bottom. The bucket is dropped into the well on a cable system with the bucket jaws open. The weight of the bucket digs the jaws into material at the bottom of the hole. The jaws then close on a load of material, which is withdrawn from the hole and dumped at the surface. Smith and Schneider[6] describe the use of the orange-peel bucket for well installation. Large diameter wells selected for closure at RMA were initially drilled with the orange-peel bucket until no further advancement could be made. Then reverse circulation drilling was employed to complete the closure.

The bottom of a well was verified based on observation of cuttings and drill rig reaction. Most wells closed with this method were constructed in the alluvium with screen set just above consolidated material. Indications that the bottom of the well had been reached included: stiff drilling, refusal, consolidated material, lack of well debris or lack of accumulated sediment.

Some problems encountered with the reverse circulation rotary drilling method included:

- Limitation of accessibility at sites due to rig size
- Large amount of water supply for circulation also requires large mud pit
- Surface collapse problems caused by the use of a large amount of water for circulation in unconsolidated (sandy) material
- Flowing sands and collapse of well casing

Some of these problems were solved by using conductor casing set inside the well casing to help keep the well open and allow circulation.

Percussion Hammer Drilling Method

A percussion (casing) hammer drill drives a double-walled steel casing into the ground with a diesel pile-driving hammer. The drilling method

can rapidly penetrate unconsolidated material including sand, gravels and cobbles.

Reverse-air circulation cools the bit and removes cuttings from the boring. Air is forced down the drill pipe that escapes through ports on the bit, lifting the cuttings back to the surface and into a cyclone where the cuttings drop out of the circulated air.[3] The cuttings can then be collected in a drop box or drums to contain any contaminated material. Water-based drilling fluid can also be used to help in the removal of drill cuttings. At RMA the dual walled drill pipe was driven over PVC casings up to 6 inches in diameter and up to 100 feet deep. Successful attempts were made to pull the well casing prior to drilling, then the boring was redrilled to remove well construction matter. This type of drilling helped alleviate the problems encountered with crooked wells. The bottom of the well was determined based on cuttings and drill rig reaction. The borings were cleaned with the reversed air circulation and grouted.

Problems encountered with the Percussion Hammer Drilling method included:

- Drilling across crooked PVC wells
- Limitations on site accessibility due to weight of the rig
- Material becoming lodged in return line (safety hazard due to potential breaking of return line)
- Drilling problems in flowing sands

WELL CLOSURE

Recommended closure methods employed during the program included standard procedures commonly used in the water well and/or petroleum industries. Modifications to these procedures were made on a case-by-case basis. All closures were performed in compliance with the requirements of the State of Colorado[4] as well as USATHAMA[7] and SDWA (UIC).

Each well to be closed was evaluated individually, with careful consideration given to the well construction characteristics and the geologic setting. Closure techniques were then adapted for each individual well to accommodate well depth and the volume of grout required to effectively seal the well was calculated. If artesian conditions existed, the sealing operation was designed to confine the water and prevent transfer of groundwater between aquifers.[4]

Standard closure practices included removal of all materials which would hinder the sealing operation, including screen and casing (Fig. 8). If the casing was in good condition, an attempt was made to remove it by fishing with cables, tools or sand-locking techniques. If the casing was in poor shape, an attempt was made to either overdrill or wash out the soil surrounding the casing to facilitate its removal. If the casing could not be removed, it was cut, torn or perforated to allow the grout to completely seal the annular space. At a minimum, casing was removed 50 feet into the formation below the contact with the alluvium (as specified by Colorado regulation). The targets for perforations were
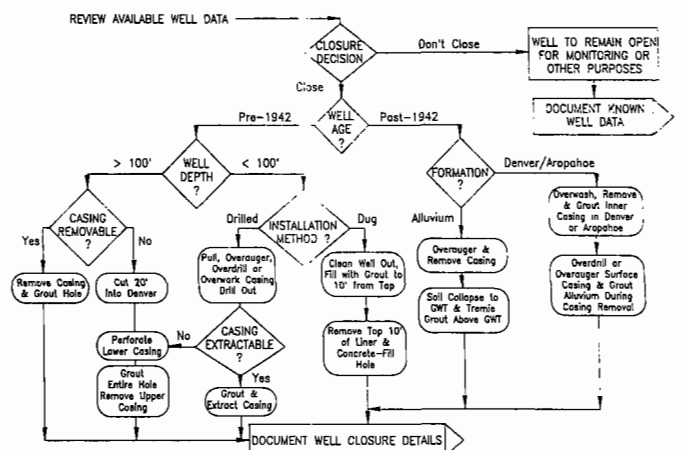
Figure 8
Standard Well Closure

zones of permeability, sand zones or contacts, where it is important to have a good seal to prevent potential cross-aquifer contamination.

Large-Diameter Hand Dug Wells

Wells at RMA with diameters of 24 to 60 inches and depths of 30 to 90 feet (hand dug or drilled) were typically constructed with cement, stone, or brick liners. Prior to closure, debris was removed from these wells by fishing tools with cables, reverse rotary drilling or cable tool methods. The bottom of each well was then inspected for drilled, cased extensions. These types of wells were closed by filling the wells with sand to within 10 feet of the surface, followed by capping with commercial concrete to three feet below grade. The remaining space was allowed to collapse and fill with matrix soil (Fig. 9). Those wells found to have drilled, cased extensions were closed as drilled wells by grouting in the extension portion, followed by closure of the upper portion as described above.
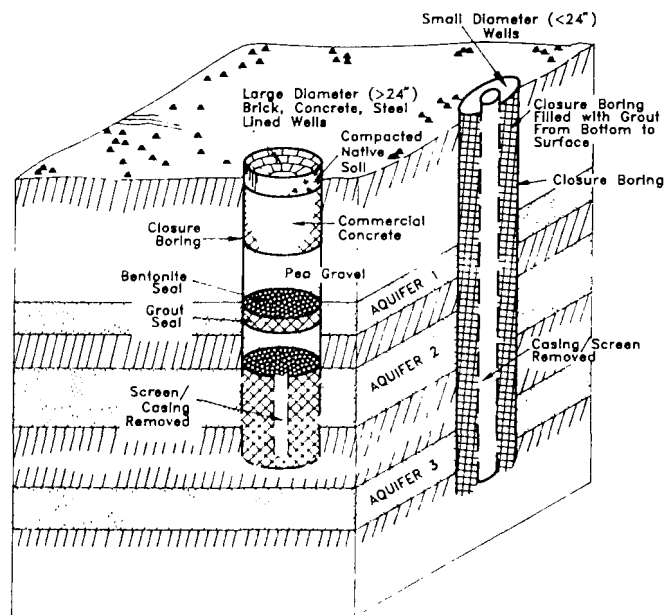
Figure 9
Well Closure Methods

Deep Drilled Wells

Methods selected for the closure of deep (>200 feet) drilled wells were based on available well construction information review. These wells were effectively cleaned and closed using mud rotary methods. Due to the depths of these wells, geophysical logs were run to determine the condition of the casing in the well and to aid in decision-making on perforations and casing removal.

Borehole geophysical logs were evaluated for determination of screened intervals and lithology of the borehole. The condition of the casing and the location of casing and screen connection joints (CCL log) were taken into consideration to help define zones that needed perforation to seal the well.

Mechanical perforation methods were originally proposed but determined to be unfeasible due to poor well conditions and small well diameters. Class A explosives in shaped charges were utilized to cut holes in steel casing, concrete and the formation behind the casing.

Following perforation activities, the well was grouted from the bottom to a preselected interval. The grout was allowed to cure for 24 hours, then well casing overdrilling was used to remove the upper portion of the well. Following removal of the well casing, the boring was grouted from the bottom to the ground surface (Fig. 9).

Shallow Monitoring Wells

Shallow monitoring wells were usually constructed of PVC or steel casings with short screened intervals in unconsolidated alluvial materials or water-bearing formations. Auger or hammer drilling methods were normally used to close the wells following the procedure outlined in the well cleaning and closure sections. If removal or perforation of the casing was not possible, the closure technique was modified and included: backfilling the screened portion of the well with clean sand and filling the remainder of the borehole with grout to the ground surface, or drilling out the casing. If the depth of the well and the location of the screened interval extended across more than one aquifer, the entire casing and screened interval was required to be filled with grout to the ground surface (Fig. 9).

Grout Placement in Small Diameter Wells

Following removal or perforation of the casing materials, grout was mixed and placed in the borehole of small (<24 inches) diameter wells. A slurry of Type I-II cement and approximately 3 to 5% bentonite powder was prepared. This slurry was pumped under pressure through a tremie pipe to within one foot of the bottom of the borehole by the Brandenhead method. With this method, mud channels are minimized.

Grout mixtures of this composition are reported to attain an approximate density of 14 lb/gal.[9] This density is sufficient to displace the drilling fluid column. After allowing the grout column to cure, the grout column was topped off to bring the grout level to within two feet of the surface.

CONCLUSION

Contamination of aquifers is a major environmental concern to PRPs, industry and government. The closure of abandoned or unusable wells is an important method for controlling this potential migration pathway for aquifer cross-contamination.

If a well is unused, abandoned or of questionable integrity, the well should be assessed for potential current or future use for monitoring, dewatering, injection, etc. If the well does not comply with applicable regulations, then closure should be recommended.

Methods of well closure are modified from those used in the well drilling industry and vary depending upon the physical characteristics of the well. The wells must be located, if they have been damaged or buried, and characterized by visual inspection or investigation with appropriate drilling and geophysical technologies. The actual closure of the well and associated boring will be dependent upon local regulations and conditions. Well closure programs are important in minimizing or providing control to potential aquifer cross-contamination.

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Remediation of a Surface Impoundment Basin F—
Rocky Mountain Arsenal

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INTRODUCTION

In Feb. 1989, the Department of the Army, Shell Chemical Company, the U.S. EPA, the Department of Interior and the Agency for Toxic Substances and Disease Registry, entered into a Federal Facility Agreement (FFA) to establish a procedure through which the organizations will cooperate in the implementation of response actions at Rocky Mountain Arsenal. One provision of the Agreement provides that specified Interim Response Actions which are compatible with long-range cleanup goals will be implemented in advance of a final Record of Decision, not planned until 1994. The remediation of Basin F is one of 13 IRAs identified in the FFA.

Use of the Interim Response Action provisions of CERCLA at this NPL site significantly accelerated the time-frame for remediation as compared to the time that would be required for remediation after the Record of Decision. It is estimated that six years were saved by using this approach to a remedial action.

This paper presents a case history of the remediation of "Basin F," a 93-acre hazardous waste surface impoundment and as reported by other Superfund project site managers relates the challenges above and beyond typical construction project events and problems. Problems resulting from unusual weather conditions, community relations issues and reprogramming activities are highlighted rather than discussions of the normal construction and historical events.

PROJECT OBJECTIVES

Objectives of the Basin F interim action were: (1) eliminate future emissions of volatile chemicals from the basin; (2) to prevent infiltration of Basin F contaminated liquids into underlying groundwater; and (3) to eliminate potential adverse impacts to wildlife that otherwise would come in contact with the contaminated liquids, sludges and solids. All of the objectives were achieved.

IMPOUNDMENT DESCRIPTION

Basin F was constructed at Rocky Mountain Arsenal in 1956 for disposal of contaminated liquid wastes from Army and lessee chemical manufacturing operations. When constructed, Basin F was provided a 3/8 inch thick catalytically blown asphalt membrane liner. This liner was covered with a 12 inch protective soil/sand cover. Basin F covered approximately 93 acres and had a capacity of 240 million gallons. Design and construction of Basin F was a cooperative effort of the Bureau of Reclamation and the Army Corps of Engineers (COE). In addition to its life as a solar evaporation pond at RMA for 32 years, Basin F was used as the settling basin for liquid waste prior to its treatment and injection into the 12,000 foot deep well. The injection well has also been closed.

Project Phrasing - Major Events

After the contract for the remediation project was awarded, the COE issued a notice to proceed in February 1988. Site preparation began in March 1988. Initial work was designed to provide health, safety and administrative facilities for the 180 personnel who would work at the site for approximately one year. Special decontamination facilities were constructed to accommodate the 110 workers who would enter the heavily contaminated portion of the site. Initial activity included installation of a 360° air monitoring network of high volume samplers and initiation of a sampling program to characterize the surface characteristics. Borings were placed on 50 foot centers to develop waste volume estimates and to determine the extent of deposition of sludge material.

Pumping of the liquid from the impoundment into 4,000,000-gallon capacity storage tanks began in May 1988 with expectations that this storage capacity would be adequate. Stainless steel tanker trucks were utilized to transport the liquid due to its extremely difficult material handling properties.

The first of several major weather complications to impact on the project arrived in May 1988 in the form of a 20-year rain event, yielding 3.5 inches of precipitation before it ended. The immediate effect was to increase the volume of chemically-contaminated liquid to 14,000,000 gallons, 10,000,000 million gallons in excess of tank capacity. This increased volume of contaminated water also affected the site condition by expanding the shoreline to the point that it covered the planned construction areas for a 16-acre waste pile. This waste pile was supposed to contain the 480,000 cubic yards of dried waste that would be generated by the time the project ended.

Immediate relief was achieved by constructing two double lined waste ponds with 8,500,000 and 5,000,000 gallon capacities. The excess liquid was transferred to these ponds, which then were covered. These ponds also were used to collect leachate from the waste pile.

The second major weather event occurred in June 1988, with a tornado moving from west to east across the northern perimeter of the site. The tornado caused damage to heavy equipment and, as we later discovered, also placed contaminated soil particles between the layers of HDPE liner as the ponds were being constructed. It was not until one year later that contaminated leachate was found in the collection systems. This development gave rise to questions concerning the integrity of the newly constructed ponds.

Increasing volume estimates continued during later project phases. At completion of the liquid pumping, it was determined that bottom elevations used to calculate waste volumes were incorrect and that deposition of crystallized waste into a hardened solid form had dramatically misled project planners. New exploratory excavation revealed that another 4 feet of crystal waste and yet another 4,000,000 gallons of liquid waste remained entrenched in layers above the asphalt

liner.

This discovery led the Army, the U.S. EPA and the COE to begin a phase known as constructive suspension of the project to evaluate engineering and cost alternatives. To the credit of the managers involved, schedule and cost growths were authorized and a planned winter work shutdown was canceled concurrent with a decision to move forward through the winter of 1988 and to complete the project as nearly as possible to the original completion dates.

Odor Problems and Community Involvement

In parallel with increased volumes, cost growth and expanded schedules, odor problems developed in the community one mile from the site; community concerns arose in August 1988. Prior to construction, numerous air monitoring studies had evaluated the potential for VOCs emissions; no potential off-site health hazard was identified. Nonetheless, local citizens soon complained of odors causing symptoms of nausea, headaches and choking. In retrospect, it is clear that these odor problems caused decreased public confidence in the program, which, in turn, necessitated major program modifications to: evaluate and implement odor control measures; reevaluate of acute and chronic health effects (conducted concurrently by six health organizations); and operate an odor control team which responded to a telephone hot-line around-the-clock.

Unique to this project was the delivery of 40 room air purifiers to the residents to control odors in their homes. While odor problems have been reported at other cleanup sites, this factor weighed heavily on com-munity acceptance of the project even though Basin F had been known in the community for 32 years at the time of remediation.

A series of public site tours, public data exchange opportunities and question and answer sessions was implemented to respond to community concerns regarding the odor problem. Ultimately, legal action was initiated by citizens who considered themselves harmed by the odors. All parties involved acknowledged that the Basin F project was being conducted in a commercial/industrial/residential mixed area with numerous odor sources. These factors will be considered well in advance of future cleanup activity.

Again, the sponsor and regulatory agencies had to evaluate alternatives in order to proceed with the project with the potential of choose between slowing down the cleanup and extending the schedule or proceeding with controlled activity and finish as soon as possible, thereby shortening the nuisance time. Assurances from senior health officials, based on the air monitoring data and toxicological evaluation that air quality was safe, provided the answer.

BASIN F - A SUCCESS STORY

In evaluating the events at Basin F, in retrospect, one learns that not all Superfund cleanups progress smoothly. Examples exist of sites partially finished that remain on some federal court docket. Work was never begun at other sites after years of RI/FS study and analysis. Evaluation of remediated site conditions today shows that the area is safely protected from the environment as stated in project objectives. On some projects, only persistence will win the day.

Evaluation of Adsorption Processes for the Removal of Residual Chemicals from Water Treated by an Ultraviolet/Chemical Oxidation System

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ABSTRACT

As one of several Interim Response Actions (IRAs) being conducted at Rocky Mountain Arsenal (RMA) under CERCLA, the Program Manager for Rocky Mountain Arsenal (PMRMA) chose ultraviolet (UV)/chemical oxidation as the best process for treatment of approximately 300,000 gallons of hydrazine-contaminated rinsewater at RMA. The rinsewater is contaminated with hydrazine and hydrazine-derivative compounds, such as unsymmetrical dimethylhydrazine or 1,1 dimethylhydrazine (UDMH) and monomethyl hydrazine (MMH), in concentrations in excess of 1,000 mg/L, as well as N-nitrosodimethylamine (NDMA) and organic compounds such as organochlorine pesticides and chlorinated hydrocarbons.

Because the project action level for NDMA is 1.4 pg/L (ppt) and because the hydrazine fuels decompose before NDMA is destroyed to the action level, 1.4 pg/L of NDMA was targeted as the goal for treated effluent. The UV/chemical oxidation process typically can treat hydrazine compounds in 16 hours, while 35 hours are required to decrease the NDMA concentration to approximately 1 to 2 ppb (μg/L), which does not meet the treatment goal of 1.4 pg/L.

Investigating a possible secondary treatment that could reduce NDMA concentrations even further, RMA and the U.S. Army Engineer Waterways Experiment Station (WES) attempted to achieve a lower effluent level without costly additional UV/chemical oxidation treatment. Three adsorption processes, granular activated carbon (GAC), organic-based ion exchange resins and activated alumina, were evaluated by WES. None of the adsorbent manufacturers could provide any information on the NDMA removal performance and adsorptive capacity of their products. Therefore, a bench-scale treatability study was initiated at WES to evaluate the three adsorption processes for removing trace amounts of NDMA from the UV/chemical oxidation system effluent.

Results from the study indicate that GAC is the best adsorbent evaluated because of its ability to reduce NDMA levels consistently below 2 μg/L. An economic analysis comparing GAC treatment to additional UV/chemical oxidation treatment was performed and the results show that significant cost and time savings can be achieved by using GAC as a secondary treatment process.

INTRODUCTION

The Hydrazine Blending and Storage Facility (HBSF) at Rocky Mountain Arsenal (RMA) in Denver, Colorado, is owned by the U.S. Air Force (USAF) and was operated by RMA between 1962 and 1982 as a depot to receive, blend, store and distribute hydrazine fuels. The primary operation was the blending of anhydrous hydrazine and unsymmetrical dimethyl hydrazine (UDMH) to produce Aerozine 50, a rocket propellant, in response to requests by the USAF. The materials were manufactured elsewhere and shipped to RMA for blending. Other operations performed at the HBSF included loading and unloading rail cars and tank trucks carrying hydrazine fuels, destruction of off-specification batches of Aerozine 50 and storage of Aerozine 50, anhydrous hydrazine, monomethyl hydrazine (MMH), monopropellant hydrazine, hydrazine 70, UDMH and hydrazine.

Hydrazine and UDMH are ignitable, corrosive and reactive, thus meeting the identification criteria for the characteristics of a hazardous waste as defined by 40 CFR 261.[1] They are unstable in the natural environment and rapidly decompose when exposed to the atmosphere. One of the decomposition products of UDMH is N-nitrosodimethylamine (NDMA), a suspected carcinogen.[2] The NDMA detected in wastewater samples is an intermediate generated during the production of UDMH using nitrosation and the catalytic reduction of dimethylamine.[3]

When the OSHA inspected the HBSF in 1982[4] and found airborne NDMA, RMA ceased operations and closed the HBSF to all but essential personnel. All blending materials were removed and the tanks and piping were decontaminated. These activities resulted in the generation of 300,000 gallons of rinsewater, which contains approximately 1,000 mg/L of hydrazine, 160 mg/L of MMH, 1,100 mg/L of UDMH and 180 μg/L NDMA.

In the Decision Document for the HBSF cleanup, the Army agreed to attempt treatment of the NDMA in the wastewater to 1.4 pg/L, the Ambient Water Quality Criterion for NDMA. Although not applicable, the value is considered a relevant and appropriate requirement (ARAR), thus serving as the ARAR governing the cleanup of the HBSF. The 1.4 pg/L level is well below the analytical detection limit for NDMA, making verification of successful treatment very difficult.

SELECTION AND DESCRIPTION OF A TREATMENT PROCESS

After a thorough review of the possible treatment alternatives, an ultraviolet (UV) light-catalyzed chemical oxidation process was selected for the destruction of the hydrazine fuel compounds (hydrazine, UDMH and MMH) and NDMA present in the wastewater. Three UV/chemical oxidation systems were evaluated based on the results of bench-scale treatability tests performed by each vendor on samples of wastewater supplied by RMA. The treatability tests were performed by each vendor at their respective laboratories, while chemical analyses were performed by an RMA contract laboratory.[5-7] A UV/hydrogen peroxide (H_2O_2) system marketed as Perox-Pure by Peroxidation Systems, Inc. (PSI), was selected based on the results of the treatability tests. The Perox-Pure system utilizes medium-pressure UV lamps with a proprietary UV spectrum and injection of a 50% hydrogen peroxide solution.

Destruction of contaminants in UV/H_2O_2 treatment systems is
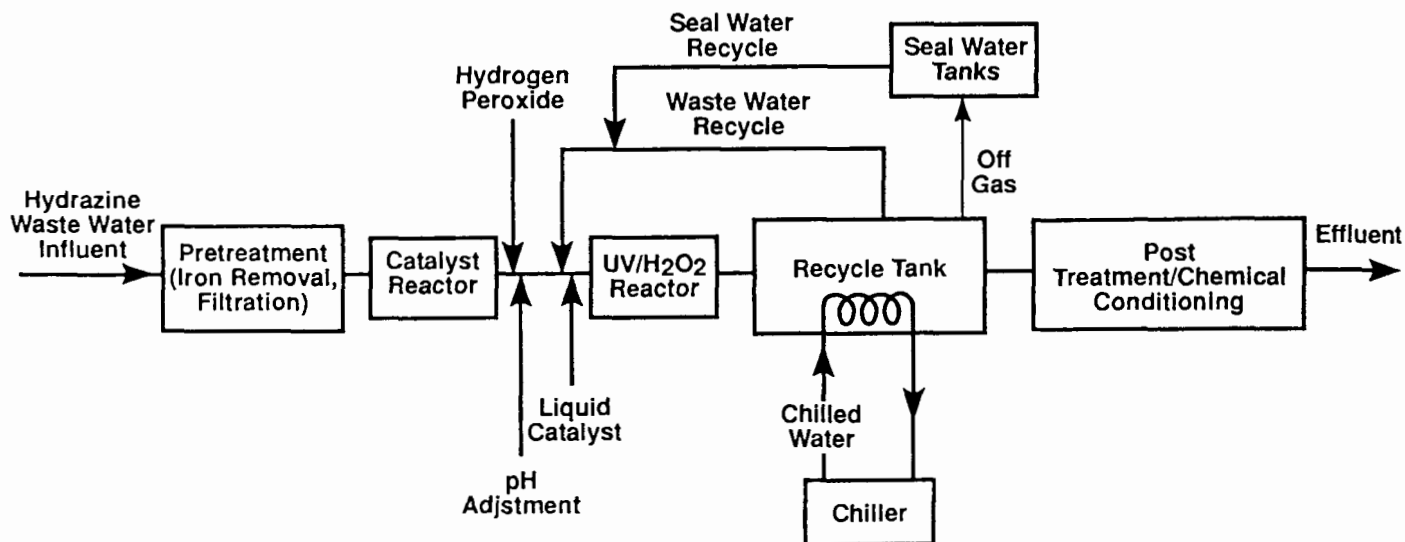
Figure 1
Process Flow Schematic
Hydrazine Wastewater Treatment Facility
Rocky Mountain Arsenal HBSF

accomplished by: (1) photolysis via UV irradiation, (2) chemical oxidation by the hydrogen peroxide and hydroxyl radicals, which are strong oxidizers produced during photolysis of hydrogen peroxide and (3) the synergistic effects of both the chemical oxidizer species and the UV light.

Based on the treatability results generated by PSI, a Model No. CW-180 was selected because of its ability to provide appropriate reactor volume and flexibility. The system is housed in a newly constructed building at RMA. A general process flow schematic of the RMA Hydrazine Wastewater Treatment Facility (WWTF) constructed to treat the hydrazine wastewater is presented in Figure 1. The total system batch capacity is 1,300 gallons.

The wastewater treated by the WWTF is pumped from a steel tank located at the HBSF through a pretreatment system for the removal of iron and suspended solids and then is stored in a feed tank. Process chemicals, including hydrogen peroxide, caustic soda, catalyst and sulfuric acid, are fed into the wastewater at a chemical injection header upstream of the UV/H_2O_2 reactor. When required, these chemicals are dispersed through the wastewater by an in-line static mixer located downstream of the inlet header. After passing through the static mixer, wastewater enters through a pressure vessel containing vertical tungsten rods arranged in a bundle. The tungsten serves as a catalyst for the hydrazine/chemical oxidizer species reaction. Before entering the UV/H_2O_2 reactor, the wastewater passes through a bag filter located downstream of the catalyst pressure vessel. The bag filter removes iron flocs carried over from the feed tank.

Treatment of the wastewater is accomplished in batch mode. A recycle module allows continuous recirculation of wastewater through the UV/H_2O2 reactor and its associated recycle tank during treatment. In the context of this report, batch time represents total system (UV/H_2O_2 reactor, chiller and recycle tank) hydraulic retention time, but actual UV/H_2O_2 reactor hydraulic retention time is 25% of the total batch time for a 1,000-gallon batch. The recirculated wastewater is cooled via a chiller module, which circulates coolant through coils in the recycle module tank to remove excess heat generated during the UV/oxidation process. The temperature of the wastewater is maintained at 125 to 140 °F.

The UV/H_2O_2 process is operated at the initial pH of the wastewater brought in from the storage tank. Because the wastewater is a basic solution with a pH of 9.1 to 9.3, the hydrazine fuels act as a reducing agent. As the destruction process takes place in the UV/H_2O_2 chamber, the favored reaction for hydrazine is oxidation to N_2.[3] The rate of hydrazine fuel destruction is measured by the decrease in pH and the

change in oxidation reduction potential (ORP) from a negative value to a positive value. Once the pH levels off at approximately 7.0, the destruction of hydrazine fuels is complete (Fig. 2).

Following treatment in the UV/H_2O_2 reactor, the wastewater is pumped to one of two effluent holding tanks for analytical characterization and pH adjustment, if necessary, prior to disposal.

DESTRUCTION EFFICIENCIES

Bench-scale studies performed by the Illinois Institute of Technology Research Institute (IITRI) and PSI indicate that hydrazine fuel compounds are initially destroyed at a rapid rate, but the rate decreases as the concentration of hydrazine fuel compounds decreases. Based on the experimental results, PSI[5] and IITRI[8] conclude that destruction of hydrazine fuels and NDMA can be accompanied by the UV/H_2O_2 process and that during the UV/H_2O_2 process, hydrazine is decomposed prior to NDMA destruction.

Pilot testing was performed by Harding Lawson Associates (HLA) under PMRMA contract using the full-scale UV/H_2O_2 treatment system to confirm the bench-scale treatability test results. The bench-scale testing indicated that hydrazine and NDMA destruction could be accomplished in 16 hours. The pilot-scale testing verified that the hydrazine fuels are decomposed prior to limited NDMA destruction and determined that the time required for successful treatment of NDMA and the hydrazine fuels is dependent on the influent concentration of NDMA. Further pilot testing indicated that treatment time of more than 50 hours may reduce the NDMA concentration below 1 $\mu g/L$, unfortunately at a significant increase in treatment cost, but still may not reach the target effluent levels of 1.4 pg/L of NDMA.

ADSORPTION COLUMN TESTING

Because of the low target treatment levels and the extremely long time required for the UV/H_2O_2 process to reach those levels, if they could indeed be reached (Fig. 3), various adsorption processes were evaluated for removal of the residual NDMA from the UV/H_2O_2 reactor effluent after hydrazine compounds were destroyed (approximately 20 hours of treatment). This evaluation was performed in hopes of meeting the NDMA action level at an appreciable cost and time savings over additional UV/H_2O_2 treatment beyond the hydrazine compound destruction end-point, which can be detected during system operation by monitoring UV/H_2O_2 reactor pH and oxidation reduction potential (ORP).
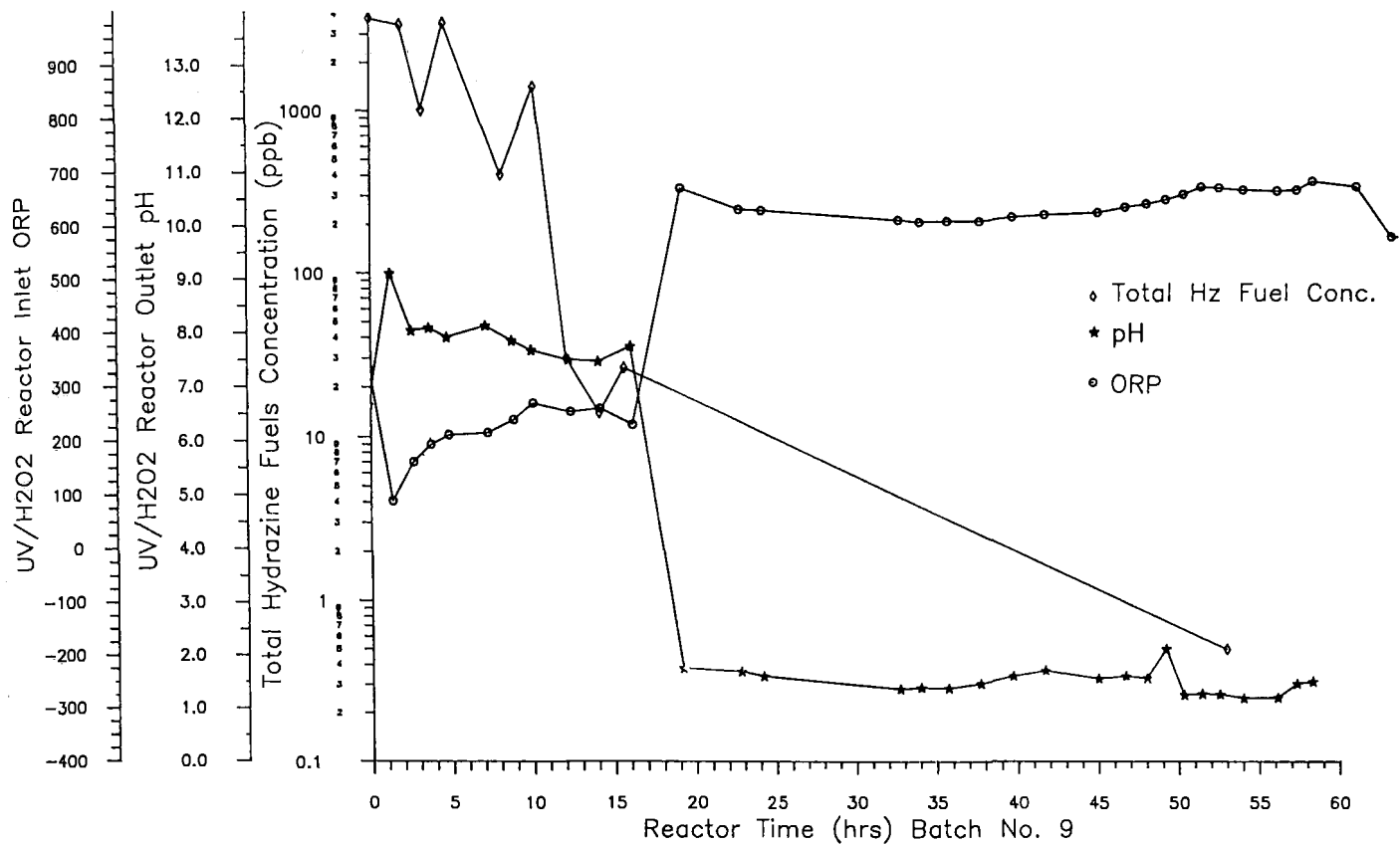
Figure 2
Total Hydrazine Fuel Destruction Utilizing
UV/H₂O₂
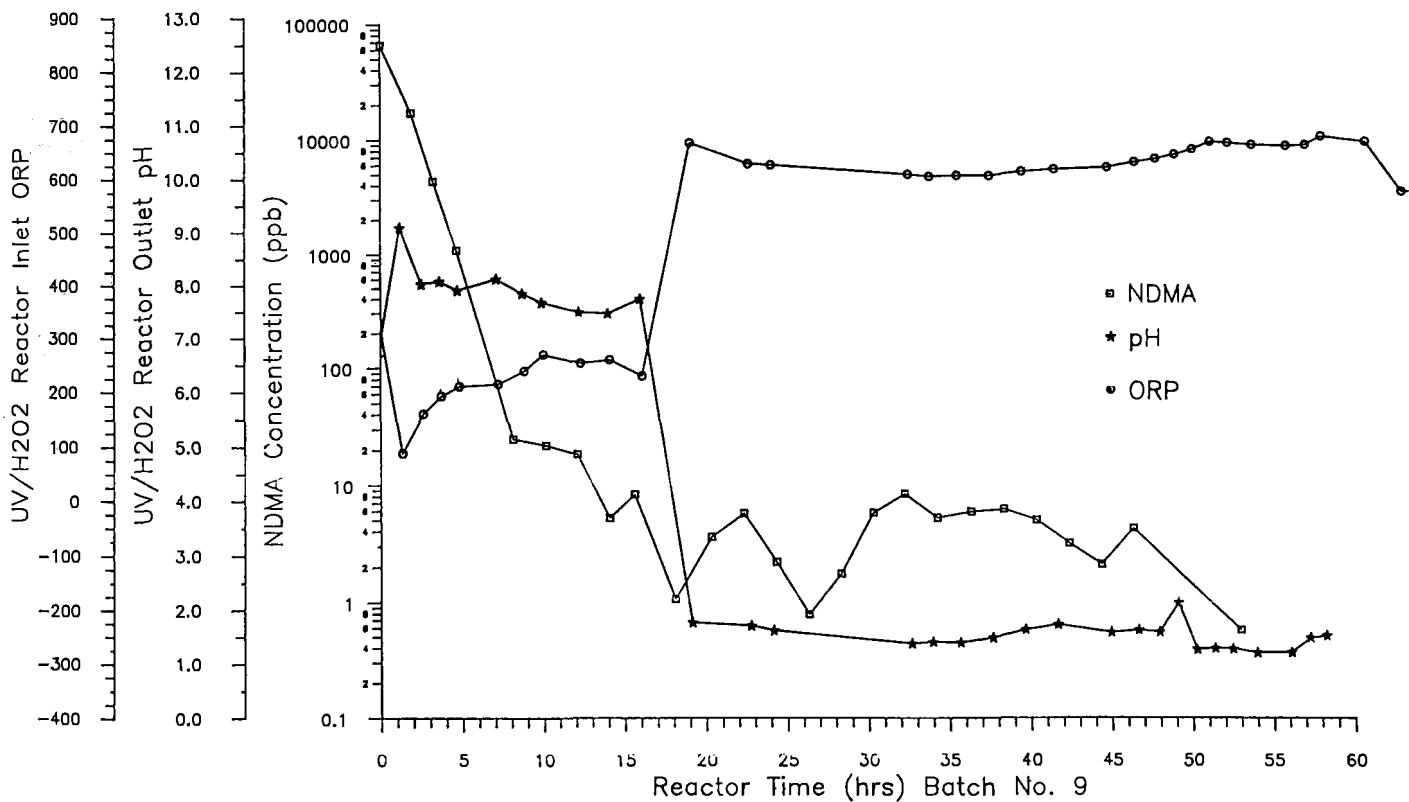
Figure 3
NDMA Destruction Utilizing UV/H₂O₂
Treatment Process

Adsorption column testing was performed at the U.S. Army Engineer Waterways Experiment Station (WES). Test influent for this study was collected from the UV/H$_2$O$_2$ system effluent tank, had a pH of 2.45, had an NDMA concentration of 66 μg/L and was shipped to WES in two 55-gallon drums.

The adsorbents evaluated at WES were granular activated carbon (GAC), activated alumina and two synthetic resins. Table 1 lists the manufacturing source, trade name and vendor for each absorbent. The columns were constructed of Plexiglas and measured 2.0 feet in length and 0.17 feet in diameter. The columns were run in an upflow mode using peristaltic pumps and flowmeters to control the influent flow rate (Fig. 4). Stainless steel screens were placed over the inflow and outflow ports of the columns to prevent the adsorbents from exiting the columns.

Table 1
Adsorbent Types and Sources

Adsorbent	Type	Brand Name	Manufacturer
Activated Carbon	Coconut Shell	CC 601	Westates
Activated Alumina	Aluminum Oxide	Celexson b CDO	Alcoa
Ion Exchange	Polyaromatic	XAD-4	Rohm and Haas
Ion Exchange	-SO3-H+ Based	Amberlyst 15 WET	Rohm and Haas
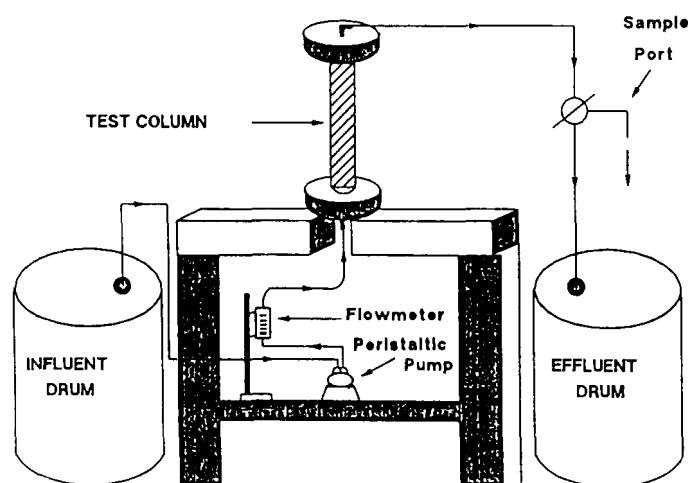
Figure 4
Adsorption Column Test Apparatus

The adsorbents were soaked for 24 hours in distilled, deionized (DDI) water before they were loaded into the columns. The columns were filled with DDI water prior to loading them with the adsorbents so that the adsorbents would stay wetted. As the adsorbents were added to the column, DDI water was removed to prevent the columns from overflowing. Each column was completely filled with the appropriate adsorbent.

All columns were run at a flow rate of 0.15 L/min, which equates to a hydraulic flux of 2.0 gpm/ft^2. The empty bed contact time (EBCT) for all columns was 8.25 minutes. NDMA samples were collected from each column at 5, 10, 20, 40 and 70 bed volumes. A bed volume constitutes an amount equal to the total volume of the empty column.

COLUMN TESTING RESULTS

The effluent NDMA concentrations from each column and the respective bed volumes at the time the samples were collected are listed in Table 2. Figure 5 is a plot of NDMA concentrations versus bed volumes passed through each column.

At 40 bed volumes, the effluents from all columns experienced increases of varying magnitudes in NDMA concentration (Fig. 5). The reason for this increase in effluent NDMA concentration is unknown. The first of the two drums containing the test influent was emptied after 40 bed volumes had passed through each column, requiring that a sample

Table 2
Adsorption Column Effluent NDMA Concentrations

Bed Volumes	Activated Carbon (ppb)	Activated Alumina (ppb)	XAD-4 (ppb)	Amberlyst 15 WET (ppb)
5	0.576	201.000	0.755	0.180
10	0.189	0.756	0.206	0.167
20	0.078	1.170	0.585	0.265
40	1.210	14.400	2.510	1.670
70	0.020	0.020	0.717	1.660

from the second drum be used to complete the study. It is possible that changing drums may have upset the adsorbent/adsorbate equilibrium, due to slight differences in influent quality, causing desorption of NDMA to occur until equilibrium was again reached with the new influent.

Table 2 shows that the activated alumina column had the highest effluent NDMA concentrations of the four adsorbents. However, activated alumina did provide significant removal of NDMA from the influent, except for bed volume No. 5 which had a concentration of 201 μg/L and was not plotted because the high value would have distorted the plot. The activated alumina bed volume No. 5 concentration is approximately three times higher than the influent NDMA concentration. The reason for this increase in NDMA concentration through the column is not understood. It is possible that sample bottle or analytical contamination could have occurred, but the QA/QC procedures associated with the NDMA analysis indicated no such problems. A second possibility is that the activated alumina initially contained NDMA produced during the manufacturing process; however, the NDMA removal achieved during subsequent bed volumes does not substantiate this conjecture unless all of the NDMA was washed from the activated alumina prior to sampling of bed volume No. 10.

The two synthetic resins had appreciable NDMA removals throughout the 70 bed volumes. The Amberlyst 15 WET resin performed slightly better than the XAD-4 resin. Also, the two resins did seem to have more consistent NDMA effluent concentrations than the other two adsorbents.

In Table 2, it can be seen that the activated carbon generally had either the lowest (bed volumes 20, 40 and 70) or the second lowest (bed volumes 5 and 10) NDMA concentrations. All of the activated carbon column effluents were less than 1.5 μg/L, with only one sample (bed volume 40) greater than 1.0 μg/L. This result is surprising because some activated carbons are actually used to purify amine compounds.

Based on the results of the adsorption studies, GAC was considered the best adsorption process because: (1) GAC generally had the lowest NDMA effluent concentrations; (2) GAC seemed less sensitive to system upset than the other adsorbents and (3) resins traditionally, are very sensitive to changes in influent quality, but GAC is much more flexible in its ability to respond positively to influent changes.

ECONOMIC ANALYSIS OF TREATMENT ALTERNATIVES

Because NDMA breakthrough was not detected in the effluent from the activated carbon column after 70 bed volumes, for sake of economic comparison it was assumed that the activated carbon column could treat at least 70 more bed volumes before NDMA breakthrough. At this loading, approximately 130 gallons of column influent could be treated per pound of activated carbon.

The cost of the activated carbon used in this study was $1.59/lb. Thus, using activated carbon to treat all 300,000 gallons of the post-UV/H$_2$O$_2$-treated water for an additional 30 hours would cost approximately $13,000 and would take approximately 600 hours. This cost estimate does not include labor or energy costs because they were considered minimal; the operation of small adsorber systems is neither labor-intensive nor energy-intensive. Labor associated with operating a low-flow (<10 gpm) GAC canister system consists of turning the system on and off daily and periodically changing the exhausted GAC canister; operator supervision of this type of system usually is not required. Energy costs associated with a low-flow GAC system consist of the operation of a small influent pump.

Conversely, labor and energy associated with the UV/H$_2$O$_2$ system costs are significant; the additional 30 hours of treatment requires direct operator system supervision and the reactor uses approximately 110
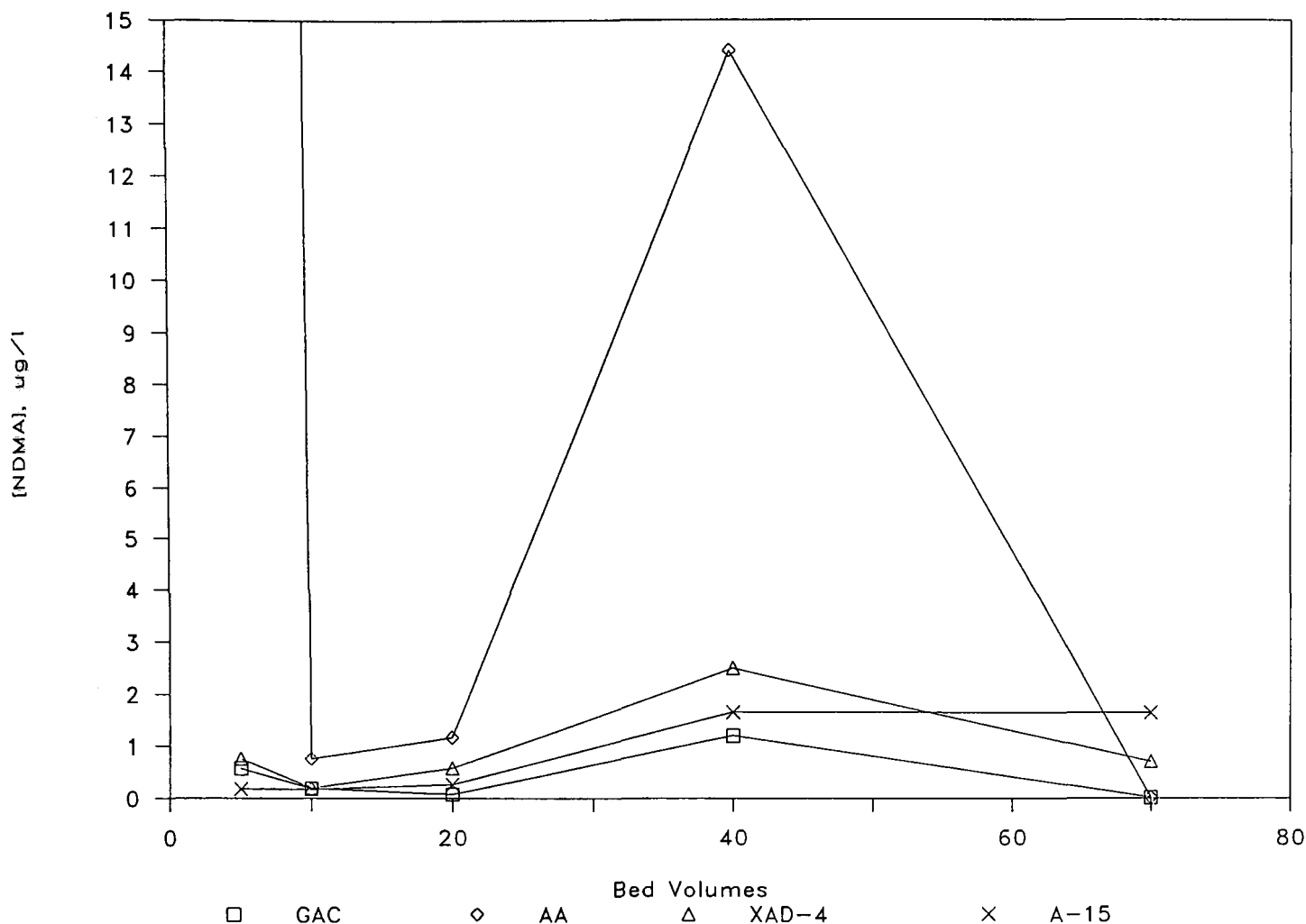
Figure 5
NDMA Adsorption Study

kw/operating hour. The cost of treating 1,000 gallons with the UV/H$_2$O$_2$ reactor for an additional 30 hours is approximately $1,450. Therefore, the cost of treating all 300,000 gallons of wastewater for the additional 30 hours is $435,000 and the time involved is 9,000 hours.

These estimated costs show that using the activated carbon system as a secondary treatment unit will result in a cost savings of approximately $423,000, which is significant compared to the overall cost of treating the 300,000 gallons of water. In addition, the time saved by using activated carbon in the test configuration is approximately 8,400 hours for all 300,000 gallons.

ADDITIONAL RESEARCH EFFORTS

Further testing will be performed using the coconut shell-based activated carbon to determine whether increased EBCTs and/or pH adjustment would result in reduced NDMA effluent concentrations from the activated carbon column and to determine actual activated carbon NDMA-adsorption capacity.

CONCLUSIONS

All adsorbents were able to remove NDMA from the test influents, except for activated alumina during the initial bed volumes. The Amberlyst 15 WET resin performed slightly better than the XAD-4 resin. Activated carbon was considered the best of the four adsorbents evaluated and will be further optimized in future studies. Also, the effluent from the GAC had consistently lower NDMA concentrations than the effluent from the UV/H$_2$O$_2$ system. It is believed that effluent

NDMA concentrations less than 100 pg/L can be reached using GAC as a secondary treatment process. Economic analysis indicates that using GAC as a secondary treatment system after 20 hours of UV/H$_2$O$_2$ treatment would result in a net savings of $423,000 and 8,400 hours of treatment time.

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Hazardous Waste Incineration: Remedy Selection and Community Consensus Building at Rocky Mountain Arsenal

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ABSTRACT

This paper discusses the selection of a technical solution to a major serious hazardous waste problem and development of widespread community support for that solution; it is a success story. Rocky Mountain Arsenal is located in the Denver metropolitan area and has frequently been called the "most contaminated piece of ground in the United States," or the nation's most serious hazardous waste site. The single most pressing and urgent problem at Rocky Mountain Arsenal is destruction of approximately 9 million gal of toxic liquid waste from Basin F, an evaporative pond dating to the 1950s. In 1989 and 1990, a remedy selection process was conducted under CERCLA, and a submerged quench incinerator was selected. The remedy selection process is of interest for several reasons:

- First, the waste is unique and has physical and chemical properties that make it hard to treat in most conventional processes (therefore this was technically challenging)
- Second, the work was done under a regulatory arrangement that made it necessary to accommodate the concerns and interests of five federal agencies, a private company and the State of Colorado
- Third, a 10-yr history of (mostly unsuccessful) treatability studies and the potential availability of promising (but untested) new technologies presented an uneven set of technical data
- Fourth, for practical and legal reasons, the remedial decision had to be made, and the cleanup completed, within about a 40-mo time frame
- Fifth, the selected remedy called for installing a hazardous waste incinerator within the Denver metropolitan area, a traditionally environmentally active area
- Sixth, a significant part of the remedy selection task was an innovative community relations program that was aimed at building consensus for a decision to avoid post-decision opposition (the Army issues a "decision document" in lieu of ROD)

The most interesting aspect of all was that no widespread public opposition to this incineration proposal was experienced when the decision was announced; on the contrary, the U.S. EPA, State of Colorado and several local citizen groups endorsed the decision. The incineration plant is being designed and will be built and operated without formal permits, and the cleanup is expected to be completed on or ahead of schedule. The key elements of this controversial and successful process are:

- A broad and imaginative technology screening process

- Early and intensive use of quantitative risk analysis (as a technology screening tool, for building public consensus for an on-site vs. off-site decision and for the detailed evaluation of remedial alternatives)
- Use of formal decision analysis techniques (to clarify issues and tradeoffs, rank the alternatives, and predict/resolve concerns arising out of the points-of-view of the many public and private groups affected by the decision)
- Consensus building through direct public participation in the technical decision, in a community relations program

PROBLEM OVERVIEW

For several years preceding 1988, remediation program managers at Rocky Mountain Arsenal (RMA) had accumulated waste treatability data that suggested that selection of an incineration remedy seemed possible if not likely at this site. In mid-1988, the Army agreed to a cleanup completion date for Basin F liquids that meant that studies, design, construction, testing and operation had to be completed in 5 yr, which is less than half of the normally required time for a hazardous waste incinerator, if that was to be the chosen remedy. Given this tight time schedule, delays of any length could not be tolerated; indeed, there was a pressing need to accelerate the program. To meet this challenge, a technical study was needed that not only addressed the subject matter and made a credible remedy selection, but also anticipated the concerns and likely reactions of the public and regulators and resolved these concerns prior to making a final decision. Furthermore, some type of community involvement program was needed that would give the public a role and a voice in the final decision, thereby building consensus and reducing the possibility of delays from local political pressure or litigation of local origin.

HISTORY OF BASIN F LIQUIDS

Rocky Mountain Arsenal

Rocky Mountain Arsenal (RMA) is an installation of the U.S. Army Armament, Munitions and Chemical Command (AMCCOM). RMA occupies more than 17,000 acres (approximately 27 mi^2) in Adams County, adjacent to and directly northeast of metropolitan Denver, Colorado. RMA is bounded on the south by industrial uses and Stapleton International Airport, on the west and northwest by residential neighborhoods ranging from medium to low density and on the north and east by agricultural lands, mostly rangeland. To the casual observer, RMA appears to be wide open, gently rolling prairie with a few widely dispersed concentrations of buildings or industrial facilities.

Wildlife is abundant, including a few threatened and endangered species such as bald eagles.

RMA was established in 1942 and has been the site of manufacture of chemical incendiary munitions and chemical munitions demilitarization. Following World War II, Congress directed the leasing of portions of RMA to private commercial interests; some of the industrial production facilities at RMA were leased to chemical companies. Agricultural chemicals including pesticides and herbicides were manufactured at RMA from 1947 to 1982. Present-day contamination problems at RMA result from both the military and agricultural chemicals manufacturing activities. All industrial activities at RMA ceased in 1982, and the Army's attention focused on cleanup of the contaminated land and water resources. Initial remedial activities were planned and implemented by the Corps of Engineers; in recent years, the mission of RMA has been redefined to be contamination cleanup, and the remediation program is now managed directly by AMCCOM, through the RMA Program Manager's Office.

Disposal practices at RMA have included routine discharge of industrial and munitions waste effluents to evaporation basins. Spills of raw materials, process intermediates and final products have occurred within the manufacturing complexes at RMA. Many of the compounds are mobile in groundwater.

History and Status of Basin F

In 1956, an evaporation pond called Basin F was constructed in the northern part of RMA. Basin F had a surface area of 92.7 ac and a capacity of approximately 243 gal. The basin was created by constructing a dike around a natural depression and lining it with a 0.375-in. catalytically blown asphalt membrane. An earth blanket approximately 1-ft thick was placed on top of the membrane to protect it. A vitrified clay pipe with chemically resistant sealed joints was installed between Basin F and the facilities where the wastes were generated. In 1962, a low dike was placed across the southeast corner of the basin to enclose an area of approximately 8 ac. From August 1957 until its use was discontinued in December 1981, Basin F was the only evaporative disposal facility in service at RMA. In 1982 the Army, Shell Oil Company, the U.S. EPA and the Colorado Department of Health agreed to start a cooperative development plan for a comprehensive remedy for the environmental situation at RMA. In 1986, the Army, Shell and the U.S. EPA, with input from the Colorado Department of Health, agreed that an accelerated remediation be undertaken pursuant to CERCLA to contain the liquids and contaminated soils in and under Basin F.

In the first part of Basin F remediation, Basin F liquids were transferred to three lined steel storage tanks and to one double-lined covered pond. Transfer of Basin F liquids to tanks and the surface pond for interim storage was initiated in May 1988 and completed in December 1988. Prior to this time, additional liquid storage capacity in the form of a lined north surface pond had been planned, since seasonal precipitation had increased the volume of liquid beyond the initial estimate. Presently, approximately 4 million gal of liquid are stored in the tank tank and 4.5 million gal in a portion of the north surface pond called Pond A.

The present Interim Response Action (IRA) for Basin F liquids addresses treatment and disposal of the contents of the storage tanks and Pond A. This IRA was initiated in September 1988. It includes characterization of the stored Basin F liquids, selection of a treatment alternative for the liquids, a community relations program that was integrated with the remedy selection process, pilot-scale demonstration of the selected treatment technology and detailed engineering design of the remedial treatment process. The first steps of this work, characterization of the liquids and selection of a preferred treatment alternative, were done in accordance with the five-step process for remedy selection prescribed generally by Section 121 of CERCLA and detailed in the NCP (Sections 300.415 and 300.430 (e)). The community rela-

tions program was in accordance with EPA guidance for community relations programs for NPL sites. The remaining steps, pilot testing and detailed engineering design, are underway and are planned to be completed by the end of 1990. This schedule will lead to completion of construction and testing in late 1991 or early 1992 and completion of the cleanup action (destruction of Basin F liquids) by mid-1993.

Characteristics of Basin F Liquid

In this study, characterization of the Basin F liquids consisted of sampling and analyzing the wastes to determine their chemical and physical properties in relation to engineering design and performance requirements of potential treatment processes and to provide the basic chemical parameters needed for a risk analysis of alternatives selected for detailed evaluation.

This testing confirmed that Basin F liquids are nearly saturated with common salts and ammonia gas. They also contain heavy metals such as copper and arsenic. In addition, they contain low levels of pesticides and byproducts of pesticide and chemical warfare agent manufacturing. The characteristics of Basin F liquids constrain the choice of treatment and disposal techniques and may require special design of treatment alternatives. For example, Basin F liquids may precipitate solid salts or release ammonia gas when stirred or combined with certain chemicals. The amounts of heavy metals, particularly copper, in the Basin F liquids may rule out certain treatments for the organic compounds also contained in the liquids. The high salt content of the liquids is corrosive to many kinds of treatment equipment.

REGULATORY FRAMEWORK

The cleanup of Basin F liquids is subject to two principal regulatory imperatives: CERCLA, and the Federal Facility Agreement for RMA. In addition, a number of other regulations and policies (ARARs) have been applied to the remedy selected for Basin F liquids, and certain other regulatory positions were considered in forming the remedial decision.

Remedial Authority

The destruction of Basin F liquid is an "interim response action" planned to be completed prior to an Arsenal-wide cleanup that is being defined in RI/FS studies. These RI/FS studies, which will lead to "final response actions," are being conducted under the Remedial Authority of CERCLA. The guidance for these RI/FS studies exists in a number of well-known U.S. EPA guidance documents with titles like, Guidance for Conducting Remedial Investigations Under CERCLA.

The interim response actions, on the other hand, are conducted under the Federal Facility Agreement and CERCLA. Guidance for studies to select appropriate interim remedies CERCLA is less well developed, occurring in sketchy form in the NCP. At the time that the Basin F remedy selection studies were conducted, no formal guidance documents existed for treatment assessment and remedy selection, and only draft guidance existed for conduct of community relations programs.

In general, CERCLA encourages a practical and expedient approach to selecting and implementing a short-term remedy for urgent contamination problems. In developing the final response actions, a comprehensive remedial investigation and risk assessment followed by a systematic feasibility study are required. For an interim response action, no remedial investigation is required and the surrogate for a feasibility study is a loosely defined "engineering evaluation/cost analysis," where cost and technical performance are the only factors that need to be considered in choosing a remedy.

The Basin F Liquids interim response action followed procedures similar to a removal under CERCLA, calling the Basin F Liquids study a "Treatment Assessment" rather than a feasibility study. The study was patterned after a CERCLA feasibility study

and was accompanied by an extensive community relations program. The treatment assessment and remedy selection were similar in appearance to a CERCLA feasibility study, but differed notably in several ways:

- Detailed engineering performance data on a number of treatment alternatives were considered at an early stage in the study, and the detailed evaluation of alternatives was limited to a small set of technical options.
- Quantitative risk analysis was included in the comparison of alternatives.
- A community relations program was relied upon for technical input to the remedy selection.

All of these measures were oriented to obtaining a practical and widely-accepted decision that could be implemented in the short 5-yr time frame. The decision that was reached could be evaluated and defended in terms of CERCLA. The process used to reach the decision was streamlined by the implementation of CERCLA at the site through the Federal Facility Agreement.

Federal Facility Agreement

In 1989, a Federal Facility Agreement (FFA) was signed by the U.S. EPA, the Army and Shell; the State of Colorado, which is given certain rights in this agreement, did not sign the Agreement, but participates in the activities outlined in the FFA. In the FFA, the Army and Shell agreed to share certain costs of the remediation, which was to be developed and performed under the oversight of the U.S. EPA, with opportunities for participation by the State of Colorado. The long-term remediation is a complex task that will take several years to complete.

The Federal Facility Agreement specified 13 Interim Response Actions determined to be necessary and appropriate to remove active sources of contamination and to prevent the spread of contaminants. Remediation of Basin F liquids, sludges, and soils is one of the 13 IRAs and is to be addressed in two parts. The first part, now completed, was removal of the liquids to secure storage and removal and stockpiling of the soils and sludges to a double-lined and capped temporary waste pile. The second part concerns Basin F liquids disposal. The time frame for completion of the second part is tied to agreed-upon limits to interim storage of Basin F liquids, and is set at 5 yr from May 1988.

The FAA states that all studies and cleanup done pursuant to the FAA will be done in accordance with CERCLA, insofar as practical, and the FFA calls for community relations programs to be implemented in accordance with CERCLA. The FFA requires that studies done under its authority conform to numerous review and comment procedures involving all the parties to the FFA.

Other Regulatory Influences

The State of Colorado has long maintained that at least a portion of the RMA cleanups are RCRA closures rather than CERCLA actions, and that the State should have privacy in directing these actions. (This disagreement is the primary reason why the State is not a signatory of the FFA.) The Army dismisses this claim specifically, but generally follows the substantive requirements of RCRA as ARARs to interim response actions planned at RMA, consistent with the expeditious implementation of solutions to urgent contamination problems. In the case of the Basin F Liquids interim response action, most of the substantive technical requirements of a typical RCRA permitting process were incorporated as ARARs, while many of the time-consuming administrative requirements of RCRA were not.

REMEDY SELECTION PROCESS

The remedy selection process consisted of three parts: a technical study, a regulatory process and a community relations program. These are discussed separately below.

Technical Study

The technical study to identify feasible treatment or disposal alternatives and select a preferred alternative consisted of five steps:

- Waste characterization
- Screening of technologies and development of alternatives
- Treatability studies
- Detailed evaluation of alternatives
- Selection of a preferred alternative

Waste Characterization

For the Basin F Liquids interim response action, characterization of the Basin F liquids consisted of sampling and analyzing the wastes to determine their chemical and physical properties in relation to engineering design and performance requirements of potential treatment processes and to provide the basic chemical parameters needed for a risk analysis of alternatives selected for detailed evaluation.

Two samples of the Basin F liquids were taken from Pond A. These samples were submitted for chemical testing and the results were compared to those from other recent Basin F liquid sampling efforts.

Screening of Technologies and Development of Alternatives

Forty different treatment technologies were identified and evaluated for their ability to tolerate the chemical and physical characteristics of Basin F liquid and achieve the general cleanup objectives of the IRA. The forty technologies encompassed all four of the basic strategies known to treatment science:

- Thermal destruction
- Immobilization
- Separation
- Chemical/biological treatment

Certain technical objectives controlled the identification and screening of alternative technologies:

- Ability to process the waste within the 5-yr time frame
- Demonstrated ability to treat the waste, based on bench-scale or pilot tests
- Ability to meet ARARs
- Orientation to the primary remedy selection objective of CERCLA, to achieve overall protectiveness of human health and the environment
- Orientation to the CERCLA guidance stressing permanent solutions that reduce toxicity, mobility or volume of hazardous substances

Of the 40 technologies, only 12 were found to be potentially feasible, given the physical and chemical properties of Basin F liquids. No separation technology was found to be feasible. The 12 potentially feasible technologies were studied further in terms of overall protectiveness, implementability within the stipulated time frame and ability to meet Applicable or Relevant and Appropriate Requirements (ARARs). In the end, five technologies were judged to be feasible, implementable within five years, protective of human health and the environment and able to meet ARARs:

- Electric Melter furnace (thermal destruction process)
- Solidification (immobilization process)
- Submerged Quench Incineration (thermal destruction process)
- Wet Air Oxidation (chemical process)
- Wet Air Oxidation with Biotreatment (chemical-biological process)

In developing remedial alternatives that would use these technologies, both on-site and off-site locations were considered. The alternatives evaluated included the following:

- Off-Site Alternatives
  - Existing Off-Site Army Facilities
  - Existing Off-Site Commercial Facilities
    - Deep Well Injection
    - Hazardous Waste Incinerators
  - Associated Transport Facilities
    - Pipeline
    - Tank Trucks
    - Rail Cars
- On-Site Alternatives
  - Existing Arsenal Facilities
  - Newly Constructed Arsenal Facilities
    - Electric Melter Furnace
    - Solidification
    - Submerged Quench Incineration
    - Wet Air Oxidation
    - Wet Air Oxidation with PACT

A brief summary of the technical characteristics and the strengths and weaknesses of these treatment alternatives is given below. All of the on-site, newly constructed treatment alternatives were capable of being designed and implemented to be protective of the community and the workers and to meet ARARs to the maximum extent practicable. Alternatives which reduce contaminant toxicity, mobility or volume are more protective of human health and the environment than alternatives that do not.

The greatest differences between the alternatives considered were seen in the areas of treatment efficiency (reduction of toxicity, mobility and volume) and implementability (feasibility, reliability and availability). The following discussion focuses on characteristics of the alternatives that make each alternative distinctive from the others.

Because of the history of the Basin F Liquids Disposal Interim Response Action, three types of alternatives which often are considered in the remedy selection process for CERCLA are not considered here. These types of alternatives include the No Action, Monitoring and Institutional Controls alternatives. Since the Interim Response Action discussed here directs the Army to choose a strategy for treatment and disposal of Basin F liquids now in storage, the No Action, Monitoring and Institutional Controls alternatives were, in a peremptory fashion, judged unacceptable for application to Basin F liquids.

Alternatives evaluated for treatment of Basin F liquids are discussed in the following sections.

Off-Site Alternatives

Existing Off-Site Army Facilities

Several U.S. Army installations operate or have operated hazardous waste incinerators for the demilitarization of chemical warfare agents or other military hazardous wastes. However, each of these facilities was constructed to address specific wastes from its respective site and none has equipment designed to operate on the particular admixture of wastes found in Basin F liquids. Thus, these incinerators are technically unsuitable. Moreover, construction of a new, technically suitable incinerator for Basin F liquids at these sites is contrary to the intent of CERCLA, which prefers on-site waste remediation where possible.

Existing Off-Site Commercial Facilities (Deep Well Injection)

With reference to off-site (or on-site) deep well injection, it was concluded that direct disposal approaches which involve no treatment are in opposition to the objectives of the Federal Facility Agreement. Specifically, these approaches will not meet the requirement of providing "permanent and significant" reduction of toxicity, mobility or volume. In addition, the deep well injection approach is irreversible and offers no opportunity for later treatment.

The Federal Facility Agreement stipulates that the Basin F liquids remediation will attain ARARs to the maximum extent practicable. Primary guidance (U.S. EPA, 1988) defines reduction of toxicity, mobility or volume as "permanent and significant reduction" through "destruction of toxic contaminants, reduction of the total mass of toxic contaminants, irreversible reduction in contaminant mobility, or reduction of total volume of contaminated media" (Section 7.2.3.3, Draft Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA, U.S. Environmental Protection Agency, 1988). Finally, deep well injection of Basin F liquids was tried in the past at RMA and failed due to the physical properties of the waste.

Existing Off-Site Commercial Facilities (Hazardous Waste Incinerators)

A survey of the capabilities of existing commercial hazardous waste incinerators showed that among all of the facilities in the nation, only three sites with liquid injection incinerators were equipped to treat Basin F liquids. However, the actual technical suitability of equipment at these installations had not been proven. In addition, each of these three commercial facilities has indicated that they would require a treatment contract that would allow the facility to refuse, at any time and at their discretion, receipt of Basin F liquids for treatment. Thus, the commercial facilities would not guarantee that Basin F liquids would be treated within the agreed-upon time frame, nor would they guarantee completion of treatment of all Basin F liquids.

Newly Constructed Off-Site Facility

A new treatment facility for Basin F liquids could be built off-site in a location that the Army could purchase or lease. Such a facility could be located such that it would be physically removed from any populated area, and thereby could presumably present a lower operational risk to humans. A new off-site facility, like any of the on-site options, could be designed and built to attain ARARs and achieve cleanup objectives. The drawbacks of a newly constructed off-site facility are the time required for permitting and the requirement to transport the waste.

On-site facilities would be constructed as a CERCLA action at a CERCLA site and would not require environmental permits from Federal, State or local agencies. An off-site facility, on the other hand, would not be considered a CERCLA facility, but rather would be viewed as a new waste treatment, storage or disposal facility (TSD) and subject to permitting and regulation under RCRA. The amount of time currently required to secure a RCRA permit for a TSD in Colorado is 3 to 5 yr, due to the complexity of application data requirements and the number and duration of agency and public reviews. When the permitting time is added to the time required to design, test, build and operate the treatment facility for Basin F liquids, the total time required for this off-site option exceeds the time available, as agreed to by the parties to the Federal Facility Agreement.

Associated Transport Facilities (Pipeline)

Conveyance of Basin F liquids through a pipeline to an off-site hazardous waste facility was considered. Although trans-state and interstate pipelines exist to convey fuel products, such as natural gas and guel oils, no pipeline suitable for liquid hazardous waste presently exists. Therefore, a separate pipeline would have to be built to transport Basin F liquids. The potential for leakage of Basin F liquids due to joint failure, corrosion failure and freeze damage under Colorado weather conditions is substantial. Additionally, since Basin F liquids are a saturated or supersaturated brine solution, they could not be piped long distances without considerable dilution to prevent salt precipitation and line pluggage. Thus, the volume of wastes would be substantially increased. The cost of constructing a suitable pipeline and supplying the power to pump the Basin F liquids long distances would

be greater than the cost of either off-site bulk transport or construction of an on-site treatment unit.

Associated Transport Facilities (Tank Trucks)

Appropriate tank trucks exist that can safely transport Basin F liquids over public highways. The scenario used here consisted of tank trucks of approximately 5,000-gal capacity used to transport Basin F liquids off-site for treatment. These trucks would be owned and furnished by a transportation contractor. To complete treatment of Basin F liquids in 1.5 yr, approximately 500,000 gal would have to be transported per month. Depending on the location of the treatment facility, this could require using more than 20 tank trucks per month (assuming five round trips each per month) to transport Basin F liquids. Based on a survey of transportation contractors, we determined that this number of tank trucks did not appear to be available from one company.

Most available tank trucks are constructed of stainless steel material, which may not be compatible with highly corrosive Basin F liquids. There were only a few lined tank trucks available at the time of the survey. The risk assessment reported in the Treatment Assessment Report indicated that the risk of transporting Basin F liquids off-site by truck was significantly higher than the risk of transporting the liquids by rail car.

Associated Transport Facilities (Rail Cars)

The use of rail cars, typically of 20,000-gal capacity, was also evaluated. The risk of transporting Basin F liquids off-site for treatment by rail car was estimated to be low relative to any other transportation mode. Specialized rolling stock exists in sufficient numbers to accommodate shipments of Basin F liquid to an off-site location. Some of the rolling stock is lined; depending on the supplier, some tank cars might need to be lined prior to receiving Basin F liquid.

On-Site Alternatives

Existing Arsenal Facilities

No treatment facilities exist at RMA that are technically appropriate, or can be modified to be technically appropriate, for Basin F liquids.

Newly Constructed Arsenal Facilities

This group of alternatives includes the five technologies identified in the screening step of the Treatment Assessment Study. They are presented here in alphabetical order.

Electric Melter Furnace

The electric melter furnace would operate at high temperatures—approximately 2300° F—to destroy organic compounds in Basin F liquids. In the furnace (similar to a glass-making furnace), the organic compounds in Basin F liquids would be destroyed almost completely. The metals would form a molten salt that would float on top of the pool of glass which lines the bottom of the furnace. The molten salt would be removed from the furnace periodically, poured into forms and cooled in preparation for final disposal. The exhaust gases would include a mixture of oxides of nitrogen and other gases. Exhaust gases released to the atmosphere from this process would be passed through air pollution control devices and would meet government standards; these exhaust gases would be monitored to assure adherence both to regulated conditions and nonregulated health risk-based operating goals.

Operation of the electric melter furnace would require the transportation of 8100 yd³ of pure liquid anhydrous ammonia and 4400 yd³ of sodium hydroxide into the Arsenal each year. Both compounds would be used in the air pollution control process. However, the risk assessment indicated that the amount and concentration of ammonia transported to the site for this alterna-

tive could present a health hazard. The electric melter furnace process would produce salts, containing metals, of about 10% of the volume of the original Basin F liquids. These salts could be disposed in a hazardous waste landfill. The form and chemistry of produced salts are not suitable for subsequent metals recovery. Of the five on-site treatment alternatives evaluated, the electric melter furnace ranked at the low end of the mid-range of costs, with an estimated total project cost of $21.1 million. The electric melter furnace has not been commercially demonstrated to be feasible for destruction of wastes like Basin F liquid.

Solidification

The solidification process would mix various chemicals with the Basin F liquids to immobilize the metals and produce a solid. Organic compounds in Basin F liquids would be incorporated into the solid but would not be destroyed or immobilized and could be leached from the solid material. Because Basin F liquids contain large amounts of ammonia and nitrogen-containing compounds, chemicals would be added to react with these compounds and prevent the release of ammonia during mixing and curing of the solid. The Basin F liquids would be pumped into two batch mixing units and mixed with Portland cement, fly ash, soil and agents to reduce ammonia emissions. Mixing units would be sealed during operation. The moist mixture would be discharged into disposable 50-gal drums and held in an adjacent building for 15 days to complete the curing process.

Control measures will be used to reduce fugitive emissions from the solidification process. Exhaust from the mixing and curing areas would be treated by air pollution control equipment to control particulates and gases. The exact nature and concentrations of emissions of organic chemicals as well as dust are not known or readily estimated for the solidification process. Due to the quantities of mixing materials handled, dust emissions could be substantial.

Solidification would require the transportation into the Arsenal of 17300 yd³/yr of phosphoric acid, plus comparably large quantities of other compounds, primarily used to reduce the amount of ammonia released during mixing. Solidification would produce solids of approximately three times the volume of Basin F liquids, which would be disposed in a hazardous waste landfill.

Solidification is a common technology for many types of wastes, but is not known to have been applied to saturated brine, ammonia-bearing wastes like Basin F liquid in a commercial-scale operation. The solidified products of this process will meet present hazardous waste landfill leachability requirements, but are close to the acceptance threshold, and leachability testing prior to disposal may be required. Of the on-site treatment alternatives evaluated, solidification ranked as the most costly, with an estimated project total cost of $71.8 million.

Submerged Quench Incineration

The submerged quench incineration process would use a vertical downfired liquid incinerator. The liquid to be incinerated would be injected at the top of the furnace along with a supplementary fuel. Burning the liquid at high temperature (approximately 1900° F) would destroy the organic compounds in Basin F liquid almost completely. After incineration, the hot gases would be forced downward and cooled in a liquid quench task to aid in washing out particulates and cleaning the exhaust gases. The high temperatures would melt noncombustible components of the Basin F liquids, producing molten salts which would flow down the walls of the incinerator and also be cooled in the quench chamber. The brine from this process could be dried to produce a salt. The exhaust gases, which would include a mixture of oxides of nitrogen and other gases, would be passed through air pollution control devices. Exhaust gases released to the atmosphere from this process would meet government standards and would

be monitored to assure adherence both to regulated conditions and nonregulated health risk-based operating goals.

Operation of the submerged quench incineration process would require the transportation into the Arsenal of 26 rail cars (200,000-lb capacity each) per year of sodium hydroxide, a caustic compound used in the air pollution control process. The submerged quench incineration process would produce salts, containing metals, of about 10% of the original volume of the Basin F liquids. These salts could be disposed in a hazardous waste landfill. The form and chemistry of the dried salts would permit a subsequent metals recovery step that would result in an innocuous residual salt product. Compared to the other on-site treatment alternatives evaluated, submerged quench incineration is the least costly, with an estimated project total cost of $19.1 million. This process has been demonstrated commercially on saturated brine wastes like Basin F liquid.

Wet Air Oxidation

In the wet air oxidation and spray drying process, Basin F liquids would be fed under pressure to an oxidation chamber operating at approximately 500° F. In the chamber, organic compounds in Basin F liquids would break down into simpler, less toxic compounds. A minimum of 95% of the toxic organics would be destroyed. The metals and many organic compounds would remain in the liquid, although some gas also would be released by the reaction. The liquid from the oxidation chamber would be treated to neutralize ammonia. Then the liquid and gas from the oxidation chamber would be fed to a spray dryer. The dried salts containing metals would be separated and packaged for shipment to a hazardous waste landfill.

The gases, which would contain some volatile organic compounds and ammonia, would be passed through air pollution control devices. Exhaust gases released to the atmosphere from this process would meet government standards and would be monitored to assure adherence both to regulated conditions and nonregulated health risk-based operating goals.

Operation of the wet air oxidation process would require the construction of a large building to house the process and the transportation into the Arsenal of 260 railroad cars (100-ton capacity each) per year of highly concentrated sulfuric acid and 22 railroad cars of 50% sodium hydroxide. The sulfuric acid would be used to neutralize ammonia, and the sodium hydroxide would be used in the air pollution control process. The wet air oxidation and spray drying process would produce salts, containing metals and some simple organic compounds of approximately 10% of the total original volume of Basin F liquids. These salts could be disposed in a hazardous waste landfill. The form of the dried salts would permit a metals recovery step, but the organic content of the salts could affect the purity of recovered metals and would remain in the salts to some degree anyway; hence, metals recovery for this process is of questionable utility. Compared to the other on-site alternatives evaluated, the wet air oxidation and spray drying process is in about the midrange of costs, with an estimated project total cost of $48.2 million.

Wet Air Oxidation with Powdered Activated Carbon Bio-Treatment (PACT)

Wet air oxidation, PACT and spray drying would destroy organic compounds in Basin F liquids by subjecting them to high pressure and moderately high temperatures in the presence of air. After passing through the pressurized oxidation chamber (operating at approximately 500° F), the liquids would be further treated by biological action to destroy organics. In the chamber, organic compounds would break down to simpler, less toxic compounds. The metals and many organic compounds would remain in the liquid, although some gases would be released by the reaction.

Before liquid from the oxidation process was treated in the

PACT process, it would be pretreated to remove copper and ammonia and diluted. The liquid then could be sent to enclosed aeration basins for PACT biotreatment. The carbon would adsorb and retain organic compounds in the aeration basins so that microorganisms would have time to break them down. After PACT treatment, the liquid would be concentrated and spray-dried in a dryer similar to that used in the wet air oxidation and spray drying process.

The exhaust gases from the dryer, which would contain some VOCs and ammonia, would be passed through air pollution control devices. Exhaust gases released to the atmosphere from this process would meet government standards and would be monitored to assure adherence to both regulated conditions and nonregulated health risk-based operating goals. Overall, the wet air oxidation, PACT and spray drying process would destroy a minimum of 99% of the toxic organics in Basin F liquids.

Operation of the process would require the construction of several large buildings to house the process and the transportation into the Arsenal of 260 railroad cars (100-ton capacity each) per year of highly concentrated sulfuric acid and 22 railroad cars of 50% sodium hydroxide. The sulfuric acid would be used to neutralize ammonia, and the sodium hydroxide would be used in the air pollution control process. The process would produce dried salts, containing some metals and simple organic compounds, of approximately 20% of the volume of the original Basin F liquids. These salts could be disposed in a hazardous waste landfill.

The process includes a metals removal step and produces a brine with very low levels of residual organics; no further metals recovery or treatment of organics is feasible for the final residual brine. Compared to the other on-site alternatives evaluated, wet air oxidation, PACT and spray drying is in the top of the midrange of costs, with an estimated project total cost of $56.2 million.

Results of Screening

The screening process concluded with the development of seven remedial alternatives:

- On-site electric melter with solid residuals
- On-site solidification with solid residuals
- On-site submerged quench incineration with solid residuals (spray drying of brine product)
- On-site submerged quench incineration, brine product, metals removal and PACT treatment of brine, no residuals
- On-site wet-air oxidation with spray drying, solid residuals
- On-site wet-air oxidation, brine product, metals removal, PACT treatment of brine, no residuals
- Off-site incineration at an existing commercial facility, with rail transportation of untreated Basin F liquid

Preliminary Risk Assessment

In conjunction with the screening of technologies and development of alternatives, a preliminary quantitative risk assessment was performed. Risks of both on-site and off-site treatment alternatives were evaluated, and the results indicated that there should be very low potential cancer risks and no significant non-cancer health hazards from any of the treatment processes themselves. However, the risk assessment indicated that there may be some potentially significant health hazards associated with the transportation of Basin F liquids (to an off-site treatment facility) or from the transportation of treatment chemicals (on-site for the electric melter furnace, one of the treatment processes evaluated).

The potential health hazard risks were associated with possible exposure to the ammonia content of Basin F liquids and possible exposure to the pure liquid anhydrous ammonia which would be required for the electric melter furnace process.

Based on this preliminary health risk assessment, off-site treatment options were not considered further in the technical study.

Treatability Studies

Bench-scale or pilot plant tests were performed on Basin F liquids using each of the 12 technologies identified in the initial screening step as potentially feasible. These treatability studies were done over an 11-yr period from 1978 to 1989. Successful bench-scale or pilot-test data exist for all of the five technologies retained in screening and used in the development of remedial alternatives, i.e., all of the alternatives selected for detailed evaluation had been demonstrated to be capable of treating Basin F liquid.

Detailed Evaluation of Alternatives

Five alternatives remained for detailed evaluation (all newly-constructed on-site facilities). Each alternative was designed at a conceptual level, and an assessment of probable performance was made. This assessment included preparation of a detailed process description; sizing of the treatment alternative to meet the waste volume and schedule for this IRA; preparation of a materials balance to estimate volumes and quantities of feed, process, discharge and residuals streams; assessment of technical performance in terms of reduction of toxicity, mobility and volume; evaluation of the implementability of the process (technical maturity, track record, etc.); estimates of capital and operating costs; and identification of regulatory issues. This information was used in the selection of a preferred remedial alternative.

Briefly stated, this is how the alternatives compared:

- *Overall Protectiveness.* Of the on-site options, the electric melter furnace and submerged quench incineration have the highest organic chemical destruction efficiencies and are therefore the most protective of human health and the environment. Wet air oxidation with PACT and wet air oxidation alone will destroy 90% or more of the organic chemicals. Solidification does not provide any treatment to organics.
- *Air Emissions.* Of the on-site options, all processes but solidification will produce emissions that meet government standards and will have monitoring to assure adherence to regulated conditions and negotiated operating goals. Solidification emissions, particularly fugitive dust, will be difficult to estimate and will present monitoring and control problems.
- *Use of hazardous chemicals.* All of the on-site options will require importation of process materials to RMA. The chemicals required for the electric melter furnace present higher risks than chemicals required for any other process. The chemicals required for submerged quench incineration present lower risks than chemicals required for any other process.
- *Residuals.* The two incineration processes produce as residuals a metal-bearing salt that can be landfilled. The salts from the submerged quench process are suitable for a subsequent metals recovery step, while the salts from the electric melter furnace are not. The wet air oxidation processes produce as interim or final residuals a metal-bearing and organic bearing salt that is not generally suitable for metals recovery, although removal of impure metals will permit subsequent organics removal (PACT) and reduce the quantity of hazardous residuals. Solidification produces a hazardous waste that can be landfilled, but which is leachable for organics and to a lesser degree for metals. The residual is not suitable for subsequent treatment steps.
- *Waste volume.* The two incineration processes and wet air oxidation produce a volume of residuals that is approximately 10% of the waste volume. The wet air oxidation process with PACT produces a volume of residuals that is approximately 20% of the waste volume. The solidification process produces a waste product that is 300% to 500% of the original waste volume.
- *Commercially demonstrated process.* Of the on-site options, the submerged quench incinerator and the wet air oxidation processes have been demonstrated commercially on saturated brine wastes like Basin F liquid. Solidification has been demonstrated commercially on many types of wastes, but not on saturated brine, ammonia-bearing wastes like Basin F liquid. The electric melter furnace has not been commercially demonstrated for liquid hazardous wastes.
- *Cost-effectiveness.* Of the on-site options, the electric melter furnace and submerged quench incinerator are the least expensive. The wet air oxidation processes are two to two and one half times as expensive as incineration, and solidification is three to three and one half times as expensive as incineration.

Selection of a Preferred Alternative

A semiquantitative scoring and ranking technique was used to evaluate the five remedial options and select a preferred alternative. The technique derived from, and was based on, multiattribute utility theory and applications of these techniques in similar decision analysis exercises. CERCLA guidance (Section 121(b) and NCP Section 300.430(e)) identify seven evaluation criteria to be used in selecting a preferred remedial alternative. These criteria are:

- Overall protection of human health and the environment
- Compliance with Applicable or Relevant and Appropriate Requirements (ARARs) to the maximum extent practicable
- Reduction of toxicity, mobility and volume
- Short-term effectiveness
- Long-term effectiveness
- Implementability
- Cost

The first step in the evaluation procedure was to develop formally correct quantitative evaluation criteria out of these seven CERCLA remedy selection criteria. To do this, these seven criteria were broken down into more specific technical factors related to the set of alternatives under review (in accordance with U.S. EPA guidance); a total of 19 technical factors was assessed for each alternative. For example, short-term effectiveness was broken down into worker safety, community protectiveness and operational environmental impact factors. A panel of chemical and environmental engineers and a risk assessment specialist assigned technical scores to each factor for each alternative, using discrete interval scales developed in consultation with a decision analyst.

The next step was to establish tradeoffs between evaluation criteria, to provide for the correct handling of preferential information in the evaluation procedure. Weights (importance values) for each of the 19 factors were elicited from the technical panel by a decision analyst, using lottery and consensus techniques. Using the factor scores and the tradeoff values, an evaluation formula was established; technical factor scores were multiplied by the weights to yield weighted factor scores, and these scores were summed to yield an overall score for each alternative. The alternatives were then ranked in accordance with the scores. Controls introduced by the decision analyst in the construction of the discrete interval scales and the elicitation of weights kept this evaluation procedure formally correct and logically rigorous, but the written record of the evaluation and the results were easily understood by the lay public.

Sensitivity studies were done on the ranking by varying the weights (importance values) for the 19 ranking factors. These studies showed how the rank order would change if some factors were considered to be more important and others less important. This approach was used to model many hypothetical points of view, such as a point of view that emphasized protection of nearby residents over all other factors, or another point of view that emphasized all factors related to short-term or long-term risk and deemphasized factors related to cost. More than a dozen hypothetical points of view were modeled, including some extreme points of view (in which one or two factors received all the weight

and all other factors were suppressed). In addition, several other diagnostic sensitivity tests were run to understand better which factors were most influential in ranking. The sensitivity studies were used to identify a set of weights and a corresponding rank order that was reasonable and realistic and could be shared by many points of view. This rank order was recommended. The top ranking alternative in this rank order is the preferred alternative.

Results

In this analysis, the on-site submerged quench incinerator was consistently the highest ranking alternative, and only under extreme and unrealistic points of view could the submerged quench incinerator be made to rank second. The poorest performer in this ranking analysis was solidification, and only under extreme points of view could it be made to rank higher. The "middle" alternatives of wet air oxidation and electric melter generally ranked far below submerged quench. The recommended rank order was:

1. Submerged Quench Incinerator
2. Wet Air Oxidation
3. Wet Air Oxidation with PACT
4. Electric Melter Furnace
5. Solidification

Regulatory Process

The treatment study proceeded from a carefully reviewed and approved work plan to conduct of technical evaluations, review of interim conclusions, preparation of a draft and final treatment assessment report and then preparation of a proposed decision document. Both the treatment assessment and proposed decision document was presented in public hearings, and subsequently a final decision document was issued. This process assured that all affected and interested agencies had ample opportunities to exert an influence on the remedial decision.

This process was complicated by the number of entities involved; in addition to the Army, Shell and the U.S. EPA, the Departments of Justice, Health and Human Services and Interior and the State of Colorado were participants. Each entity brought different interests to the process along with different styles of dealing with other agencies and the public. To accommodate the large number of interactions required by the participants in the regulatory process, the Army arranged for numerous briefings, progress meetings, special purpose committees and written materials to keep the parties up-to-date.

Community Relations Program

To assure that the community at large also had opportunities to exert an influence on the remedial decision, a community relations program was implemented. The program included informational elements, such as fact sheets and presentations, as well as participatory (consensus building) elements, such as workshops and hearings. The community relations program started at an early point, and the public was made a participant in the evaluation of technical material and the development of a remedial decision. To give the program more visibility and make it function more effectively, the Army established a community relations task force to plan and oversee all of the community relations activities.

CONSENSUS BUILDING

In 1988, the Army agreed to a 5-yr limit on temporary storage of Basin F liquid, yet any of the feasible remedial alternatives would take several years to implement. A delay in implementing the selected remedy could not be tolerated if the 5-yr storage limitation was to be observed. If there was general agreement in the community on the selection of a remedy, then the chances for a program delay due to public opposition would be reduced. Therefore, the Army set out to build consensus in the community for a remedy selection, using the community relations program to dis-

seminate technical information and receive inputs from members of the public. The main elements of this consensus-building initiative are discussed below.

Frequent informational meetings

The Army held several meetings to brief special interest groups and the public at large on the progress of the technical studies.

Workshop

The Army held a day-long public workshop on the technical studies, and gave members of the public the opportunity to have first-hand experience in evaluating the technical information. In one exercise, the detailed evaluation and ranking of the seven remedial alternatives was opened up to the public, and the participants had the opportunity to alter the ranking weights as they wished and see in real time the effect this had on the ranking scores and rank orders. This analysis showed the participants in the public meeting that the Army's selection of a particular alternative was the reasonable result of a logical process, and that under a broad spectrum of points of view, the same technology (submerged quench incinerator) would rank first. This builds consensus for the technical evaluation.

Well-planned media relations

The Denver area press were invited to all public meetings and were given special briefings. Based on the high level of information made available to the media, no single-issue special interest groups were able to divert media attention.

Letting the public make part of the decision

In the informational meetings and the workshop, numerous concerns were expressed and repeated by the public, mostly concerning the operational safety of whatever remediation was selected and the objectivity of the Army in monitoring the remedial action. At the workshop, the Army committed to address these concerns by converting these concerns into elements of the remedial decision. Thus, for example, concerns over products of incomplete combustion (PICs) were addressed by a decision to conduct a special predesign pilot test; concerns over operational safety under severe weather or upset condition were addressed by a decision to include operational controls in the design; concern over the objectivity of monitoring was addressed by agreement to have an independent third-party monitor on-site. In all, 12 discrete decision elements were added to the basic technological remedy selection; all of these elements were shown in the decision document to be directly derived from public concerns. While the Army reserved the responsibility to select the remedial technology, the public owned a significant part of the decision concerning how the selected technology would be operated.

Advance resolution of all sensitive issues

The Army used an "open-handed" approach, by bringing up and resolving sensitive public issues early in the process, before they became points of contention. These issues included on-site versus off-site remediation, health risk studies, the effects of incineration, etc.

Establishment of standards-setting and dispute resolution procedures

The Army included standards-setting and dispute resolution procedures in the ARARs section of the decision document to give form to the operating guidelines and lasting commitment to safety and community interaction by the Army.

CONCLUSION

When the Decision Document describing the selected remedy was issued in March 1990, there was no widespread public opposition to the selection of a submerged quench incinerator for the

Basin F Liquids at RMA. On the contrary, state officials commended the Army on its selection process and lent their weight to the decision. There has not been any organized opposition to this incinerator since the decision was announced. The incinerator is in the final stages of design at the moment, and construction is scheduled to begin in a few months. Some of the principal lessons learned in this remedy selection and consensus building process are:

- Among the benefits of intensive planning is early identification and resolution of sensitive technical issues;

- Formal risk analysis is a cost-effective screening and evaluation tool because it addresses the top concerns of the public and most agencies;

- Sensitivity analysis of a formal ranking method is insightful and useful for planning consensus building activities;

- Early involvement of the public is key to building support for the decision;

- Direct use of public input in the technical decision improves the quality of the decision and avoids downstream delays.

Interim Response Actions: An Approach to Short-Term Remediation (Ahead of the Record of Decision)

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ABSTRACT

The environmental restoration of Rocky Mountain Arsenal (RMA) in Denver, Colorado, is a nationally prominent CERCLA project. An outgrowth of the settlement between the Federal Government and Shell Oil Company is a unique Interim Response Action Program being implemented at the Arsenal by the U.S. Army with technical assistance from Shell under U.S. EPA oversight.

Interim Response Actions (IRAs) were identified in the RMA Federal Facility Agreement as beneficial measures that could be taken prior to the final ROD for the entire Arsenal. A specially structured process was developed for the IRA program that simplifies the U.S. EPA's standard RI/FS program guidance. The IRA process starts with the assumption of utilizing existing data which correlate with the RI/FS site characterization. The next IRA process step, assessment, is the functional equivalent of the RI/FS steps of development and screening of alternatives, treatability studies and detailed evaluation of alternatives. The IRA decision document step corresponds to the RI/FS ROD. The IRA process also adds an implementation/design document step prior to remediation.

The unique features of the IRA process include the range of measures possible, how the process is administered, the regulatory review involved and the community relations program intended to encourage public involvement. In addition to the organizations already mentioned, the Department of Interior, the U.S. Fish and Wildlife Service and the Colorado Department of Health are afforded a nearly equal participation in the IRA process.

In practice, the IRA process has been an unqualified success. Beneficial mitigation is being accomplished at 13 IRA sites. The IRAs range in scope from treating and disposing of 8.5 million gallons of liquid to groundwater treatment systems to in situ soils treatment. The most notable of the IRAs is the Basin F site — one example of how well the IRA process works. The Basin F IRA has involved two separate phases that entailed the removal and temporary storage of contaminated soils and liquids, followed by final remediation of the liquids. Final remediation of the soils will be accomplished through the ROD. The first phase of the Basin F IRA has been completed and the second phase has just passed the Decision Document step.

INTRODUCTION

The environmental restoration of Rocky Mountain Arsenal (RMA) in Denver, Colorado, is a nationally prominent Superfund project. Out of the litigation between the Federal Government and Shell Oil Company has risen a unique solution for accelerated remediation of certain sites at the Arsenal. The Interim Response Action (IRA) program is being implemented by the U.S. Army with technical assistance from Shell under U.S. EPA oversight.

Interim Response Actions were identified in the RMA Federal Facility Agreement (FFA) as beneficial measures that could be taken prior to the final ROD for the Arsenal. Because IRAs are near-term remediation projects, they must be consistent, to the maximum extent practicable, with the final remediation to be defined by the ROD. Through the FFA, a specially structured process was developed for the IRA program that simplifies the U.S. EPA's standard RI/FS program guidance.

HOW THE IRA PROCESS WORKS

The IRA process is similar, but not identical, to the CERCLA RI/FS process (Fig. 1). After utilizing existing data to characterize the site of the IRA, the IRA process begins with the preparation of an alternatives assessment. The assessment step is equivalent to the RI/FS steps of development and screening of alternatives, treatability studies and detailed evaluation of alternatives. The goal of the assessment is to evaluate alternatives that can achieve the objectives of the IRA. The evaluation of alternatives follows general CERCLA guidelines and may include factors such as effectiveness, protection of human health and the environment, mitigation of the threat to human health, the reasonableness of cost and timeliness. Concurrent with the assessment, a proposed applicable or relevant and appropriate requirement (ARAR) determination is developed and issued. The principal signatories of the RMA Federal Facility Agreement (FFA) (i.e., U.S. Army, U.S. EPA Region VIII, U.S. Department of Interior and Shell Oil Company), referred to as the Organizations, are given 30 days in which to comment on the draft assessment and proposed ARARs. Although not a signatory of the FFA, the State of Colorado is allowed the same review of and comment on IRA documents as the Organizations.

Once the assessment and ARARs are finalized, based on comments received, a Proposed Decision Document is prepared to provide the rationale for the selected alternative and the revised ARAR decision.

BASIC CERCLA	RMA IRA
TECHNICAL STUDY (FS)	TREATMENT ASSESSMENT
COMMUNITY RELATIONS PROGRAM	COMMUNITY RELATIONS PROGRAM
REMEDIAL ACTION PLAN	DECISION DOCUMENT
RECORD OF DECISION	IMPLEMENTATION DOCUMENT
IMPLEMENTATION PLAN	
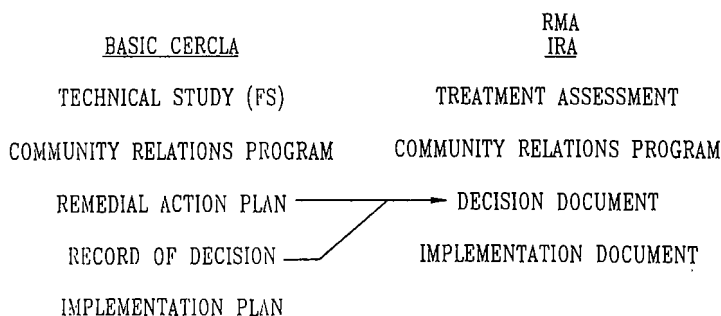
Figure 1
IRA vs. CERCLA Remedy Selection Process

The Decision Document step is equivalent to the RI/FS ROD. The Organizations and State (OAS) and the public are given 30 days to comment on the Proposed Decision Document and ARARs. At least one public meeting is held during the comment period to inform the community in the vicinity of RMA.

Following receipt of comments on the Proposed Decision Document from the OAS and the public, a Draft Final Decision Document is prepared. The Organizations then have 20 days to review the Draft Final Decision Document and to raise any objections. If no dispute is raised, the Draft Final Decision Document automatically becomes the Final Decision Document.

The final step in the IRA process is the additional requirement of an Implementation Document, which includes the final drawings, specifications, design analysis, cost estimate for implementation and deadlines for completion. During design or implementation, an Organization may advise the others if it believes that the IRA is being designed or implemented in a way that will not meet the IRA objectives as set forth in the Final Decision Document.

Disagreements that may arise between the Organizations are resolved through a mechanism called dispute resolution. The dispute resolution process consists of review of the issue at progressively higher levels of corresponding management authority among the Organizations. The dispute resolution process continues as necessary until it culminates at the final review committee level, where the Administrator of the U.S. EPA makes a binding decision for the Federal Government. Shell may seek judicial review if still unsatisfied with the decision. To date, no dispute has been raised to the final review committee.

At any time prior to the ROD, any Organization may request consideration of the need for additional IRAs or modification of existing IRAs. Additional IRAs have been considered and may be implemented in the future at RMA.

SPECIFICS OF THE IRA PROGRAM

In practice, the IRA process has been an unqualified success. Beneficial mitigation is being accomplished at 13 IRA sites (Fig. 2). The IRAs range in scope from treating and disposing of 8.5 million gallons of liquid to groundwater treatment systems to in situ soils treatment.

The FFA identifies 13 cleanup areas for the IRA program:

- Groundwater Intercept and Treatment System North of the Arsenal
- Improvement of the North Boundary System and Evaluation of all Existing Boundary Systems
- Groundwater Intercept and Treatment System North of Basin F
- Closure of Abandoned Wells on the Arsenal
- Groundwater Intercept and Treatment System in the Basin A Neck Area
- Basin F Liquids, Sludge and Soils Remediation
- Building 1727 Sump Liquid
- Closure of the Hydrazine Facility
- Fugitive Dust Control
- Sewer Remediation
- Asbestos Removal
- Remediation of Other Contamination Sources
- Pretreatment of CERCLA Liquid Wastes

When the IRA program was formulated in 1987, a combination of proposed one-time and ongoing actions was considered. Thus, ongoing projects such as application of dust suppressant and removal of asbestos were exempted from the requirement of a Decision Document and a public meeting. Other projects such as the construction of recharge trenches at the North Boundary System and the closure of abandoned wells were exempted from the requirements of an assessment and public meeting.

The IRA program can be broken into two broad cleanup areas. For example, IRAs A. B. C and E deal exclusively with the interception and treatment of groundwater contamination. All other IRAs can be grouped as removal or treatment actions.
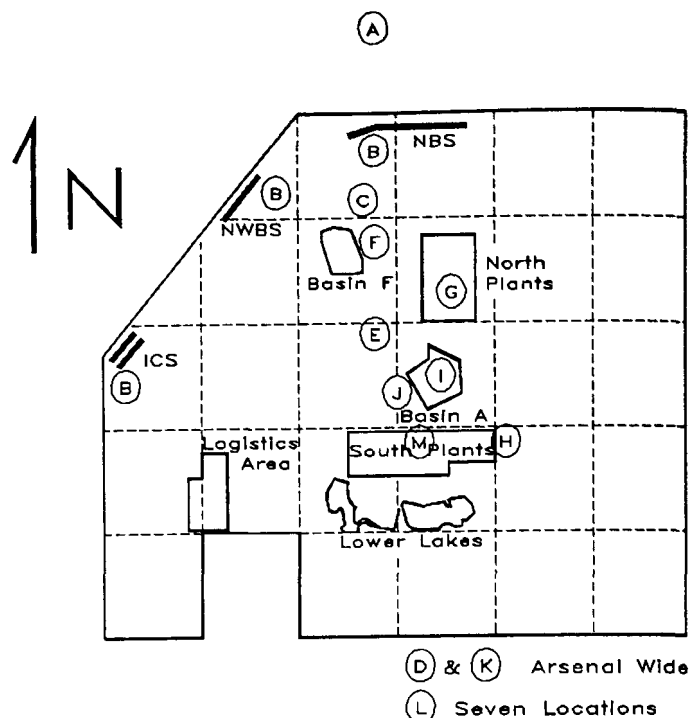
Figure 2
Approximate IRA Locations
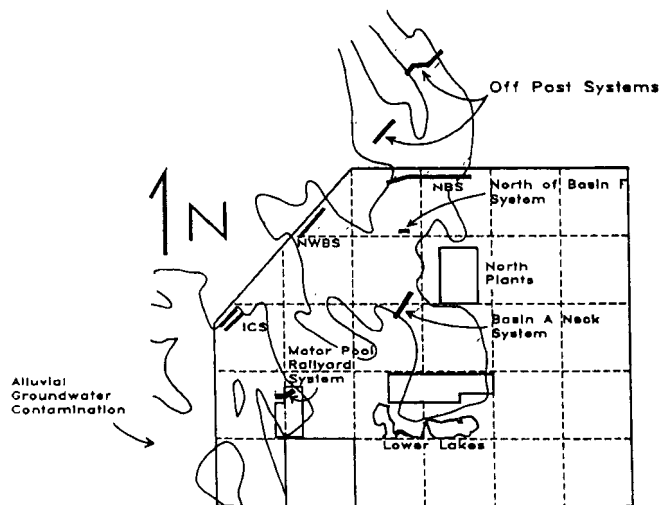
Figure 3
Groundwater Intercept and Treatment IRAs

GROUNDWATER INTERCEPT IRAS

The IRA for Groundwater North of the Arsenal (IRA A) was initiated to clean up the area just north of the Arsenal where contaminated groundwater had migrated off the Arsenal before the North Boundary System was installed (Fig. 3). The groundwater presented a threat of further migration and so was considered important enough to assess the need to construct one or more pump-and-treat systems in the area. The design of two interconnected intercept systems has been completed and the implementation document was issued in October 1990. Construction is scheduled to begin in 1991.

IRA B, Improvement of the North Boundary System and Evaluation of all Existing Boundary Systems, consists of three parts: (1) assessment of the need for improvements (such as expansion) to the North Boundary System and assessment, selection and implementation of any

necessary improvements to the system; (2) assessment of the other two boundary systems (Irondale and Northwest) and assessment, selection and implementation of any necessary improvements; and (3) implementation of the groundwater recharge trenches to increase the rate of reinjection of treated groundwater at the North Boundary System. Currently, construction of improvements to the North Boundary System is underway and is expected to be complete in December 1990. Assessment of the Northwest Boundary will be complete in December 1990, as well. The groundwater recharge trenches at the North Boundary are complete and have been operating since June 1990. The three boundary systems treat all contaminated groundwater approaching the boundaries before it leaves the Arsenal.

The Groundwater Intercept and Treatment System North of Basin F (IRA C) and the Groundwater Intercept and Treatment System in the Basin A Neck Area (IRA E) were designed to intercept and treat contaminated groundwater flowing through small channels the Basin F and Basin A. These systems are interior to the Arsenal and will treat water before it reaches the boundary systems. Treating contaminated water in this way will significantly speed up the final remediation after the ROD. These two IRAs are relatively close in location, so the Basin A Neck treatment system of granular activated carbon (GAC), which was complete and online in July 1990, will treat the North of Basin F groundwater after it is treated by an air stripper. The North of Basin F intercept system was complete in September 1990.

OTHER IRAS

From June 1988 until February 1990, 352 old and deteriorating farm wells and unused Arsenal wells were located and closed under IRA D, Closure of Abandoned Wells. The success of this IRA in closing wells on the Arsenal that had the potential to spread shallow groundwater contamination to deeper aquifers has prompted U.S. EPA to suggest an expansion to areas off the Arsenal where Arsenal contaminants exist in the groundwater.

IRA G, Building 1727 Sump Liquid, was initiated in May 1987. The sump, which was a central collection sump for the North Plants manufacturing complex, was filled to capacity with contaminated run-off from the other buildings. A 5-gpm treatment system was installed during the assessment portion of the IRA to begin liquid treatment and to alleviate the potential for overflow. More than 350,000 gallons of wastewater were treated by an activated alumina (AA) and GAC process, which removed the principal contaminants of fluorine, arsenic and diisopropyl methylphosphonate (DIMP). Continued operation of the small temporary system was eventually determined to be the preferred solution and the implementation has included expansion of treatment capacity to 7.5 gpm. IRA G served to treat water that would have had to be stored until after the ROD was issued and that could have leaked into the groundwater.

An assessment of the Closure of the Hydrazine Facility (IRA H) was already underway when the FFA was finalized. The facility had been closed since 1982 when the blending operations ceased. Fuels were removed from their holding tanks, which were triple-rinsed. The rinsate is unlike any other on the Arsenal and requires a unique treatment process. The preferred option for treating the remaining 300,000 gallons of hydrazine-contaminated rinsate is an ultraviolet (UV)/chemical oxidation system. In addition, the facility is to be dismantled once the wastewater has been treated and disposed. Implementation is scheduled to begin in early 1991.

IRA I, Fugitive Dust Control, consists of a periodic application of dust suppressant in Basin A. The application is necessary because Basin A no longer is filled with liquid and consists of highly contaminated soil. This situation creates a risk of windblown dust contaminating other areas of RMA and possibly locations beyond the boundaries. One application has been made since the IRA was initiated in 1988 and a second is planned for 1991.

The sanitary sewer system at RMA was included as IRA J because of its deteriorating condition in the area of the South Plants manufacturing complex and its location within saturated, contaminated alluvium in the Basin A area during seasonal high groundwater levels. The preferred alternative was in-place abandonment of the sewer in the South Plants and Basin A area. Most of the South Plants area will be abandoned, but remaining activities in the vicinity of South Plants will likely be linked by a new line to the rest of the sewer system. The replacement line will be constructed first, followed by in-place abandonment as South Plants buildings are closed. This IRA is presently being implemented.

IRA K, Asbestos Removal, was an outgrowth of ongoing Arsenal programs to remove asbestos from occupied buildings. U.S. EPA has decided that the IRA will eventually address all buildings at RMA prior to demolition. Asbestos has been removed from 10 occupied structures. More than 1,000 structures may eventually have asbestos removed prior to demolition.

"Hot Spots" is the title often used for IRA L, Remediation of Other Contamination Sources. This IRA addresses as a group those sites of suspected contamination that on their own might not warrant inclusion as a separate IRA (Fig. 4). To date, seven sites have been assessed and Final Decision Documents have been issued for six of those. The selected treatments range from in situ vapor extraction and in situ vitrification to groundwater extraction and treatment to capping and/or groundwater monitoring. This IRA is unique in that it allows the inclusion of new sites within its procedural mechanism upon approval of the Organizations.
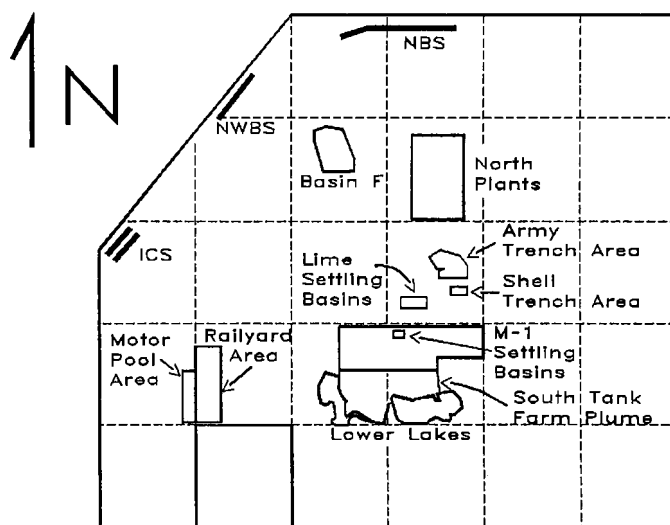
Figure 4
Locations of Other Contamination Sources IRA

The Pretreatment of CERCLA Liquid Wastes (IRA M) consists of the design, construction and operation of a wastewater treatment system to treat water generated by ongoing remedial investigation activities, feasibility study testing, laboratory wastes and other IRAs. This IRA is presently in design and completion of construction and startup will occur in the fall of 1991. The constructed treatment facility will continue treating wastewater as the final remediations are being implemented after the ROD.

Basin F IRA

Although the Basin F IRA is included in the "other" category, its extreme complexity and cost warrant a separate, detailed discussion. Basin F was built as a state-of-the-art, asphalt-lined evaporation pond in 1956 and was used as the primary disposal system for Army and Shell wastes until 1982. From its maximum capacity of 240 million gallons, it was estimated that approximately 4 million gallons of concentrated brine and waste remained by the summer of 1987. As the only remaining basin containing liquid, coupled with the wide variety of wastes it received and its lengthy operating history, Basin F represented one of the most complex cleanups at the Arsenal. It also represented a potential threat to wildlife, groundwater quality and air quality.

Two separate phases were recognized as necessary in remediating Basin F. In the first phase, conducted in 1988 and 1989, the liquid was removed from the basin and was stored and the most contaminated sludges and soils were consolidated into a double-lined, capped waste pile. Treatment of the liquid is to be carried out as a second phase within approximately 5 years from the time it was stored. The waste pile will be examined in the ROD.

Due to a heavy unexpected rainfall and the discovery of a false basin floor formed from crystalline condensate from the liquids stored there, a total of approximately 11 million gallons of liquid were removed from Basin F by September 1988. To accommodate this unexpected increase in liquid, an 8 million-gallon pond was constructed in addition to the originally planned 4 million-gallon tank storage capacity. By the time the pond was covered in May 1988, evaporation had reduced the total amount of stored liquid to approximately 8.5 million gallons. This amount has increased slightly over time due to the addition of leachate from the waste pile.

Approximately 500,000 yd^3 of contaminated material were placed in the waste pile. The material consisted of the Basin F walls, the liner, approximately 6 inches of material below the liner and the overburden of sludges above the liner (Fig. 5).

The second phase of this IRA was initiated in September 1988. Submerged Quench Incineration by the T-Thermal Sub-X Liquid Datur (TM) incinerator has been selected as the preferred treatment technology after an exhaustive review and assessment of treatment possibilities was conducted from 1979 through 1989. Design will be completed in December 1990, and installation on the site will begin in the spring of 1991. A trial burn has tentatively been scheduled for January 1992. Operations are expected to take place from May 1992 through the fall of 1993, thus completing liquid treatment within the 5-year limit.

LONG-TERM BENEFITS

By affording the Army and Shell an efficient regulatory process under which important actions can be accomplished prior to the ROD, the IRA program has played a significant role in the initial cleanup of RMA. Approximately $200 million in cleanup actions will have been completed by the time the ROD is issued (Fig. 6). Completion of the IRAs will simplify the eventual cleanup and, in the meantime, this approach will decrease the potential health threat of various sites on the Arsenal. Significantly, the cleanup of Basin F is now a greatly reduced cleanup action under the ROD simply because of the IRA. Only the waste pile soil, possible limited underlying soils and empty liquid storage facilities will remain after the IRA is complete.

Figure 5
Basin F IRA - Phase One
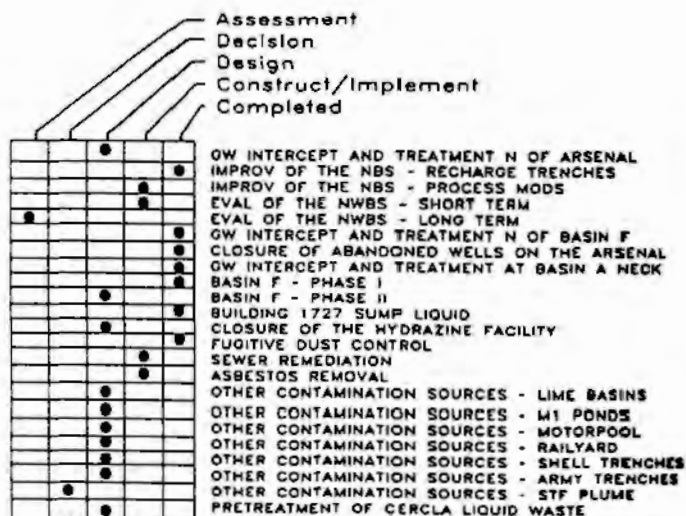
Figure 6
Summary of IRA Program Status

ACKNOWLEDGEMENTS

Selecting a Chemical Oxidation/Ultraviolet Treatment System and Successful Treatment of Hydrazine Wastewater at Rocky Mountain Arsenal

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ABSTRACT

The unique quality of wastewater and the stringent treatment requirements imposed by regulatory agencies can drastically impact the type of treatment selected for any site. Remediation options for treatment of 300,000 gallons of hydrazine-contaminated wastewater at Rocky Mountain Arsenal (RMA) in Denver, Colorado, are affected by the presence of hydrazine fuel compounds and n-nitrosodimethylamine (NDMA), a decomposition byproduct, as well as part per trillion (ppt) limits on NDMA in the effluent from the treatment system. Although ultraviolet (UV)/chemical oxidation treatment is a fairly common process for destruction of organic constituents in water, the treatment method has only recently been used to destroy more exotic chemicals such as the hydrazine fuel compounds and their by-products.

Steps taken in the development approach for the treatment system include a rigorous treatability testing and equipment selection program, the analytical method development and certification process for the hydrazine fuel compounds and NDMA, and development of the optimal treatment equipment configuration and operating parameters during design, construction and full-scale startup testing, all within significant time constraints set forth in the RMA Federal Facility Agreement (FFA).

INTRODUCTION

The Hydrazine Blending and Storage Facility (HBSF) at Rocky Mountain Arsenal (RMA) northwest of Denver, Colorado, was constructed in 1959 and operated for 23 years from 1959 to 1982. The 10-acre site (Figure 1) consists of two tank yards and a connecting pipeline and was used as a depot to receive, blend, store and distribute hydrazine fuel compounds. The primary operation was blending anhydrous hydrazine and unsymmetrical dimethyl hydrazine (UDMH) to produce Aerozine 50, a rocket propellant. The materials were manufactured elsewhere and were shipped to RMA for blending. Blending operations were not continuous and occurred in response to U.S. Air Force requests. Other operations at the HBSF included loading and unloading rail cars and tanker trucks, destroying off-specification Aerozine 50 and storing Aerozine 50, anhydrous hydrazine, monomethyl hydrazine (MMH), monopropellent hydrazine, hydrazine 70, UDMH and hydrazine.

Hydrazine and UDMH are unstable in the natural environment and rapidly decompose when exposed to the atmosphere. One decomposition byproduct of UDMH is NDMA, a suspected human carcinogen. In 1982, the U.S. Occupational Safety and Health Administration (OSHA) surveyed the HBSF and detected the presence of airborne NDMA within the facility. In May 1982, RMA ceased operations and closed the HBSF to all but safety-essential or emergency-response entries. In the process of closing the HBSF, piping and tanks were cleaned, and 300,000 gallons of decontamination water from these cleaning operations were generated. This wastewater is currently stored in three tanks (Figure 2). Each tank was sampled at four depths, and the ranges of concentrations of analytes found in the wastewater are summarized in Table 1. Analytes showing the highest concentrations include the hydrazine fuel compounds, NDMA, aniline and iron.
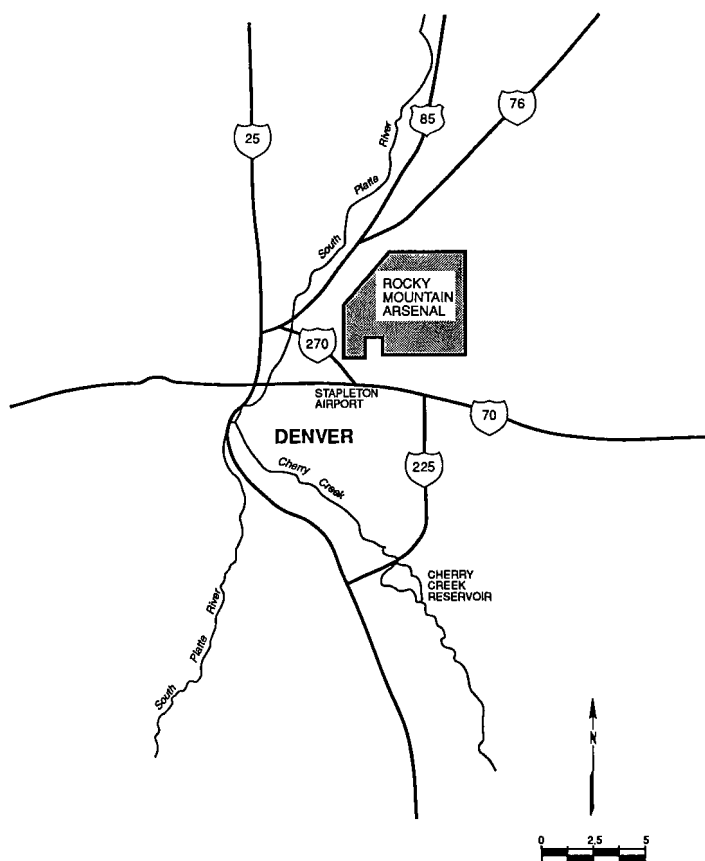
Figure 1
Location Map

In February 1989, a Federal Facility Agreement (FFA) was signed for cleanup of RMA, and a number of Interim Response Actions (IRAs) were initiated to alleviate certain concerns prior to the final remedial action. Before implementation of an IRA, the IRA process requires

Table 1
Range of Concentrations of Analytes Found in Hydrazine Wastewater at RMA

Analyte	200,000 gallon Tank (µg/l)	50,000 gallon Tank (µg/l)	In-ground Sump (µg/l)
Hydrazine Fuel Compounds/Nitrosamine			
Hydrazine	11,000 - 85,000	22,000 - 60,000	380 - 2100
Monomethyl hydrazine	14,000 - 18,000	50,000 - 36,000	
Unsymmetrical dimethyl hydrazine	11,000 - 79,000	11,000 - 82,000	85 - 1600
N-Nitrosodimethylamine	53 - 60	470 - 790	1.4 - 5.8
Volatile Organics			
Acetone	23.8 - 32.0	50.7	
Benzene	2.25 - 2.66	53 - 112	
Chlorobenzene		41.6	
Chloroethane		2000	
Chloroform	96.6 - 106	3000 - 4750	
Chloromethane	7.25 - 25.6	45.3	
1,2-Dichloroethane	1.61 - 1.67	66 - 143	
1,1-Dichloroethane	3.66 - 3.89	96 - 570	
1,1-Dichloroethene		13.1	
1,2-Dichloropropane		26.0 - 89.1	
Dimethyl sulfide	46 - 61	4.87 - 14.2	
Methylethyl ketone/2-butanone			13.3
Methylene chloride	61 - 110	2600 - 13,000	
O, P-xylene		1.84	
Tetrachloroethene		2.60	
Toluene		5.09	96 - 680
Trichloroethene		5.16	
Vinyl acetate		134 - 186	
Vinyl chloride		78.3	
Semivolatiles			
Aniline	1500 - 6400	1200 - 1460	
Atrazine	4.52 - 5.50	33.1 - 44.0	8.86 - 150
Benzothiazole	2.97 - 14.9	2.47 - 2.92	
4-Chloroaniline	2.88 - 2.94		
Malathion			0.574
4-Methylphenol			45.5 - 320
Naphthalene		8.18 - 9.68	
Parathion			3.78
Phenanthrene			
Phenol			4.12 - 4.52
Vapona		19.1	
bis(2-Ethylhexyl) phthalate	11.0	2.00	2.14
Metals			
Arsenic	16.1 - 20.4	43.1 - 66.3	220 - 288
Cadmium			0.601 - 1.88
Chromium	6.62 - 7.61	5.22 - 6.87	5.8 - 10.7
Copper		7.48	
Iron	6330 - 12,100	48 - 81,000	700 - 1080
Mercury	0.241 - 0.658	0.738 - 0.868	
Silver	0.224	0.462	
Zinc	12.4 - 22.8	12.2 - 28.9	24.6 - 55.4

µg/l = micrograms per liter

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completion of an Assessment Document, a Decision Document that includes applicable or relevant and appropriate requirements (ARARs), and a draft Implementation Document that includes design specifications. The Decision Document also specifies that the UV/chemical oxidation process is to be used to treat the hydrazine wastewater that currently is stored at the HBSF. The action levels for the contaminants of concern are shown in Table 2. NDMA's action level, also an ARAR, was derived from an overriding health-based goal of a 10^6 lifetime excess cancer risk. In an extremely conservative approach, discharge to ambient water immediately following treatment was assumed. Therefore, treating NDMA to the ultra-low level in the reactor was examined.

The decommissioning of the HBSF is to occur in two phases: (1) treatment of hydrazine wastewater and subsequent discharge of the wastewater to the RMA sanitary sewer system, and (2) decontamination of tanks and piping and demolition of all aboveground structures such as buildings, concrete, piping and support systems and storage tanks.

The objectives of the hydrazine wastewater treatment portion of the IRA include: (1) developing analytical methods and certifying the methods and laboratories that will perform the analyses under the Program Manager for Rocky Mountain Arsenal's (PMRMA) analytical certification program, (2) conducting a treatability test to determine whether qualified manufacturers can reduce the concentrations of

hydrazine fuel compounds present in the wastewater stored at the HBSF to concentrations near the action levels identified in the Decision Document, (3) selecting an appropriate UV/chemical oxidation treatment system and designing and constructing a full-scale treatment system to include one UV/chemical oxidation reactor, (4) conducting full-scale startup testing of the treatment system using approximately 10,000 gallons of hydrazine wastewater stored at the HBSF, (5) gathering sufficient process information from the full-scale testing to more specifically define operational treatment requirements, including kinetic data to predict treatment time necessary to achieve action levels identified in the Decision Document and (6) preparing an Implementation Document defining the step-by-step procedures for installation of a second treatment unit and treatment of the remaining hydrazine wastewater at the HBSF.

ANALYTICAL PROGRAM

Before any testing could be accurately conducted, methods for analyzing the hydrazine fuel compounds and NDMA had to be developed and certified in order to ensure that the ultra-low levels specified in the action levels could be reached in treatment. An analytical method for NDMA was previously certified under the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) certification program at a level of 200 ppt. Hydrazine, UDMH and MMH were not previously certified under the USATHAMA certification process because methods of analysis for these compounds had been shown to be unstable. Extensive research was conducted during the method development stages, and methods for NDMA and MMH were certified. The method for analysis of UDMH still is not certified because it remains unstable. Certified reporting limits are shown in Table 3.

One difficulty encountered in implementing this IRA is that analytical certification was not achieved at or below the action levels specified for this IRA. This can be seen by comparing the action levels in Table 2 with the reporting limits in Table 3.

TREATABILITY TESTING PROGRAM

Neither a literature review nor the manufacturers of UV/chemical oxidation equipment could provide much information regarding the treatment of hydrazine fuel compounds and NDMA by UV/chemical oxidation. Thus, the primary objectives of the treatability testing were to: (1) determine whether qualified manufacturers could reduce the concentrations of hydrazine fuel compounds and NDMA present in the wastewater stored at the HBSF to concentrations near the action levels; and (2) generate design and operational information for the full-scale treatment system. Bench-scale and pilot-scale testing were performed at the manufacturing facilities of three qualified vendors of UV/chemical oxidation equipment using representative wastewater collected from the largest tank in which hydrazine wastewater is stored at the HBSF. Peroxidation Systems, Inc., and ULTROX International performed bench-scale testing, while SolarChem Environmental Systems performed pilot-scale testing of their respective UV/chemical oxidation equipment. Analytical testing was performed by an independent laboratory. Hydrazine wastewater was collected, sampled and shipped in stainless steel drums to the three vendors. A sample of influent wastewater was analyzed for the hydrazine fuel compounds, NDMA, purgeable halocarbons and metals, and the results served as the influent baseline for all three vendors.

Visits were made to each vendor's manufacturing facility during the treatability testing to witness the testing and to assess the capabilities of each manufacturer. Effluent wastewater samples from the treatability testing were analyzed for NDMA and the hydrazine fuel compounds by developmental analytical methods not yet certified under the PMRMA program. Purgeable halocarbons and metals were analyzed using standard U.S. Environmental Protection Agency (EPA) methods.

Performance results from the treatability testing (Table 4) indicate that the hydrazine fuel compounds and NDMA were reduced by all three vendors to the respective detection limits of the developmental methods used for analysis. Purgeable halocarbons also were reduced to below detection limit levels. Thus, all three vendors met the objective of reducing the influent concentrations to action levels for the compounds of concern. Recommendations from the treatability testing for
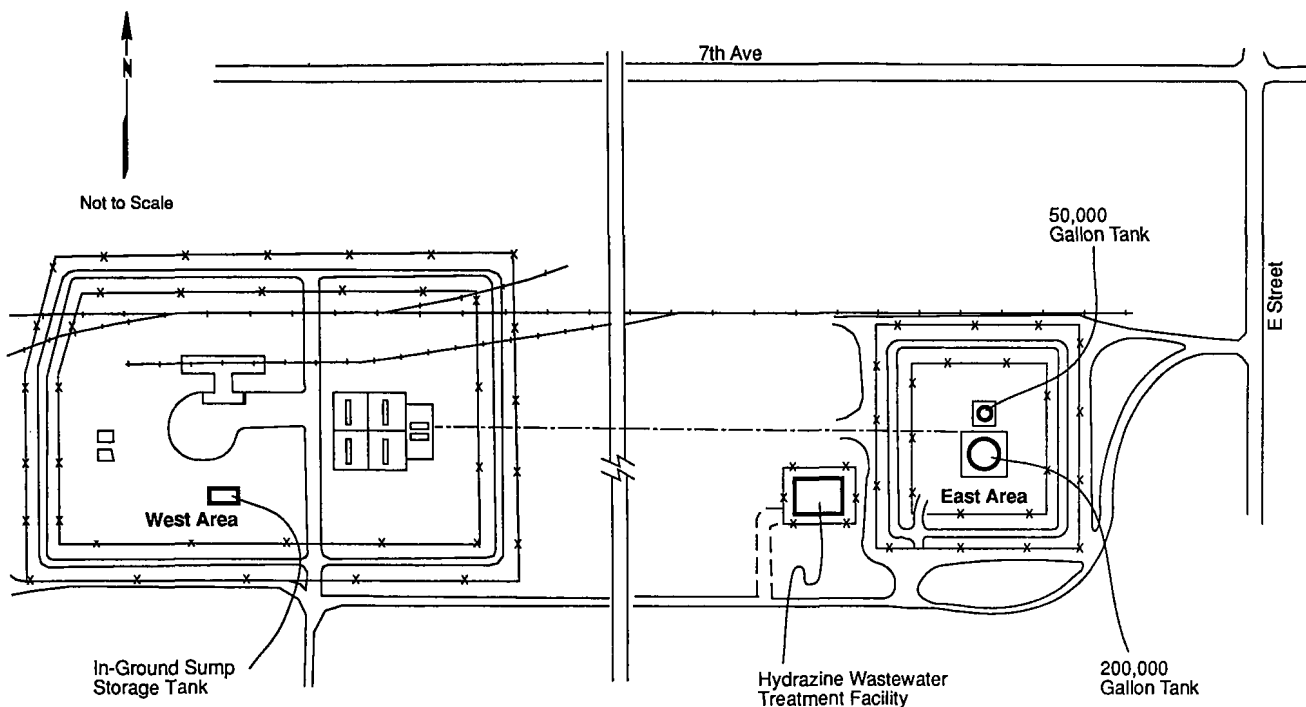
Figure 2
Location of Storage Tanks and Wastewater Treatment
Facility at HBSF

Table 2
Action Levels for Contaminants of Concern

Parameter	Action Level From IRA Decision Document
NDMA	1.4 ppt
Hydrazine	2.5 ppb
UDMH	25 ppb
MMH	20 ppb

ppb = parts per billion
ppt = parts per trillion

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Table 3
Certified Reporting Limits for Contaminants of Concern

Parameter	Certified Reporting Limit (CRL)
NDMA	42 ppt
Hydrazine	9.9 ppb
UDMH	25 ppb*
MMH	7.4 ppb

* Action level only. UDMH was not certified.

ppb = parts per billion
ppt = parts per trillion

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full-scale operation were similar for all three vendors and included: (1) treatment in batch mode, (2) treatment time of between 8 and 16 hours using an ozone and/or hydrogen peroxide chemical oxidant concentration greater than the stoichiometric concentration, (3) maintaining a solution pH of between 3 and 5 throughout treatment and (4) use of a metal-based catalyst.

The selection of Peroxidation Systems, Inc., to provide the UV/chemical oxidation equipment was based in part on the analytical results from the bench- and pilot-scale testing program. Other evaluation criteria that were considered included capital and operating costs, potential for generation of off-gas, ease of installation and operation, experience, delivery time and anticipated response and support services. These other criteria were evaluated based upon information contained in the treatability testing reports and gained from visits to the vendor facilities during treatability testing.

DESIGN/CONSTRUCTION

Full-scale design criteria resulting from the treatability testing pro-

gram included: (1) UV-enhanced oxidation of the high-strength hydrazine wastewater should be performed in the batch treatment mode in order to maintain a reasonable reactor size; (2) the temperature of the wastewater should be maintained at 140 °F or less; and (3) the pH of the wastewater should be maintained between 3 and 5 for the most effective reduction of NDMA. Based on these and other criteria, a full-scale treatment system, incorporating the unit processes indicated in Figure 3, was designed and constructed within a 4-month period. The heart of the system includes the UV/chemical oxidation reactor, recycle tank and pump, and chiller (Figure 4). Other appurtenant unit processes include influent and effluent transfer and storage systems, bag filtration of the influent, hydrogen peroxide, concentrated sulfuric acid, liquid catalyst, caustic chemical storage and feed systems, a tank and reactor off-gas collection system, a hydropneumatic potable water system, air monitoring and safety subsystems. The off-gas collection system was included to collect and treat air displaced in the headspace of tanks and to treat any gases that might be generated in the reactor.

The treatment system is housed in a 40- by 60-foot insulated

Table 4
Analytical Results from Treatability Tests

Analytes	Vendor A Untreated Wastewater μg/l	Vendor A Treated Wastewater μg/l	Vendor B Untreated Wastewater μg/l	Vendor B Treated Wastewater μg/l	Vendor C Untreated Wastewater μg/l	Vendor C Treated Wastewater μg/l
Hydrazine Fuel Compounds						
Hydrazine	1,100,000	<20	1,500,000	<10	610,000	43
MMH	62,000	<990	580,000	<250	99,000	<1,000
UDMH	960,000	<20	1,800,000	<5	540,000	56
NDMA	120	0.02	72	0.07	37	0.20
Purgeable Halocarbons						
Chloroethane	<10	<0.5				
Chloroform	60	32	44	<0.5	160	<5
Chloromethane	<10	<5.0				
Methylene chloride	31	8.8	18	1.2	200	12
Tetrachloroethane	<5					
Metals	NA				NA	
Total arsenic		11	18	19		16
Total chromium		300	<10	260		50
Total copper		75	<25	70		
Total mercury		0.5	0.2	1.9		0.6
Total molybdenum		200				
Total nickel		220	404	170		260
Total thallium		100				
Total zinc		60	<20	280		90
Total iron		2,900	5,600	14,000		220

NA = Not applicable; sample not received or analysis not required.

< indicates not detected at or below specified reporting limit.

μg/l = micrograms per liter

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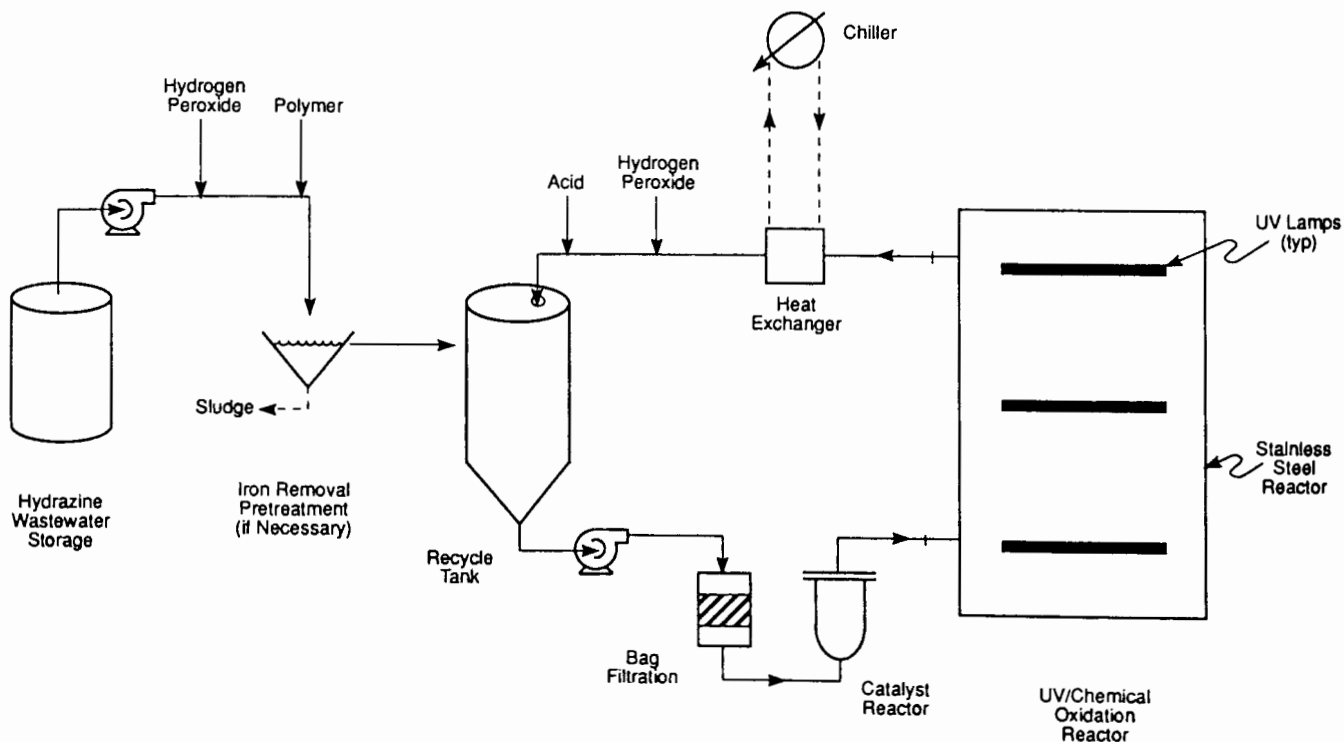
Figure 3
Schematic of the UV/Chemical Oxidation Process
for Destruction of Hydrazine Wastewater

preengineered metal building. All tanks and equipment are located within a secondary containment curbing; lined sumps are included to collect and remove any spilled liquids; and the floor of the facility is protected with a nonslip, chemical-compatible, protective coating system.

FULL-SCALE STARTUP TESTING

Once the treatment building was complete, full-scale startup testing of the hydrazine wastewater treatment system was conducted from January to May 1990, using nine batches of wastewater ranging in volume from 700 to 1,300 gallons. The purposes for startup testing were to: (1) address equipment and related startup concerns, (2) perform any necessary physical and operational modifications to the system and (3) gather process and analytical data to define the operational requirements for treatment of the approximately 300,000 gallons of hydrazine wastewater.

Wastewater was pumped via a submersible pump suspended at an intermediate depth in the largest tank, which the characterization data indicated has the highest concentration of the hydrazine fuel compounds and NDMA. During treatment of each batch, the operating parameters included pH, oxidation/reduction potential (ORP), temperature, hydrogen peroxide concentration, catalyst type, recycle rate, total treatment time and wastewater volume (Table 5). For those parameters that varied during treatment, both initial and final values are presented.

Pretreatment of all batches consisted of filtration through 50- and 5-micron pore-size bag filters arranged in series. Iron fouling of the quartz sheaths that surround the UV bulbs in the reactor during Batches 1 and 2 resulted in modifications to the system including adding a 1-micron pore-size bag filter in-line with the reactor and recycle tank, replacing the liquid ferrous sulfate catalyst with an in-line solid tungsten

Figure 4
UV/Chemical Oxidation Reactor, Recycle Tank and Chiller

rod reactor and attempting to oxidize and remove iron using hydrogen peroxide and polymer chemical addition, slow mixing and settling. Because the influent concentration of NDMA varied greatly between batches, the attempt to remove iron seemed to be oxidizing the UDMH and creating NDMA. Thus, pre-oxidation and polymer addition were discontinued for pretreatment of Batches 8 and 9.

Batch 1 was treated using the recommended operating parameters

Table 5
Summary of Full-Scale Startup Testing results

Parameter	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9
pH (units) (initial/final)	2 - 5	9/3	7/1.3	8 - 2	1.6/1.6	1.5/1.5	1.4/1.4	9.3/2	9/2
Catalyst	Ferrous sulfate solution	None	Tungsten rods	Tungsten rods	Tungsten rods	Tungsten rods	Tungsten rods	Tungsten rods	Tungsten rods
Cumulative treatment time for batch (hours)	43	60	100	46	48	50	68	33.5	53
Total volume treated (gallons)	700	1300	1300	1300	1300	1300	1300	1300	1300
Recycle Rate Range (gpm)	65 - 147	65 - 151	76 - 134	68 - 76			NA		
ORP Range (mv) (initial/final)	301 - 684	-138 - 692	-43 - 667	-21 - 625	567 - 619	552 - 631	590 - 610		
Maximum Operating Temperature (°F)	130	122	136	130	130	122	127		
Hydrazine (ppb) Influent/lowest Level achieved	1,000,000/ < 2.5	NA/ < 2.5	1,200,000/ < 0.25	250,000/ < 0.25	96,000/ < 0.25	51,000/ < 0.25	490,000/ < 0.25	65,000/ < 0.25	130/ < 0.25
UDMH (µg/l)	810,000/ < 2.5	NA/ < 2.5	5,300,000/ < 0.25	380,000/ < 0.25	250,000/ < 0.25	56,000/ < 0.25	940,000/ < 0.25	2,000,000/ < 0.25	100/ < 0.25
MMH (µg/l)	320,000/ < 2.5	NA/ < 2.5	89,000/ < 0.25	120,000/ < 0.25	20,000/ < 0.75	64,000/ < 0.25	180,000/ < 0.25	110,000/ < 0.25	2,600/ < 0.25
NDMA (µg/l)	106/ 0.228	NA/ 0.255	285/ 0.062	23,500/ 0.467	59,200/ 0.679	40,000/ 25.8	28,300/ 1.39	3,880/ 5.00	66,000/ 0.107

< indicates parameter not detected at or above specified reporting limit
NA = parameter not analyzed
mv = millivolts
µg/l = micrograms per liter

from the bench-scale testing program. The literature suggests that hydrazine fuel compounds are destroyed best via an oxidation process at a pH above neutral, while destruction of NDMA is enhanced at a pH less than 4. Thus, for Batches 2, 3, 4, 8 and 9, the influent pH of between 7 and 9 was maintained at the beginning of each batch in an attempt to enhance the destruction of the hydrazine fuel compounds. The pH was later reduced in these runs to promote NDMA reduction. In an attempt to avoid the formation of NDMA by oxidation of UDMH, Batches 5, 6 and 7 were run at a pH of less than 2 units for the entire run time.

Three types of wastewater samples were collected during each batch: influent, process stream and effluent. Influent samples were collected after the pretreatment steps to obtain baseline water quality data. Process stream and effluent samples were collected from the same location downstream of the reactor. Process stream samples were collected at planned intervals throughout each batch and were analyzed to determine: (1) the concentration of NDMA and the hydrazine fuel compounds as a function of time, (2) reaction rate kinetics and (3) the time required to reach the lowest effluent NDMA and hydrazine fuel compound concentrations. Process stream samples were collected at 2-hour intervals during Batches 3 and 9 to develop reaction kinetics data.

Results from the nine batches treated during the full-scale startup testing period are shown in Tables 5 and 6 and in Figures 5 and 6. The results indicate the following:

- The UV/chemical oxidation process very successfully in reduced the levels of hydrazine fuel compounds, NDMA and other organics present in the hydrazine wastewater at RMA. In particular, the removal of the suspected carcinogen, NDMA, ranged from 99.785 to 99.999%. The hydrazine fuel compounds were consistently reduced to below detection limits in all batches. Where data are available, it appears that the hydrazine fuel compounds are destroyed in the initial 10 hours of treatment time. Other organic compounds also were reduced or destroyed in the process.
- Analytical method limitations do not allow measurement of NDMA to the ARAR (1.4 ppt) required for this IRA. Nevertheless, the detection limit for NDMA was not reached in any process stream or effluent sample through the full-scale testing program. It is therefore assumed that the limits of the UV/chemical oxidation technology, with respect to NDMA, were established during this testing.
- Iron fouling of the quartz sheaths that surround the UV bulbs occurred during Batches 1 and 2 and appeared to inhibit the treatment capability of the reactor.
- Pretreatment of hydrazine wastewater to remove iron appeared to enhance the formation of NDMA.
- A treatment scenario involving treatment at the initial pH of between 7 and 9 until the hydrazine fuel compounds are reduced to below detection limits, followed by reducing the pH to less than 4, appeared to provide the lowest effluent NDMA concentrations in the shortest treatment time. The data from Batch 9 suggest that effective reduction of the compounds of concern may be achieved in approximately 16 hours. Using this treatment scenario, it appears that the hydrazine fuel compounds may be reduced to below detection limits, while NDMA reduction to less than 2 ppb may be consistently achieved.
- Influent concentrations for the hydrazine fuel compounds and NDMA appear to vary significantly throughout Batches 1 through 9.
- Influent concentrations of NDMA and the hydrazine fuel compounds can vary greatly, even when taken from the same depth in the same tank.

RECOMMENDATION FOR FULL-SCALE TESTING

Based on the results from the full-scale startup testing, the following recommendations are made for treatment of the approximately 300,000 gallons of hydrazine wastewater stored at the HBSF:

- Each batch should be treated by not adjusting initial pH and by adding hydrogen peroxide in an amount exceeding the stoichiometric requirement. After the hydrazine fuel compounds are destroyed, which is indicated by a drop and subsequent leveling off of pH, the pH of the waste stream should be reduced to 2 for destruction of NDMA. Verification testing will be conducted during treatment of batches in the next phase of the IRA to determine whether the

Table 6
Full-Scale Testing Treatment Results for Other Parameters of Concern

Analyte	Batch 1 Influent Concentration μg/l	Batch 1 Effluent Concentration μg/l
Volatile Organics		
Acetone	32.0	32.5 – 52.3
Chloroform	106	< 5
Chloromethane	< 10.0	36 – 37.5
Methylene chloride	110.0	18.8 – 23.2
Semivolatiles		
Dieldrin	0.0601	< 0.0539
Benzothiazole	14.9	< 1.14
Dimethyl disulfide	53.0	< 1.16
Metals		
Arsenic	16.1	6.32 – 6.58
Cadmium	< 0.2	3.0 – 3.2
Chromium	< 22.4	641 – 645
Copper	< 10.0	15 – 16.6
Mercury	0.658	0.962 – 1.100
Silver	0.224	0.968 – 1.130
Zinc	< 20	114 – 118

< indicates parameter not detected at or above specified reporting limit
μg/l = micrograms per liter

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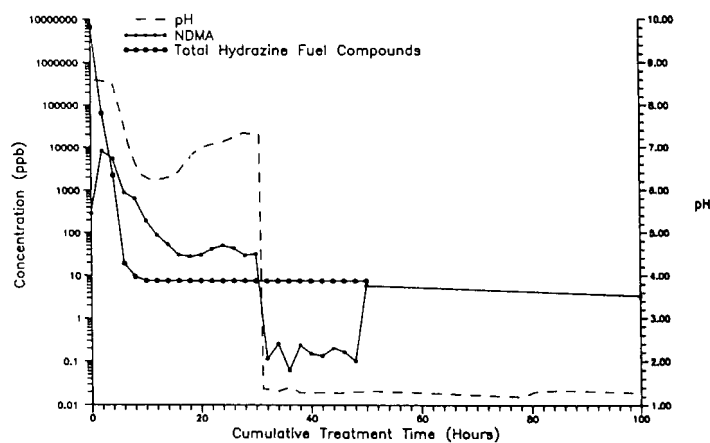
Figure 5
Operating Results—Batch 3
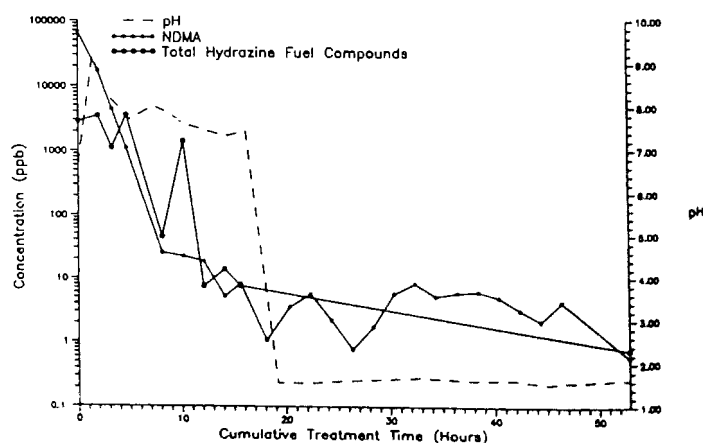
Figure 6
Operating Results—Batch 9

recommended treatment scenario is effective.

- The treatment system should be modified to eliminate "dead spots" in the reactor, recycle tank and interconnecting piping.
- The reactor and associated steel piping should be modified such that all connecting parts are made of 316 stainless steel in order to reduce the "battery" effect caused by the high concentrations of acid in the reactor.
- Treatment time should be approximately 16 hours, but actual time should depend on the concentrations of hydrazine fuel compounds and NDMA in the influent.

CONCLUSION

The results of the treatability testing and the startup testing suggest that the UV/chemical oxidation reactor can successfully treat the wastewater; however, the limits of the reactor have been reached when treating the hydrazine-contaminated wastewater at the HBSF. Additional treatment time does not significantly reduce the concentration of NDMA below 1 to 2 ppb. Therefore, the exposure pathways must be examined to determine whether NDMA levels of 1 to 2 ppb may still achieve the overriding health-based goal of 10^{-6} lifetime excess cancer risk rate. If the health-based risk goal cannot be achieved, additional treatment with adsorption media or a solar evaporation pond must be performed. A risk assessment is being conducted, and the methods of additional treatment are currently being tested.

A Systematic Approach to Analytical Method Development to Meet Ultra-Low-Level-Based ARARs, Rocky Mountain Arsenal, Denver, Colorado

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ABSTRACT

In many cases, health-based action levels or applicable or relevant and appropriate requirements (ARARs) are established that require treatment of chemicals in environmental media to ultra-low levels that are often below currently available method analytical detection limits. For this reason, analytical method development must be undertaken to achieve the lowest level of detection possible to demonstrate that ultra-low-level ARARs can be met. Two approaches to method development include: (1) modification of currently available analytical methods to improve performance while not restricting the flexibility of the overall analytical approach and (2) methods development when published methods are not available for contaminants that are stipulated for regulation under a recently developed technology or health-based ARARs.

Modifying the current U.S. Environmental Protection Agency (EPA) Method 607 became necessary at Rocky Mountain Arsenal (RMA) for the analysis of N-nitrosodimethylamine (NDMA) in treated wastewater to evaluate the practicality of achieving an Ambient Water Quality Criteria (AWQC)-based ARAR of 0.0014 parts per billion (ppb) for NDMA. In conjunction with method modification for analysis of NDMA, method development for analyses of hydrazine (HYDZ), monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine or 1,1-dimethylhydrazine (UDMH) also was necessary because published methods were neither available nor adequate to meet program-stipulated ARARs. Methods are evaluated using a systematic approach and a rigorous quality assurance/quality control (QA/QC) program developed by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and adopted by the Program Manager for Rocky Mountain Arsenal (PMRMA). The PMRMA QA/QC program substantiates that modified method results or results generated using newly developed methods meet or exceed U.S. EPA or state agency requirements for analytical precision, accuracy, representativeness, completeness and comparability.

Conservative risk assessment-based ARARs may be analytically unachieveable, considering the current state of technology, and must be evaluated before signing the record of decision (ROD) to ensure the action levels selected are practicable and protective of human health. Well-documented method development programs will improve the understanding of the analytical constraints that must be considered when selecting final treatment levels.

INTRODUCTION

During 1989, the U.S. Army, U.S. EPA Region VIII, Shell Oil Company (Shell) and the Department of Interior (DOI) agreed on a plan for safe disposal of hydrazine-contaminated wastewater and for decommissioning of facilities previously used for blending of hydrazine rocket propellants at the Rocky Mountain Arsenal (RMA). The plan was defined by a Decision Document in which a preferred remedial alternative was recommended. Action levels were established for four compounds in the wastewater at the Hydrazine Blending and Storage Facility (HBSF): (1) NDMA at 0.0014 ppt, (2) HYDZ at 2.5 parts per billion (ppb), (3) MMH at 15 ppb and (4) UDMH at 25 ppb. The Interim Response Action (IRA) program for RMA defined by the Federal Facility Agreement (FFA) provides that "IRAs shall, to the maximum extent practicable, attain ARARs."

Development of the ARAR established for NDMA was based on a health-based standard because NDMA is not directly governed under any state or federal regulatory laws. At the time of signing the HBSF IRA Decision Document, the Ambient Water Quality Criteria (AWQC) was selected as the ARAR for NDMA. Because no health-based criteria are currently available, the action levels selected for the hydrazine fuel compounds (i.e., HYDZ, MMH and NDMH) were based on unpublished analytical method detection limits.

The AWQC for NDMA of 0.0014 ppb was developed pursuant to Section 304(a)(1) of the Clean Water Act, 33 U.S.C. 1314(a)(1). Under this section of the Clean Water Act, the U.S. EPA must periodically review and publish criteria for water quality that accurately reflect the latest scientific health and welfare knowledge. The NDMA ARAR of 0.0014 ppb represents a 1×10^{-6} cancer risk factor for an average person who consumes a total of 2 liters of NDMA-contaminated water per day during 70 years and an average 6.5 grams of NDMA-contaminated fish per day during the same 70-year lifetime. This AWQC was developed and published by the U.S. EPA during 1980 as guidance when establishing ARARs for site remediation. The ultimate utility of any such site-defined ARAR depends on two essential elements under the Superfund Amendments and Reauthorization Act (SARA). A new level of treatment can be redefined after an ARAR has been agreed upon only if: (1) the new level of treatment can be shown to be protective of human health or (2) the established ARAR can be shown to be unpracticable.

To show the levels to which ARARs are set are practical and achievable, two elements of any pilot-scale or bench-scale treatment program must be carefully examined: (1) efficiency of the treatment system to meet program ARARs and (2) the reliability of the analytical method when evaluating the treatment system efficiency.

Many methods currently are available for evaluating the efficiency of analytical methods. The U.S. EPA uses a statistical approach for calibration standards that evaluates method accuracy based on seven replicate analyses run during a single day. The approach is designed to evaluate instrument sensitivity and accuracy. However, this method of determining method detection limits does not consider sample preparation and extraction efficiencies, which generally control and dictate analytical method reliability.

During the early 1980s, USATHAMA introduced a statistical method to evaluate method detection limits that was designed to account for sample preparation and extraction efficiencies. This program requires that a series of calibration standards and investigative samples be prepared and analyzed over the entire estimated range of method performance. Four consecutive days of extraction and analysis are required to be evaluated using a series of standard statistical tests. The U.S. EPA method startup protocols, which prepare and analyze samples in quadruplicate during a single day and compare results to a national data base, are most comparable to the USATHAMA method design plan; however, the investigative samples prepared and analyzed under the U.S. EPA method startup protocol are run only at a single level of concentration and are analyzed during a single day.

Under a prime contract to perform several different studies at RMA, Harding Lawson Associates (HLA) designed and tested an ultraviolet (UV)/chemical oxidation treatment system for the HBSF wastewater. To accomplish this task, HLA researched and developed analytical methods to attempt to satisfy the program-stipulated ARARs set forth in the HBSF Decision Document.

CHEMICAL PROFILE OF NDMA

The major uses, sources and regulatory constraints on human exposure to NDMA are very important for understanding the nation-wide significance of the analytical technology available for analyzing the presence of NDMA.

Before April 1976, NDMA was used as an intermediate in the production of UDMH, a liquid rocket propellant believed to have contained up to 0.1% NDMA as an impurity. NDMA also forms from the chemical breakdown of UDMH. NDMA has been used as an industrial solvent; as an antioxidant; in lubricants and condensers to increase the dielectric constant; as a nematocide; as a softener for copolymers; as an inhibitor of nitrification in soil; and in active metal anode-electrolyte systems.[4]

Nitrosamines, including NDMA, are present in a wide variety of food as reported by Fine[5] and Scanlan.[6] Nitrosamines are found most commonly in cured meats (particularly cooked bacon); beer; Scotch whiskey; some cheeses (especially Gouda and Edam types); nonfat dry milk and buttermilk; and sometimes fish.[4] Levels of total volatile nitrosamines are generally less than 5 μg/kg in these foods. The average daily intake of volatile nitrosamines from food is estimated to be approximately 1 μg per person. NDMA is also found in rubber pacifiers, baby-bottle nipples and occasionally in cosmetics. Smokers are exposed to an estimated 6.5 nanograms (ng) of NDMA per cigarette from mainstream smoke; undiluted sidestream smoke may contain 20 to 100 times as much NDMA as mainstream smoke.[3]

NDMA does not appear to be common in drinking water or ambient air. Brodzinsky and Singh[7] compiled all available atmospheric monitoring data for a number of organic compounds, including NDMA, for 404 locations. In rural and remote areas the median concentration of NDMA was 0.018 μg/m^3; the median concentration in urban and suburban areas was 0.028 μg/m^3 and in source-dominated areas, 0.042 μg/m^3. Indoor levels of NDMA measured in restaurants and other public places have been between 0.01 and 0.24 μg/m^3 and are attributed primarily to tobacco smoke.

REGULATORY STATUS OF NDMA

The following is a brief summary of the March 1, 1989, nationwide regulatory status of NDMA. This summary is provided to inform the reader of manufacturing and other industrial situations that may result in the release of chemicals discussed in this paper. The regulatory environment is rapidly changing in relationship to NDMA and HYDZ, MMH and NHMH. A clear understanding of the state of current regulations governing these chemicals will provide the reader a better understanding of the potential effect that method development, such as that described in this paper, will have on the ultimate success or failure of any remedial action. Not only can the following discussion help to clarify the regulatory constraints currently applicable to the specific chemicals discussed in this paper, but it also can provide insight into how method development will affect remediation programs for

chemical compounds, other than those discussed in this study, for which legal constraints are not yet clearly defined.

Federal Programs

Clean Water Act (CWA)

NDMA is listed as a toxic pollutant, subject to general pretreatment regulations for new and existing sources and to effluent standards and guidelines. Effluent limitations specific to NDMA have been set in the following point source categories: electroplating, steam electric power generating and metal finishing. Limitations vary depending on the type of plant and industry.

Resource Conservation and Recovery Act (RCRA)

NDMA is listed as an acute hazardous waste and a hazardous waste constituent. This chemical is subject to land-disposal restrictions when its concentration as a hazardous constituent of certain wastewaters exceeds site-specified designated levels. NDMA is included on the U.S. EPA's groundwater monitoring list. The U.S. EPA requires that all hazardous waste treatment, storage and disposal facilities monitor their groundwater for chemicals on this list when suspected contamination is first detected and annually thereafter.

Comprehensive Environmental Response Compensation and Liability Act (CERCLA)

NDMA is designated a hazardous substance under CERCLA. It has a reportable quantity (RQ) limit of 0.454 kg. NDMA is designated an extremely hazardous substance under SARA Title III Section 302. Any facility at which this chemical is present in excess of its threshold planning quantity of 10 pounds must notify state and local emergency planning officials. If NDMA is released from a facility in excess of its RQ, local emergency planning officials must be notified.

Marine Protection Research and Sanctuaries Act (MPRSA)

Ocean dumping of organohalogen compounds as well as the dumping of known or suspected carcinogens, mutagens or teratogens is prohibited except when they are present as trace contaminants. Permit applicants are exempt from these regulations if they can demonstrate that such chemical constituents are nontoxic and nonbioaccumulative in the marine environment or are rapidly rendered harmless by physical, chemical or biological processes in the sea.

Occupational Safety and Health Act (OSHA)

Employee exposure to NDMA should be avoided. This chemical is designated an Occupational Safety and Health Administration (OSHA) carcinogen. Detailed regulations exist in 29 CFR 1910.1016 for areas where NDMA is manufactured, processed, used, packaged, released, handled or stored. These include requirements for reporting maintenance and decontamination.

Hazardous Materials Transportation Act (HMTA)

The U.S. Department of Transportation (DOT) has designated NDMA as a hazardous substance with an RQ of 0.454 kg, subject to requirements for packaging, labeling and transportation.

State Water Programs

All states have adopted the AWQC criteria as their promulgated state regulations, either by narrative reference or by relisting specific numeric criteria. The following states have promulgated additional or more stringent criteria:

- *Kansas* - Kansas has an action level of 0.0014 ng/L for NDMA in groundwater.
- *New York* - New York has a maximum contaminant level (MCL) of 50 μg/l in drinking water.
- *Oklahoma* - Oklahoma has set an enforceable Toxic Substance Goal of 0.8 ng/L for nitrosamines in surface waters classed for public and private water supplies.

Proposed Regulations

- *Federal Programs* - No proposed regulations are pending.

- *State Water Programs*

    Most States - Most states are in the process of revising their water programs and proposing changes in their regulations that will follow the U.S. EPA's changes when they become final. Changes are projected for 1989-90.

    Minnesota - Minnesota has proposed a Recommended Allowable Limit (RAL) of 0.007 µg/L for drinking water.

CHEMICAL PROFILE OF HYDRAZINE/HYDRAZINE FUELS

For the purpose of demonstrating the significance of the hydrazine fuel compounds to programs nationwide and in an attempt to not provide an exhaustive narrative, hydrazine is presented as an example of the industrial uses and regulatory environment surrounding hydrazine fuel compounds. Hydrazine is similar in chemical composition and in many of its industrial applications to UDMH and MMH. However, distinctly different industrial and regulatory constraints govern each of these compounds. For a more detailed discussion of these topics, the reader should contact a local regulatory agency for further guidance and reference materials.

Hydrazine is used in industry as a chemical intermediate in the manufacture of pharmaceuticals and plastic blowing agents and is used as an oxygen scavenger in boiler feed-water treatment and in fuel cells. It also is used as a missile propellant and in auxiliary power units of the space shuttle orbiter and solid rocket boosters. Each F-16 aircraft carries 6.5 gallons of a 70% hydrazine/30% water solution used in an emergency power unit to supply electrical and hydraulic power.

Information on sources of exposure to hydrazine is limited. The primary source of human exposure appears to be smoking, because hydrazine is a component of mainstream cigarette smoke. No data were found by HLA on its presence in the ambient environment. However, UDMH is a common breakdown product for the plant growth regulator Alar, applied to many fruits such as peaches and apples.

The following is a summary of the regulatory status for hydrazine as of March 1, 1989:

Federal Programs

Safe Drinking Water Act (SDWA)

In states with an approved Underground Injection Control program, a permit is required for the injection of hydrazine-containing wastes designated as hazardous under RCRA.

RCRA

Hydrazine is identified as a reactive, toxic hazardous waste and listed as a hazardous waste constituent.

CERCLA

Hydrazine is designated a hazardous substance under CERCLA. It has an RQ limit of 0.454 kg. Reportable quantities have also been issued for RCRA hazardous waste streams containing hydrazine, but these depend on the concentrations of the chemicals in the waste stream. Hydrazine is designated an extremely hazardous substance under SARA Title III Section 302. Any facility at which hydrazine is present in excess of its threshold planning quantity of 1000 pounds must notify state and local emergency planning officials annually. If hydrazine is released from the facility in excess of its RQ, local emergency planning officials must be notified. Under SARA Title III Section 313, manufacturers, processors, importers and users of hydrazine must report annually to the U.S. EPA and state officials their releases of this chemical to the environment.

MPRSA

Ocean dumping of organohalogen compounds as well as the dumping of known or suspected carcinogens, mutagens, or teratogens is prohibited except when they are present as trace contaminants.

Occupational Safety and Health Act

Employee exposure to hydrazine shall not exceed an 8-hour time-weighted average (TWA) of 0.1 ppm. Employee skin exposure to

hydrazine shall be prevented/reduced through the use of protective clothing and work practices.

HMTA

The DOT has designated hydrazine as a hazardous substance with an RQ of 0.454 kg, subject to requirements for packaging, labeling and transportation.

Food, Drug and Cosmetic Act (FDCA)

Hydrazine may not be used as a boiler-water additive in any amount in the preparation of steam that will contact food.

State Water Programs

All states have adopted U.S. EPA AWQC and National Discharge Permit Water Restrictions (NDPWRs) as their promulgated state regulations, either by narrative reference or by relisting the specific numeric criteria. The U.S. EPA has not currently published any AWQC for hydrazine. Only New York has promulgated additional or more stringent criteria:

New York has an ambient water quality standard for hydrazine of 5 µg/L at less than 50 ppm hardness and 10 µg/L at greater than or equal to 50 ppm hardness for Class A, A-S, AA, AA-S, B, and C surface waters. New York also has an ambient water quality standard for hydrazine of 50 µg/L at less than 50 ppm hardness and 100 µg/L at greater than or equal to 50 ppm hardness for Class D surface waters.

Proposed Regulation

- *Federal Programs* - No proposed regulations are pending.
- *State Water Programs* - No proposed regulations are pending. Most states are in the process of revising their water programs and proposing changes in their regulations that will follow the U.S. EPA's changes when they become final.

After review of the current state of regulations for compounds such as NDMA or hydrazine fuels, it is apparent that regulatory constraints will most likely be based, at least in part, on the level of detection achievable.

METHOD DEVELOPMENT FOR THE ANALYSIS OF NDMA IN WATER

U.S. EPA-approved methods for analysis of NDMA in aqueous samples include U.S. EPA Methods 607, 625 and 1625. The method detection limits published for these methods are 0.150 ppb or ug/l (Method 607) and 50 ppb (Method 1625). No detection limit for Method 625 is published. Because the AWQC-based ARAR for NDMA under the HBSF IRA program is 0.0014 ppb, none of these U.S. EPA methods, in their current state of development, were adequate to meet required objectives.

Some potentially applicable analytical work on the analysis of ultra-low levels of NDMA was reported by Jody[8] and others from the Illinois Institute of Technology Research Institute. In Jody's paper, "Ozonation of Hydrazine Fuels and Their Associated Impurities," he reported that levels of NDMA detection using a rotary-evaporation sample concentration technique coupled with a gas chromatograph and nitrogen phosphorus detection (GC/NPD) system were approximately 0.010 ppb. The IITRI method was essentially a modified U.S. EPA Method 607.

HLA contacted IITRI and requested they repeat their previous analytical work and subject it to the statistical programs utilized by PMRMA. The PMRMA certification program for systematically evaluating method performance involves a two-step process that ultimately yields a certified reporting limit (CRL) for the analyte(s). The initial step, or precertification, is used to evaluate instrument stability and linearity over the proposed testing range of concentration. The program involves preparing two separate sets of calibration standards and analyzing them in the sequence that will be used during daily calibration. IITRI's analytical results were found to satisfy all linearity and instrument sensitivity requirements. Table 1 shows that instrument sensitivity and reproducibility were acceptable down to the 0.020 ppb level of concentration. Instrument response to NDMA was evidenced

at the 0.0075 ppb level, but reproducibility was poor. Linearity of calibration checks was acceptable, as shown in Figure 1.

During the second step of method certification using the systematic approach used by PMRMA, four consecutive days of instrument calibration and spiked-sample extraction analysis were performed and subjected to statistical analysis. Table 2 shows the results for spiked samples analyzed using the IITRI, U.S. EPA Method 607 modification during 4 days of analysis. Recovery values were found to be erratic. Figure 2 shows the data were not linear and failed to meet linearity criteria. Thus, it became apparent that investigation into the development of better sample extraction procedures was required to analyze for the presence of NDMA at ppt levels.

Table 1
IITRI Precertification Results

Target Value (in µg/l or ppb)	Instrument Values in Area Units Standard G	Standard H
0.0075	0.0161	0.0098
0.020	0.0306	0.0353
0.050	0.0749	0.0656
0.100	0.1451	0.1265
0.250	0.3190	0.3590
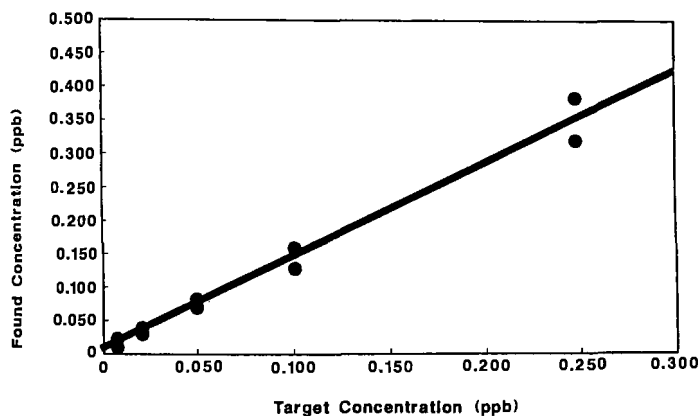
Figure 1
Found Concentration vs. Target Concentration
IITRI Precertification Results for NDMA
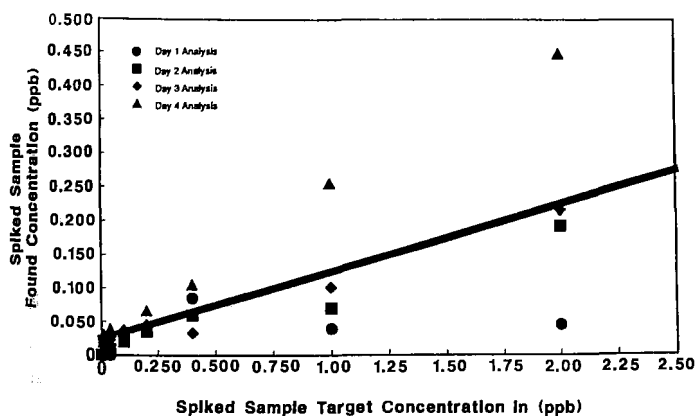
Figure 2
Found Concentration vs. Target Concentration
IITRI Certification Sample Results for NDMA

Table 2
IITRI Certification Sample Results for NDMA

Spiked Concentration (µg/l or ppb)	Day No. 1 Reported Concentration	Percent Recovery	Day No. 2 Reported Concentration	Percent Recovery
2.000	0.045	2.26	0.192	9.60
1.000	0.040	4.00	0.070	7.05
0.400	0.085	21.40	0.060	15.00
0.200	0.035	17.70	0.035	17.60
0.100	0.031	30.90	0.020	20.60
0.040	0.000	0.00	0.009	22.20
0.020	0.002	11.80	0.019	93.50
0.010	0.000	0.00	0.020	195.00
Method Blank	0.000		0.000	

Spiked Concentration (µg/l or ppb)	Day No. 3 Reported Concentration	Percent Recovery	Day No. 4 Reported Concentration	Percent Recovery
2.000	0.216	10.80	0.448	22.40
1.000	0.102	10.20	0.256	25.60
0.400	0.033	8.20	0.106	26.50
0.200	0.046	22.90	0.067	33.40
0.100	0.038	37.50	0.038	37.50
0.040	0.023	57.50	0.039	98.20
0.020	0.020	102.00	0.023	114.00
0.010	0.014	140.00	0.031	308.00
Method Blank	0.000		0.000	

Published QC acceptance criteria listed in U.S. EPA Method 607 for NDMA-spiked samples at 20 ppb in water are 13 to 109 percent recovery. The reported method detection limit based on the analysis of seven replicate calibration standards is 0.150 ppb. This indicates that a sample with an NDMA concentration as high as 1.15 ppb could potentially be reported as not detected at the U.S. EPA Method 607 detection limit of 150 ppt if sample recovery were only 13%. This level of method performance was not acceptable using the PMRMA two-step certification process.

DataChem Laboratories in Salt Lake City, Utah, had previously successfully certified a method for the analysis of NDMA at 0.200 ppb. Precertification was rerun by Datachem for the analysis of NDMA using instrument conditions similar to those used by IITRI; the data were found to be comparable. In an attempt to improve spiked sample results, the florisil column cleanup recommended in U.S. EPA Method 607 was eliminated from the extraction procedure because it drastically reduced NDMA extraction efficiency. Separatory funnel extraction, used in U.S. EPA Method 607, was substituted with the use of liquid-liquid continuous extraction at a pH between 5 and 9.

After an 8-hour liquid-liquid continuous extraction using the extraction solvent methylene chloride (MECL2), sample concentration was found to be most efficient by adding 15 mLs of methanol (MeOH) to the 300 mLs of MECL2 extract and then concentrating the extract in a cool-water bath at 65 °C, using a Kuderna-Danish. When the extract reached a volume of 100 mLs, a hot-bath concentration step at 90 °C was used to reduce the sample to a volume of 5 to 8 mLs. A nitrogen blowdown step was then used in a cold-water bath at or below 30 °C. Numerous types of concentration methods were examined, such as condensers, turbo-evaporators and micro-snyder columns. In all cases, the preferred method that yielded at least 40% NDMA recovery was the one that utilized the Kuderna-Danish coupled with a nitrogen blowdown.

Table 3 shows the results of 4 days of spiked-sample extraction and analysis using the described modifications to U.S. EPA Method 607. The range of concentrations tested is a subset of the actual range over which the method was tested. The method was tested initially over a range of concentration from 0.010 ppb to 2 ppb. However, over this range the method was found to be not linear, so higher levels tested were eliminated and a selected low-end subset of the analytical results that

provided the lowest CRL possible was presented. From the analytical results in Table 3 and the graphical display of these data in Figure 3, it is obvious that some analytical variability exists even at the reported levels of spiked-sample concentrations listed. This resulted in a statistically determined CRL of 0.042 ppb and a working range that extended only to 0.150 ppb. Because the program objective was to obtain a CRL as close to 0.0014 ppb as possible, this limited range did not cause problems.

Table 3
DataChem Certification Sample Results for NDMA

Spiked Concentration (ug/l or ppb)	Day No. 1 Reported Concentration	Percent Recovery	Day No. 2 Reported Concentration	Percent Recovery
0.020	0.014	68	0.009	47
0.050	0.035	69	0.030	60
0.100	0.064	64	0.052	52
0.200	0.136	68	0.058	29
Method Blank	0.000		0.000	

Spiked Concentration (ug/l or ppb)	Day No. 3 Reported Concentration	Percent Recovery	Day No. 4 Reported Concentration	Percent Recovery
0.020	0.013	67	0.004	21
0.050	0.030	61	0.028	56
0.100	0.043	43	0.044	44
0.200	0.140	70	0.084	42
Method Blank	0.000		0.000	
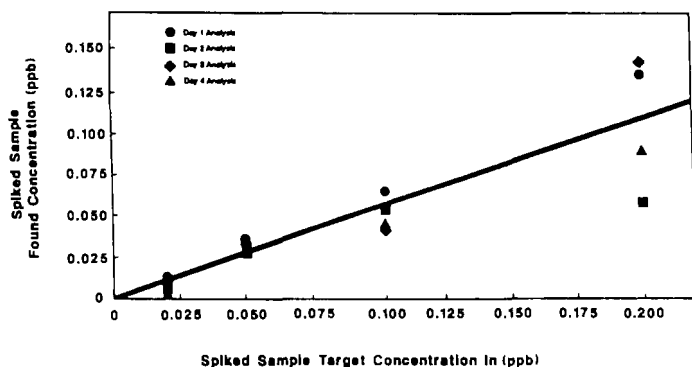
Figure 3
Found Concentration vs. Target Concentration
DataChem Certification Sample Results of NDMA

However, in addition to strict analytical considerations of precision, accuracy, completeness and comparability, the representativeness of analytical results was also considered when attempting to evaluate the practicality of ultra-low-level- based ARARs such as that for NDMA in the HBSF IRA program. Table 4 shows a list of method blank results obtained during some of the analyses performed during Phase I of the HBSF IRA program. Table 4 shows that when attempting to analyze high-level samples, special considerations needed to be added to the method to eliminate cross-contamination. After analysis of method blank samples shown in Table 4, individual ventilation units were placed over each sample extraction vessel and concentration steps for low- and high-level samples were segregated. This, along with adopting additional cleaning procedures and eliminating a step using a pipetting apparatus, eliminated the previously observed cross-contamination.

METHOD DEVELOPMENT FOR THE ANALYSIS OF HYDRAZINE FUEL COMPOUNDS IN WATER

The hydrazine fuel compounds are not included among the U.S. EPA-designated priority pollutants, and a U.S. EPA-approved procedure for

Table 4
Hydrazine Blending and Storage Facility
Method Blank Summary for N-Nitrosodimethylamine, Phase I
Commerce City, Colorado

Blank ID	Related Investigative Sample	Blank Sample Concentration (in ug/l or ppb)	Sample Concentration (in ug/l or ppb)
JDR001		.123	
	IRAH-11-I		23400
	IRAH-21-KB		13000
	IRAH-23-KB		9190
	IRAH-25-KB		5910
	IRAH-16-KA		147
	IRAH-19-KA		47.7
	IRAH-20-KA		8.79
	IRAH-22-KA		4.32
	IRAH-24-KA		2.34
	IRAH27KAMS		1.82
	IRAH-27-KA		1.50
	IRAH-12-I		.302
	IRAH-17-KA		.174
	IRAH-18-KA		<.020
	IRAH-25-KA		<.020
	IRAH-26-KA		<.020
JKC001		.263	
	IRAH-17-I		66000
	IRAH-27-KB		17200
	IRAH-28-KB		4390
	IRAH-29-KB		1090
	IRAH-30-KB		25.0
	IRAH-31-KB		22.0
	IRAH-32-KB		18.5
	IRAH-45-KB		8.30
	IRAH-48-KA		5.70
	IRAH-33-KB		5.21
	IRAH-47-KA		3.59
	IRAH-18-I		3.37
	IRAH-46-KA		1.07

the analysis of hydrazine fuel compounds is not currently available. However, one analytical method recommended for the analysis of azo compounds, hydrazines and derivatives involves derivatization and analysis by GC/NPD, mass spectrometer (MS) or a flame ionization detector. Numerous other methods for the analysis of hydrazine in air and soil have been published and were investigated during the method development process.

The only directly applicable method for analyzing hydrazines in water was developed by Environmental Science (ES) for the Facilities Management Division (ASD/PMDA), Headquarters Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, and several other Air Force bases, and was published in February 1988. In this experimental method, derivitization using 2-furaldehyde, benzaldehyde, 2,4-pentanedione, methylethyl ketone and cinnamaldehyde was evaluated. The reaction of the target compounds with 2-furaldehyde produced the most successful results using an internal standard, nitrobenzene, for quantitation. No work was performed by ES concerning absolute recovery efficiencies. This method utilizes procedural standards whereby calibration standards and analytical samples are derivatized before analysis. Using such procedural standards, and standard U.S. EPA-type statistical methods for determination of method detection limits, the 2-furaldehyde method detection limit for hydrazine was 21 ppb, for MMH was 15 ppb, and for UDMH was 18 ppb.

Based on the QC results published by ES on their 2-furaldehyde method, Vista Laboratories, Wheat Ridge, Colorado, was asked to conduct method development and evaluation of the ES method utilizing the systematic program used by PMRMA.

The method development effort began with a review of the existing method developed by ES as well as other methods developed by NIOSH for monitoring hydrazine fuels in air. The existing methods did not meet the project objectives of obtaining a CRL of 2.5 ppb for hydrazine and 20 ppb for UDMH; however, the existing methods showed the promise of improvement to attain these goals.

The laboratory study began with the reaction of 2-furaldehyde (furfural) with the hydrazines to create hydrazone derivatives that would be of sufficient molecular weight to extract and of sufficient stability to chromatograph. Following the evaluation of the derivatives of their detector response, optimal GC conditions were developed for all three derivatives on the primary DB-1 and confirmatory DB-608 columns. Phenylhydrazine was investigated as a potential surrogate for the method and the phenylhydrazine derivative was successfully chromatographed. Two compounds, 2-picoline and nitrobenzene, were evaluated as potential internal standards for the method. Nitrobenzene was chosen because of retention time considerations.

Hydrazine derivatives were synthesized in ethyl acetate solutions. Because of the insolubility of furfural in hexane, the sample extract solvent of choice for nitrogen phosphorus detectors was ethyl acetate. Calibration standards were prepared in hexane. "Micro-extraction" techniques were evaluated for extraction of the derivatives from water samples. Sample aliquots of 100 mLs were extracted with 2 mLs of hexane, yielding recoveries of 1 to 10% for the hydrazones. MECL2 was evaluated as an extraction solvent followed by a solvent exchange with hexane. Initial tests of the concentration and solvent exchange revealed the hydrazine derivatives were stable through these steps, with recoveries ranging from 75 to 100%. One-liter samples were extracted with MECL2 and the extracts were concentrated and exchanged to hexane. Excess 2-furaldehyde was co-extracted and formed a nonmiscible layer with MECL2 during concentration. Recoveries of the hydrazones ranged from 10 to 40%; thus, it was decided to seek another extraction solvent.

Hexane extraction was again attempted on a "macro-extraction" scale. Aliquots of 100 mLs of hexane were concentrated to see if the hydrazones would survive the higher water-bath temperatures required to concentrate hexane versus MECL2. Recoveries from the concentration step ranged from 83 to 95%. One-liter samples were extracted with hexane, and the extracts were concentrated to 1 mL. Recoveries of the hydrazones ranged from 7 to 40%, indicating no improvement in using hexane over using MECL2.

Because ethyl acetate had been used in some of the existing methods, it was decided to evaluate it as an extraction solvent. Samples 100 mL in size were extracted with ethyl acetate and extracts concentrated. Recoveries ranged from 40 to 94%. Samples were prepared covering a range from 2.5 to 250 ppb, and recoveries ranged from 65 to 100% for hydrazine, 45 to 75% for UDMH and 2 to 10% for MMH. The 2-furaldehyde derivative of MMH yielded such a low response it was decided to use another derivatizing agent for this compound. A method using 2,4-pentanedione to derivatize MMH was evaluated with success.

The sensitivity of the GC system to the derivatives was then evaluated. Solutions of the hydrazones were prepared to place 10 ng (absolute) of the hydrazine fuel derivatives on column. Sufficient instrument response was observed to estimate that a 100-mL sample volume would be adequate to meet the target reporting limit concentrations.

The two methods were again evaluated over the previously established testing range. Sample aliquots of 100 mLs were derivatized with 2-furaldehyde for hydrazine and UDMH and 2,4-pentanedione for MMH and then extracted with ethyl acetate. Nitrobenzene proved to be a suitable internal standard; however, the hydrazone of UDMH either was not recovered or disappeared from the extract. The methods performed favorably for hydrazine and MMH.

The methods were then redrafted to include "preparatory" procedural standards rather than the "externally derivatized" standards used to this point. It was believed that any inefficiency in synthesis or extraction of the derivatives would be accounted for by preparing standards in a manner identical to sample preparation.

Precertification of the method for MMH was successful. Phenylhydrazine recoveries were very erratic; subsequently, this compound as a surrogate standard was abandoned. Precertification of the method for hydrazine and UDMH was attempted with very poor results. Very poor chromatography was observed for the hydrazine derivative at lower concentrations. The DB-608 column was replaced with a newer version of the DB-608 column and NPD detector perfor-

mance improved. A DB-17 column was installed and adopted as the confirmatory column.

Because of the variability and introduction of chromatographic interference from the ethyl acetate, it was decided to evaluate a different extraction solvent. Diethyl ether was chosen because of its similar polarity properties.

Diethyl ether was found to be a suitable extraction solvent. Precertification was attempted using ethyl acetate in addition to diethyl ether as a keeper during solvent concentration; however, retention time shifts were noted during GC analysis, which invalidated the precertification. Precertification was again attempted, and successful, using hexane as a keeper to remove the previously observed retention time shifts. Precertification for MMH was also attempted, and successful, using the diethyl ether/hexane solvents.

After precertification, approval was given to attempt certification of the methods. Certification was successful for MMH, yielding a CRL of 7.5 ppb, which was sufficiently below the program ARAR of 20 ppb. During the certification attempts it was revealed that the concept of initial calibration checks and daily single-point calibrations for hydrazine and UDMH would not be successful. Although any single calibration curve was reasonably linear, the slope of the curve varied from preparation to preparation. A scheme of daily five-point calibrations was, therefore, drafted and included in the method.

The second certification attempt proceeded and yielded CRLs of 9.9 ppb for hydrazine and 30 ppb for UDMH. Because these CRLs did not meet the ARAR targets of 2.5 ppb and 25 ppb respectively, a third certification attempt was scheduled.

During the third certification attempt, a problem with the disappearance of the UDMH derivative was observed, as it had been during previous analyses. The derivative appeared to be synthesized, but would rapidly disappear, from the derivatized extracts. Analyses of a single extract performed one-half hour apart indicated a loss of 50% or more of the UDMH hydrazone.

After experiencing the problems with UDMH disappearance, it was determined that the method would be recertified as a qualitative method at the level required by the ARAR. Recent developments have pointed to the possibility that the antioxidant L-ascorbic acid may provide some relief from the observed UDMH disappearance problem.

SELECTION OF PROTECTIVE AND TECHNOLOGICALLY FEASIBLE REGULATORY LIMITS

When establishing ARARs or cleanup goals at any hazardous waste site, careful consideration of the analytical constraints that govern the reliability of analytical data must be reviewed and compared to proposed health-based criteria. Analytical method development, using an exhaustive QA procedure similar to that used by PMRMA, is essential before establishing final cleanup goals for unregulated chemical constituents for which methods are not available.

Table 5 compares the oral carcinogenic potency factor, the 1×10^{-6} calculated cancer risk factor for two commonly known human carcinogens, benzene and vinyl chloride, to the SDWA-stipulated MCLs. The 10^{-6} cancer risk factor can be directly related to the cancer potency factor, provided the route of exposure is the same. Comparing the 10^{-6} cancer risk factor to the SDWA MCL, it is obvious that the MCLs for both benzene and vinyl chloride are significantly above the 10^{-6} cancer risk level of concentration. The 1×10^{-4} cancer risk factors (i.e., the generally accepted level of protectiveness by most regulatory agencies) for benzene and vinyl chloride (Table 5) are 100 and 1.5 ppb, respectively. The U.S. EPA has chosen the MCL for these two compounds by rounding the vinyl chloride 10^{-4} risk factor of 1.5 to 2.0 ppb (which is the generally accepted practical quantitation limit (PQL) for the U.S. EPA-accepted method for analysis of vinyl chloride) and has set the MCL for benzene on the U.S. EPA Method PQL alone.

The rationale used to establish cleanup goals is similar to that used to establish ARARs: (1) the selected cleanup goal should be protective of human health, or between the 10^{-4} and 10^{-6} estimated cancer risk level, and (2) the selected cleanup goal should be practically achievable given the current state of available analytical technology. Based on this

Table 5
Comparison of Health Risk versus
Analytical Quantitation Limits

Compound	EPA Classification	Oral Carcinogenic Potency Factor (mg/kg/day)$^{-1}$	One-in-one-Million Drinking Water Risk Concentration (ppb)	SDWA MCL (ppb)
NDMA	B2 Probable Human Carcinogen	51	1.4×10^{-3}	
Benzene	A Human Carcinogen	0.029	1	5
Vinyl chloride	A	2.3	0.015	2

line of reasoning, the analytical constraints on the detection of unregulated chemical compounds should play a critical role in the selection of final treatment objectives at any hazardous waste site.

SUMMARY AND CONCLUSIONS

In the case studies reviewed, it is apparent that a target treatment level of 0.0014 ppb for NDMA is realistically unachievable given the current state of analytical technology. However, the technology currently available can yield reliable data in the 10^{-4} to 10^{-6} cancer risk factor range between 0.140 ppb and 0.0014 ppb. In the case of hydrazine fuel compounds, it was discovered that currently available methods of analysis can verify treatment to higher levels of protection for the compound MMH, but the method for analysis of hydrazine is insufficiently reliable at the levels currently stipulated in the HBSF IRA Decision Document.

For UDMH significant analytical problems still exist that must be overcome before the reliable quantitation of UDMH can be performed, but program objectives can be satisfied through the use of a qualitative

approach until further method improvements can be implemented.

The role of analytical chemistry in the conscientious selection of ARARs and final treatment objectives is often over-shadowed by the desire to obtain a solely health-based protective solution to chemical contamination problems at hazardous waste sites. Provided that a level of cleanup is protective, it is critical that the analytical methods reliably portray the level of contamination or remediation that may be required by a program ARAR. Therefore, a careful selection and QA review of health-based and technology-based criteria must be performed before selecting final treatment or regulatory limits.

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Timing—The Critical Element in a Successful Community Relations Program at the Rocky Mountain Arsenal The Basin F Liquids Story

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ABSTRACT

Early community relations planning and implementation at controversial Superfund sites can enhance the quality of decisions made and help keep projects on schedule. A case study at the Rocky Mountain Arsenal in Denver, Colorado, demonstrates that at a site with complex technical issues and regulatory framework, where incineration is a likely decision and where the local populace is opposed to incineration, an aggressive community relations program can be a technical tool for achieving technical objectives. The project worked within a framework of a community relations task force, briefed a wide range of interested parties (including the governor's staff), offered a community workshop and responded to community concerns in the decision document or with written responses.

PREMISE:
COMMUNITY RELATIONS ENHANCES DECISIONS, SUPPORTS SCHEDULES

During confirmation hearings for U.S. EPA administrator William K. Reilly, the U.S. Senate asked for an evaluation of the Superfund program and how it could be improved. Reilly returned with a management review in 90 days with *A Management Review of the Superfund Program*, known internally as the "90-day Study." In the study, the U.S. EPA announced a new long-term strategy for the Superfund program. One element is to encourage full participation by communities in cleanup decisions. The 90-day Study made 50 recommendations for improving the Superfund program. Of the 50 recommendations, 10 deal with community involvement. One key recommendation was: "Strongly support increased public involvement in Superfund decisions and accept occasional delays as the result of greater public involvement."

While we applaud the increased emphasis on public involvement, it has been our experience that an active community relations program initiated early in the process actually helps avoid delays, rather than causing them. The case study that follows shows not only that citizen involvement can help us stay on schedule, but that it can improve the quality of Superfund decisions.

CASE STUDY:
THE ROCKY MOUNTAIN ARSENAL

In March 1990, the U.S. Army at Rocky Mountain Arsenal (RMA) announced it would act quickly to use on-site incineration to handle its most complex and controversial waste problem. This decision was endorsed and supported by the U.S. EPA, the State of Colorado, officials of the local affected community and several citizen interest groups.

The nature of this decision bears examination, because it was so widely accepted and yet it contains so many elements of controversy. Citizen involvement was not by itself the critical element in this

widespread acceptance. As this case study will show, it was the timing of that involvement that made a difference. In a nutshell, our challenge was to:

> "Site a moderately-sized hazardous waste incinerator near Denver, a large, environmentally conscious city, to treat 8,500,000 gallons of toxic liquid waste at the nation's worst military hazardous waste site under a tight, legally mandated deadline."

At first glance, these conditions might seem to define a hopeless situation. To reach a remedial decision, the Army required some relatively complicated technical studies. It also needed to build enough comprehension and confidence in the community to ensure citizens could comment knowledgeably and the U. S. Army would have time to respond. We believed if we could do this, the solution finally selected could be put in place on time without fostering opposition or creating discomfort among the people affected by the cleanup. How the Army faced this challenge is the subject of this paper.

HISTORY:
MUNITIONS AND CHEMICAL HANDLING AT RMA

The Rocky Mountain Arsenal was established in 1942 on more than 17,000 acres (27 mi^2) adjacent to Adams County, Colorado. The installation is located approximately 10 miles from downtown Denver just north of Stapleton International Airport. The Arsenal has been the site of the manufacture of chemical materials such as mustard gas, white phosphorous and napalm. In the 1950s, the Army produced GB nerve agent and continued munitions-filling operations until 1969. Later, the Army initiated a program to destroy chemical munitions, which continued until the 1970s. To offset operating costs at the end of World War II, Congress directed the Army to lease selected facilities, including the Arsenal, to private industrial chemical manufacturers. Shell Chemical Company (now Shell Oil Company), a major lessee, manufactured agricultural chemicals at the Arsenal from 1952 to 1982.

In 1956, Basin F, a state-of-the-art evaporation pond, was constructed by building a dike around a natural depression and lining it with a 0.75-inch asphalt membrane. A one-foot layer of earth was placed on top of the asphalt to protect it. The pond could hold approximately 243,000,000 gallons of wastewater. From August 1957 until its use was discontinued in early 1982, Basin F was the only lined evaporative disposal facility in service at the Arsenal.

In February 1989, two administrative agreements were signed to ensure the Rocky Mountain Arsenal cleanup program was carried out in a smooth and responsible manner. The Federal Facility Agreement (FFA) and the Settlement Agreement (SA) define how appropriate remedial actions will be determined and the technical and financial responsibilities for each party. The FFA also defines how the interim

response actions (IRAs) will be carried out, consistent with the NCP. The IRAs are designed to support and be consistent with the final ROD on how the Arsenal will be cleaned up. When this decision is made in late 1993, the IRAs will either be completed or be incorporated into the final cleanup actions.

STRATEGY AND ISSUES:
AGGRESSIVE COMMUNICATIONS IN
A NEGATIVE ATMOSPHERE

The remedial objective of the Basin F Liquids IRA is to destroy Basin F liquids or render them harmless by June 1993. For a number of reasons discussed below, this schedule is exceedingly restrictive. To help achieve this objective on time, the Army needed a community relations program that would do more than simply inform the public of a decision after all the technical assessment had already been completed, with hopes the public would support the decision—or, at a minimum, not be so opposed that there would be delays in the schedule. The Army needed the public's help and participation in framing a decision that responded to citizen concerns even as it was developed. The key to the Army's approach was designing the community relations program to be a technical tool that helped to shape the remedial decision and thereby built consensus. The design of the community relations program was, therefore, based on the following premises:

- It should accommodate the full range of issues and community concerns generated by the technologies under consideration for Basin F (as well as those technologies that were excluded).
- It should provide a means of active public participation in technical issues that would have impact on significant portions of the remedial decision (i.e., response to public concerns should form a part of the decision and thereby build consensus and active support for the decision);
- It should have a substantial outreach component to ensure that all appropriate constituencies and affected parties are informed and involved;
- It should strive to achieve a "win-win" result. Early citizen involvement should improve the quality of the decision and help the Army stay on schedule.

Within the framework of this approach, the community relations program was influenced by several issues that were either peculiar to RMA or inherent in the nature of the Basin F liquids problem and its potential solutions. These issues were:

Complex Technical Issues

Basin F liquids are unique and unusual and cannot be handled by most conventional treatment methods. The waste is corrosive to most treatment equipment, has high concentrations of ammonia and contains significant concentrations of metals and organic chemicals (as many as 80 species). Scores of experimental treatability tests have been done over a 10-year period and a number of commercial hazardous waste facilities have tried without success to treat Basin F liquids. A few innovative technologies still in developmental stages seemed to be potentially promising, but the limit on temporary storage of the wastes ruled out all but proven approaches, none of which had been tried on wastes exactly like Basin F liquid.

Generalized Aversion to Incineration

This issue is not local, but rather reflects a national fear and mistrust of hazardous waste incineration. The Army evaluated 40 different treatment technologies, but the final set of five feasible technologies included two incineration techniques and two quasi-incineration techniques. Hence, from an early point in the study, it was apparent that incineration was the major technology under active consideration. All the design and risk studies subsequently showed incineration to be the safest and most reliable alternative. Nevertheless, the public in general and some groups in particular, were predisposed against incineration and expressed fears about explosive hazards and deleterious health effects of incinerators that were taken to be common knowledge.

The Superiority of One Incineration Technology
Over All Other Alternatives

Perversely, the problem of dealing with the widespread aversion to incineration was made "worse" by the results of our remedy selection study; they showed that one type of incinerator was so much better in nearly every way than the other alternatives, that it was almost impossible to define a set of decision-making priorities where this incinerator would not be the preferred solution. Thus, not only did we think that incineration was the best solution while the public was predisposed to think it was the worst solution, but also our technical case for incineration was so strong that the public was likely to think that we had manipulated the data.

Local Aversion to Incineration

Colorado—and Denver in particular—is environmentally conscious and has a history of objecting to any type of disposal practices that might result in air emissions into the already polluted atmosphere. As a consequence, we knew the cumulative impact of any IRA alternative on air quality would be carefully scrutinized by the public. Incineration, often referred to by citizen activist groups as a "landfill in the sky," would undoubtedly be a target of Denver's concern if it were proposed as a preferred alternative.

Complex Regulatory Framework

The cleanup of RMA is a Superfund action, but a history of litigation, unapproved consent decrees and settlement agreements has shaped the content and procedures of the cleanup program. In 1989, a Federal Facility Agreement (FFA) was signed that defined the roles and responsibilities of the participating organizations, who are: (1) the U.S. Army; (2) the U.S. Environmental Protection Agency; (3) Shell Oil Company; (4) the State of Colorado (not a signatory); (5) the U. S. Department of Justice; (6) the U. S. Department of Interior; and (7) the Agency for Toxic Substances and Disease Registry.

Two committees have an active role in remedial oversight. The RMA Committee, which consists of representatives of all of the agencies listed above, oversees most investigation and remediation programs. The Technical Review Committee (TRC), which consists of representatives of a number of local health and utility agencies, at-large citizen representatives, local government and representatives of the Army, was established by the FFA. In addition, day-to-day decisions on the community relations program are subject to the guidance of the Community Relations Task Force, which includes representatives of the Army, U.S. EPA, Shell and their contractors.

The FFA states that community relations at RMA will be done in accordance with U.S. EPA regulations. Interim Response Actions, such as the Basin F Liquids IRA, are performed under the Superfund removal authority, for which the community relations requirements are not well defined and for which there is no formal guidance aside from the public hearing and comment period requirements. At RMA, the Community Relations Task Force can recommend to the RMA Committee, which approves the action, on the direction and content of community relations programs for IRAs.

The overall regulatory picture, then, consists of a complex legal history, a complicated interagency agreement, seven major players with widely differing agendas, committees making decisions and committees making committees and reliance on a law that gives no clear-cut directions for community relations programs for large-scale, removal-authority actions like the Basin F Liquids IRA.

Multiple Conflicting Interests

All parties to the FFA and the State of Colorado shared a common interest: destruction of Basin F liquids by mid-1993. Each party, however, had other interests that had to be considered in the planning and implementation of the community relations program.

For example, the Army and U.S. EPA, facing a multidecade cleanup program, are individually concerned about establishing precedents for the future and the adequacy of the public participation and decision-making process as well as the effectiveness of the selected IRA alter-

native. Shell urges caution in all matters that it believes might have a bearing on present or future litigation. DOJ is concerned that concepts and commitments are correctly presented and consistent with other declarations of the federal government. The State maintains that it should manage the Basin F cleanup as a RCRA action. The State usually takes the position that the Army is not in compliance with RCRA and is therefore in willful breach of the law. The State is concerned that its official position should be correctly stated as final approval authority on the project. The Department of Interior is charged with protecting Arsenal wildlife, including the endangered bald eagles and the threatened ferruginous hawks. All this is to say that, in addition to overcoming the complexity of technical and community issues in working with the public, we had to devote substantial energy to overcoming the complexity of the RMA Committee members' interests.

Community Sensitivities

In 1988, Basin F liquids were removed from the basin and the soils and sludges were scraped up and placed in secure storage. The process of moving these soils and sludges unexpectedly released strong ammonia-like odors to the atmosphere. The odors drifted into neighborhoods adjacent to the Arsenal and residents complained strenuously. Some neighbors said that the odors caused serious health problems, but the Army, the U.S. EPA and the Colorado Department of Health (CDH) were unable to document any problems or detect harmful concentrations of contaminants with ambient air monitors.

Nevertheless, the odor problem was covered closely in the press and lasted for several months. The memory of this problem, reinforced by periodic mention in the press, lingered. Many residents perceived that the Army and its contractors had not taken adequate precautions to prevent this hazard, that the hazard had adverse health effects and that the Army either failed to own up to its actions or had tried to cover up a serious community health problem. Thus, a general climate of bitter memories and mistrust of the Army prevailed as the Basin F Liquids IRA study began.

In short, this was a tough technical problem with many of unusual conditions. In spite of this situation, or perhaps because of it, we wanted residents to understand these technical issues so that they could participate effectively in the critical elements of our decision: selection of one remedy from a small group of feasible technologies and determination of how that technology would be operated to ensure that it would both be safe and achieve cleanup objectives.

Based on the nature of these issues and the tight schedule for implementation of a Basin F liquids remedy, Community Relations Task Force members recommended to the management of their respective organizations that an innovative approach be taken to informing the public of incineration's probable preferred alternative status. Instead of waiting for the Draft Decision Document to be released and then holding a public meeting to hear from the citizens, the Community Relations Task Force recommended that a public education and involvement process start earlier than required in the FFA. The Task Force recommended that the Army hold a series of briefings for elected officials, special interest groups, the media and the general public to inform them of what technologies were being investigated and the pros and cons of each technology.

The Army approved this approach and within a week after the Draft Treatment Assessment Report was released, more than 200 people received background information on the technologies being considered. During these briefings, the Army made it clear that incineration was the leading candidate. The approach was significant because it was the first time the Army had "gone public" with a Draft Treatment Assessment Report. This departure from the norm was not only a first, but as was demonstrated, was key to the Army's success in gaining community support for its eventual decision.

In addition to the briefings, the Army hosted an informal workshop and invited interested citizens to attend. The workshop was designed not only to provide more in-depth technical information to the public on all the technologies being studied, but more importantly, to also provide the Army with in-depth knowledge of the public's questions and concerns. Having learned of the public's concerns and questions, the Army was then in a position to demonstrate its sensitivity to the community by addressing its concerns orally at the workshop, at the formal public meeting held at the start of the comment period two months later and in the Army's Final Decision Document.

The effectiveness of the Task Force's community relations efforts can be measured by the overwhelming lack of negative reaction to the Army's decision. The community relations program and individual techniques that were employed are described below.

THE PROGRAM:
BUILDING CONSENSUS THROUGH INTERACTION

The two basic building blocks of our community relations program were the development of a community relations plan and strategy and the implementation of aggressive community relations activities. These activities were undertaken under the combined guidance and review of the Community Relations Task Force.

The Community Relations Task Force

The Task Force represented the diverse interests of the Army, the U.S. EPA and Shell Oil Company. The group met frequently and attendance at any given meeting included some or all of the following: the Army's technical, community relations and legal staff and consultants; Department of Justice attorneys; Shell's public relations and technical staff and consultants; and U.S. EPA's community relations coordinators. The purpose of this group was to discuss, coordinate and agree on community relations activities planned for the Arsenal.

The Community Relations Plan and Strategy

To provide a useful framework for understanding and responding to community concerns, Superfund guidance required development of a Community Relations Plan (CRP) tailored to the community that surrounds and is potentially affected by, the Arsenal. Using documents and information previously developed by Shell and the U.S. EPA as a basis, the Army conducted a community assessment that included telephone interviews with Arsenal neighbors and other interested parties. All of this information was then distilled into a CRP that provided background and guidance not only for the Basin F Liquids IRA, but also for the program as a whole.

Further, the Task Force developed a Communication Strategy targeted specifically to the vigorous public information effort launched in conjunction with release of the Draft Treatment Assessment Report. The document identified messages, audiences and a briefing schedule. Out of this overall planning process, we identified several categories of interested individuals, each with its own unique set of interests and concerns. While it might be natural to assume that we could take a single approach to the information needs of a particular group, we discovered through the community assessment that we had to differentiate the information needs and concerns even within categories. For example, in the case of key federal officials, members of Congress not only had different concerns from the U.S. EPA, but different concerns from one another. These varied audiences are described below:

- **Federal officials**, including both regulatory agencies and Members of Congress who have expressed continued and active interest in cleanup plans for the Arsenal. Members of Congress have most often expressed concern about the cleanup schedule and the long-term uses of Arsenal land. The U.S. EPA sought the highly technical information in our Treatment Assessment Report and was very sensitive to state and community acceptance of our alternative.
- **State officials**, including four different groups: the Governor's office, the Colorado Department of Health, the Attorney General and state legislators, who at any given time had divergent agendas for the Arsenal. For example, the Attorney General's office sought and reviewed information on the Basin F Liquids IRA with litigation issues as the foremost concern, while the Colorado Department of Health wanted detailed information about cleanup technologies and eventual uses of the land.
- **Local government**, including the affected counties, cities and water

district were most concerned about immediate and long-term health effects, long-term operation and maintenance costs and negative impacts on their communities and property values.

- **Arsenal neighbors**, including citizen groups such as Citizens Against Contamination that had organized to address Arsenal issues and had concrete, specific concerns and information needs about where, when and how cleanup technologies would be implemented.
- **Special interest groups**, such as Citizens' Intelligence Network, the National Toxics Campaign, the League of Women Voters, the Sierra Club and the Audubon Society, whose interests spanned the range of environmental issues.
- **The media**, including the major metropolitan print and electronic media, national media and two Commerce City newspapers, all of which covered Arsenal activities with great interest, cast doubt on the Army's credibility and commitment to cleanup and often sensationalized new developments at the Arsenal.

Even when everyone agreed on the importance of a specific issue, individual information needs were different. For example, almost everyone was concerned about cleanup standards, i.e., how clean is clean? For some audiences, this meant we had to speak in concentration units ppb; for others, in precedents set at other locations; and for others, in terms of the long-term uses of the land that the standards would allow. As a result, we knew not only that a single community relations technique would not suffice, but also that even individual techniques, such as briefings, would have to be tailored to individual audiences.

Community Relations Activities

Taking into account the varied audiences and the aforementioned issues that were impacting the Basin F Liquids IRA alternative selection process, we embarked on the community relations activities described below.

Official briefings

Over a period of a week after the release of the Draft Treatment Assessment Report, the Army presented tailored briefings to key target audiences described above. We devoted considerable effort to the briefings through the preparation of the following materials:

- A **slide show** to provide background for the Basin F Liquids Interim Response Action, the alternatives evaluated and the preferred alternative.
- **Information kits** that included the following information:
  — Five fact sheets describing the five alternatives we evaluated;
  — Fact sheets on the Federal Facility Agreement, Risk Assessment, Notes on Chemicals in Basin F Liquids and the Remedy Selection Process
  — A U.S. EPA fact sheet on Public Involvement in the Superfund Program
  — A Brief History of the Rocky Mountain Arsenal
  — A Background Paper on the Basin F Liquids Interim Response Action, including a detailed description of alternatives

Media briefings

After briefing key officials, we briefed the media, drawing upon and tailoring our repertoire of information and support materials.

Workshop

To help interested citizens understand the complex technologies and evaluation process, we invited them to a half-day workshop so that we could begin to address their questions and concerns in detail. The workshop was designed to accomplish the following objectives: (1) help residents understand the alternatives evaluated for Basin F liquids; (2) respond to concerns that had been expressed up to that point regarding the alternatives; (3) help residents understand the selection process and provide the opportunity to manipulate weighting of the selection criteria; and (4) provide responses to new questions that the workshop generated. Activities associated with each of these activities are described below.

Basin F liquids alternatives

For this presentation, we drew upon key portions of the basic slide show that had been used for the briefings and tailored the presentation to a lay audience of neighbors.

Response to previously expressed concerns

To make sense out of the high-tech information related to Basin F liquids, we took a low-tech, down-to-earth approach to answering persistent questions that had been generated previous to the workshop. For example, to help people understand the physical properties of Basin F liquids, we presented a one-liter graduated cylinder of simulated Basin F liquids (made with water, food coloring and coarse kosher salt) to demonstrate how a supersaturated brine (like that from Basin F) looks and behaves. We used this demonstration to show how difficult it is to pass the liquid through a normal pipe and to call attention to the corrosive nature of the liquid, both of which severely constrained the alternatives that could be considered.

Then we used half-pint (250 Ml) jars to demonstrate the quantity of waste that would remain after treatment with the various technologies we had evaluated: from one liter of actual Basin F liquid (the same volume as our demonstration model), we demonstrated, that either of the two incineration alternatives would leave 250 Ml (one jar) of residue. Either of the two quasi-incineration alternatives would leave 750 Ml (three jars) of residue and solidification, the fifth alternative, would leave 2,250 Ml (nine jars). To demonstrate the quantity of residual pesticides remaining in the off-gas production from incinerating the entire 8,500,000 gallons of Basin F liquid during the 18-month operation of the incinerator, we used a 0.5 oz vial, which could fit in the palm of our presenter's hand.

The selection process

For this discussion, we changed gears and brought the power of the computer to the workshop. We set up the raw technical scores against the selection criteria and then projected this matrix from a computer screen onto an overhead screen. After explaining and demonstrating how the selection process worked, we changed the weightings of any of the selection criteria to meet the preferences of members of the audience—live and on-screen.

It is worth noting that in preparing for the workshop, this portion of the agenda caused the most discussion and consternation. Some members of our Task Force said that putting this kind of information in the hands of ordinary people was similar to "handing them a gun." Others said that allowing people to manipulate the values themselves was essential in order to persuade people that the Army had not skewed the results to favor its own preferred alternative. Alternate proposals were set forth to provide hard copies of different scenarios or to demonstrate the selection technology on the overhead computer screen without allowing citizens to manipulate the values. Our Program Manager decided to use the full information approach that included manipulation of weightings.

New questions

To maximize opportunities for participants to ask questions, we divided into small, interactive groups moderated by neutral facilitators. While we committed ourselves to a flexible format for these meetings to allow group dynamics to drive the way they operated (which turned out to be rather differently from one another), in general we structured them to be moderated by a neutral, non-Army employee, with a resource person assigned to each group to assure that the group did not go off on a tangent based on factually inaccurate information. In general, the resource persons spoke only when spoken to; they also synthesized the public concerns and comments to feed back to the Army's technical policy staff for response by the end of the workshop. The questions generated also were recorded on large flip-charts. The U.S. EPA had an observer in each small group; but all Army and Shell staff left the room, in order to encourage the free flow of questions.

At the end of this part of the agenda, the groups categorized their questions and identified a representative to report to the full group.

When the group questions and concerns were reported, the Program Manager and his technical staff responded to questions that could be answered at that time. Other questions were deferred until more information was available. Some concerns were incorporated into the design of the final decision.

Public comment period and public meeting

We held a 30-day public comment period, during which we held a public meeting to receive comment.

Information repositories and information center

To make the full range of technical information available to the interested public, copies of the full technical documents were placed in the Arsenal's Joint Administrative Record and Document Facility (JARDF) and five libraries in the Denver area.

Tours

Tours of the Arsenal are an ongoing feature of the community relations program.

Mailing List

We compiled a mailing list from our own and the U.S. EPA's sources to create a combined list of key contacts to whom we could send information. We also used this list and a professional calling service to call interested citizens to invite them to the workshop and the public meeting.

THE IRA DECISION: THE PUBLIC MAKES A DIFFERENCE

Effects on Implementation and Operation Objectives

One of the comments the public most commonly make regarding the public involvement process for hazardous waste remediation is, "You, (the Army) say that you want public input to your decision. But I am sure that if we come to the end and you favor one remedy and the community favors another remedy, you are going to go with your preferred alternative."

Our experience at the Rocky Mountain Arsenal clearly demonstrated that, as public involvement experts, we must recast the "them-us" perception and the "thumbs up/thumbs down" approach to decision-making. Involving the community early in the process allows us to work together to develop a solution to the contamination. At the end of the studies, we should share some common understandings about the nature of the problems and the attendant complexities.

In the case of the Arsenal, we were able to refocus the discussion from "incineration/not-incineration" to consideration of the best ways to protect the public both from negative health effects and from worry about the technology that was most appropriate for the overall management of Basin F liquids.

We did this in one of two ways: (1) we incorporated public concerns into the decision document itself, and (2) we responded in writing to public concerns about incineration and other issues related to final disposal of Basin F liquids. Thirteen supplemental provisions for implementation and operation of a Submerged Quench Incineration treatment facility were added to the decision document as a result of public involvement. These supplemental provisions concern how the treatment system will be developed and operated, to assure that government agency and private citizen concerns for safety and environmental protection are met.

The concerns fel into seven general categories with one to six subtopics in each category. Each subtopic was addressed in one of the two ways mentioned above. To document how the Army addressed each of the concerns, the decision document included a matrix with a bullet-list of the concerns and how the Army responded to them (Table 1). The matrix was followed by a description of the decision elements listed in the matrix.

For example, under general concerns about incineration, the Army incorporated specific provisions in the decision document to respond to four of the six specific subtopical concerns. One of these, the concern about other uses of the incinerator after the Basin F IRA is completed, resulted in this commitment in the decision document: "Following completion of the Basin F Liquids IRA, the incinerator will be shut down, decontaminated, decommissioned and disassembled under the closure provisions described in Section 9.0." The other two concerns that were subtopics under the general category of incineration received written responses.

Table 1
Expressed Concerns and Form Response[1]

MAJOR TOPIC	SPECIFIC CONCERN	FORM OF RESPONSE*
Treatment Process in General	Odor	Written Response
	Operational controls re: weather, upset conditions	Decision Element (4,5)
	Location of facility	
	Off-site disposal of residuals or wastes	Decision Element (1)
	How the process works	Written Response
		Written Response
Incineration	Characteristics of submerged quench incinerator	Written Response
	Operational controls re: weather, upset conditions	
	Products of incomplete combustion (PICs)	Decision Elements (4,5,8)
	Safety of SQI technology	
	Use of incinerator after Basin F IRA	Decision Elements (2,8,11)
	Screening and selection of incinerators	Decision Elements (3,6)
		Decision Element (13)
		Written Response
Health Effects	Transportation risks	Decision Element (7)
	Treatment process risks	Decision Elements (4,5,8,9,11)
		Written Response
	Long-term effects	
Trust/Credibility	Objectivity and quality of monitoring	Decision Elements (8,9,10)
	Existence and enforceability of standards for many emission compounds of concern	Decision Elements (2,8,11)
	Army's commitment to safety	Decision Elements (3,4,5,7,8,9)
Ranking	Details on ranking	Written Response
	Constraints to study	Written Response
Public Involvement	Expand opportunities for interaction	Written Response
	Permanent hotline and response log	Decision Element (12)
Regulatory Process	Scope of IRA in relation to other cleanup activities	Written Response

* Written response to expressed concerns occurs in Appendix A to the Treatment Assessment Report. Concerns from the public workshop are grouped separately from other concerns and comments submitted by government agencies and parties to the federal facility agreement.

"Decision Element" means that the Army's response to the expressed concern has been made a part of the proposed decision described in Section 6.0 of this decision document. The decision element numbers (in parentheses) shown here correspond to the numbered "Implementation and Operating Objectives" presented in Section 6.2 of this document. [See below]

Public and State Response

Response to our approach was very positive. At the end of the workshop, for example, one person commented that for the first time, he understood what the problems at the Arsenal are and how the technology will help solve the problems. Another person said, "The workshop was important to communicating to the citizens of this area the concern of the Army."

There has been no groundswell of opposition to the final decision. In fact, when the National Toxics Campaign criticized the Army for its decision, the Colorado Attorney General's Office came to the Army's defense, noting that the Army had made extraordinary efforts to involve and respond to citizens regarding the Basin F Liquids IRA.

LESSONS LEARNED: BENEFITS OF PUBLIC INVOLVEMENT

In many Superfund programs, the community relations program is tangential to the more central attractions of the RI/FS. The common model is to use technical studies to reach decisions and the community relations program to inform the public of these decisions and answer any questions about the decisions. For the Basin F Liquids IRA, however, we moved the community relations effort to center stage and gave the program a substantive role in shaping the technical decision. The effectiveness of this approach provides us with several lessons for the future on how similar technical decisions can be made in a fair and timely fashion.

Involve the Public Early

Citizens expect to have a role in environmental decision-making and laws such as those that gave us the Superfund program guarantee them that right. Superfund requirements, however, do not compel the Army to provide for public input until the official comment period, which is held after the Army has developed a preferred alternative. Being asked to comment under these circumstances, however, invariably perturbs

the public and often results in opposition to a project based not so much on its merits, but rather on how the initial decision was made, i.e., with the public excluded. For the Basin F Liquids IRA, it was evident that involving the public at a predecisional stage met with wide approval amongst not only the public, but also the various state and federal agencies with oversight responsibilities. In other words, no one opposed the Army's decision on procedural grounds. Timing on this project was absolutely key.

Incorporate the Public's Input Into the Decision-making Process

It is not enough simply to listen and record the public's questions and concerns. These concerns must be addressed and considered in a meaningful way. Timing of the community relations program for the Basin F Liquids IRA demonstrated that it was possible to get the public's input early enough in the process that the remedial alternatives could be crafted to enhance adherence to Superfund provisions that require consideration of state and community acceptance.

Document Your Response to the Public's Input

Too often a federal agency gets no credit for the portion of the public's input that it does incorporate, only criticism for the input it apparently discounts. In its Final Decision Document for the Basin F Liquids IRA, however, the Army went to great lengths to document its full understanding of the community's concerns and addressed them in concrete terms through the addition of more than a dozen supplemental provisions. By developing the matrix of community concerns and Army responses (Table 1), the Army got credit for being responsive to the community and the community could clearly see that it had been included in the decision-making process.

Include Community Relations as a Technical Tool to Achieve Technical Objectives

Incorporating citizens' input was not designed simply to make them feel better about the process; it improved the quality of the decision itself. It is all too easy to be condescending in our attitudes toward public input, believing that because we are the experts, we have all the answers and could not possibly have overlooked anything. The addition of 13 supplemental technical provisions to the decision document based on public comments demonstrated that educating the public early helps residents contribute constructively to the decision-making process. The result is a technical solution that better addresses the safety and environmental protection objectives of the IRA.

For example, the Army responded to citizen concerns about products of incomplete combustion by agreeing to "...conduct a special predesign pilot test of the incinerator, planned specifically to collect and analyze data on products of incomplete combustion or PICs. Information from this test will be used both in design and in planning of operational controls... [and] will be presented to the Organizations and the State in a design review."

An Aggressive Community Relations Effort Speeds, Rather Than Delays, the Decision-making Process.

Working under the tight time frame that the Army had for implementing the Basin F Liquids IRA, it would have been easy to conclude that there "wasn't time" for up-front community relations. The experience for this IRA demonstrates clearly that the real potential for delays was not in involving the public, but in making a decision that would be challenged by the community and oversight agencies. Given the issues involved in the Basin F liquids problem, the Army knew that such challenges were not just possible, but probable. Timing of the Army's up-front community relations effort clearly demonstrated the potential for building consensus out of controversy.

If You Have a Pattern That Works, Use It Again.

As the Army embarks on evaluation of remaining IRAs, we expect to include community relations planning as an integral part of our technical work. In this process, we expect to identify community issues and concerns, respond to those concerns as we go and thereby work within our time constraints. We expect to foster the free flow of technical information and community concerns between the Army and the community and to build a decision tree that includes public input. Thus, we feel that by anticipating and responding to issues, we can not only stay on schedule, but also end up with better solutions to the Arsenal's contamination problems.

Remediation of a 115,000-Gallon Petroleum Pipeline Leak

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ABSTRACT

A rupture in a buried petroleum pipeline released 115,000 gallons of diesel fuel, contaminating soil and groundwater at a site in Milwaukee, Wisconsin. Emergency and interim response actions resulted in the recovery of more than 70,000 gallons of product from the ground surface, a nearby creek and recovery trenches. Based on the results of a contamination assessment, an evaluation of remedial alternatives indicated that the most cost-effective and technically feasible remedial method included low temperature thermal desorption for treating the impacted soils and discharge of impacted groundwater via an automated interception trench to a sanitary sewer. The implementation of the thermal desorption process was the first application of its type in the State of Wisconsin.

Approximately 10,000 cubic yards of soil, with a total petroleum hydrocarbon (TPH) concentration of up to 24,000 parts per million (ppm), were treated at the site using the thermal desorption system. Using a feed rate of between 15 and 30 tons per hour, the impacted unconsolidated materials, varying in composition from gravelly sand to silty clay, were heated to between 400 and 500 °F in a propane-fired rotary kiln. The petroleum vaporized from the soils and was completely oxidized in an afterburner operating at 1450 °F. After processing, the soil was replaced in the excavation with a TPH concentration of less than 10 ppm.

Groundwater remediation continues at the site. Impacted groundwater is intercepted by a 225-foot long collection trench. An automated pumping system recovers impacted groundwater which is subsequently discharged to a sanitary sewer. Dissolved organic compounds total less than 5 ppm, therefore, no treatment is required prior to discharge to the sewer.

INTRODUCTION

On June 4, 1988, approximately 115,000-gallons of No. 2 diesel fuel leaked from a ruptured underground pipeline. The pipeline rupture occurred in a county park in a residential area of Wauwatosa, Wisconsin. Some of the product from the pipeline rupture gushed to the surface where it flowed downhill and into an adjacent creek. The leak was immediately discovered by pipeline pressure monitoring at which time the pipeline was shut down. All relevant authorities were immediately notified including the local police and fire departments, the Wisconsin Department of Natural Resources (WDNR) and the Department of Transportation (DOT).

Emergency response actions included controlling access to the site, excavation and replacement of the ruptured pipeline segment, and recovery of free product. Free product was recovered from the pipeline repair excavation and from the ground surface using vacuum trucks. Absorbent booms and pads were placed in the creek to contain and collect product from the surface water. During the week after the leak,

additional back-hoe pits were dug in the vicinity of the release to recover subsurface free product with vacuum trucks. These immediate response actions recovered approximately 70,000 gallons of free product.[1]

SITE INVESTIGATIONS

Site investigations were required to define the nature and extent of impacts to soil and groundwater. The investigations Hydro-Search, Inc. conducted included the installation of soil borings with soil sampling to characterize the geology and determine the lateral and vertical extent of impacted soils, and the installation and sampling of observation wells to characterize the rate and direction of groundwater flow and the extent of impacted groundwater. In addition, a site survey was performed locating all sampling locations as well as site features and utilities including overhead power lines, storm sewers, sanitary sewers, gas pipelines and petroleum pipelines.

Geology

Regional information regarding the geology at the spill site was obtained from 41 private well logs located within one-half mile of the site. Site-specific geologic information was obtained from more than 40 soil borings constructed during the site investigation.

Geologic materials at the site consist of unconsolidated glacial deposits underlain by dolomite bedrock. The thickness of the unconsolidated deposits vary regionally from less than 10 feet to several hundred feet.[2] The unconsolidated materials consist of intermixed silty clay, sand and gravel. Figure 1 shows an east-west regional geologic cross-section through the spill area. The cross-section information is based on private well logs located in the area. At the site, the thickness of the unconsolidated deposits is at least 30 feet. The unconsolidated material consists of approximately 0.5 to 1.0 feet of clayey silt topsoil, between 1 and 4 feet of silty sand and gravel fill material, occasionally a 1 to 2-foot thick buried black clayey silt soil horizon, and intermixed glacial silty sand, clay, and gravel.[3] Figure 2 presents a northeast to southwest geologic cross-section across the site.

Underlying the unconsolidated glacial deposits is the Niagara dolomite, a white to gray, fine to coarsely crystalline dolomite. The Niagara dolomite dips gently to the northeast into the Michigan Basin.

Hydrogeology

The water table at the site occurs in the unconsolidated glacial deposits approximately 5 to 7.5 feet below ground level. Based on water level measurements obtained on several occasions from seven monitoring wells and Underwood Creek, local groundwater flow across the spill site is west towards the local discharge point, Underwood Creek. Figure 3 shows a water table map which indicates the local flow direction.[1] Regional groundwater flow deeper within the bedrock aquifer is to the east towards Lake Michigan.[2]
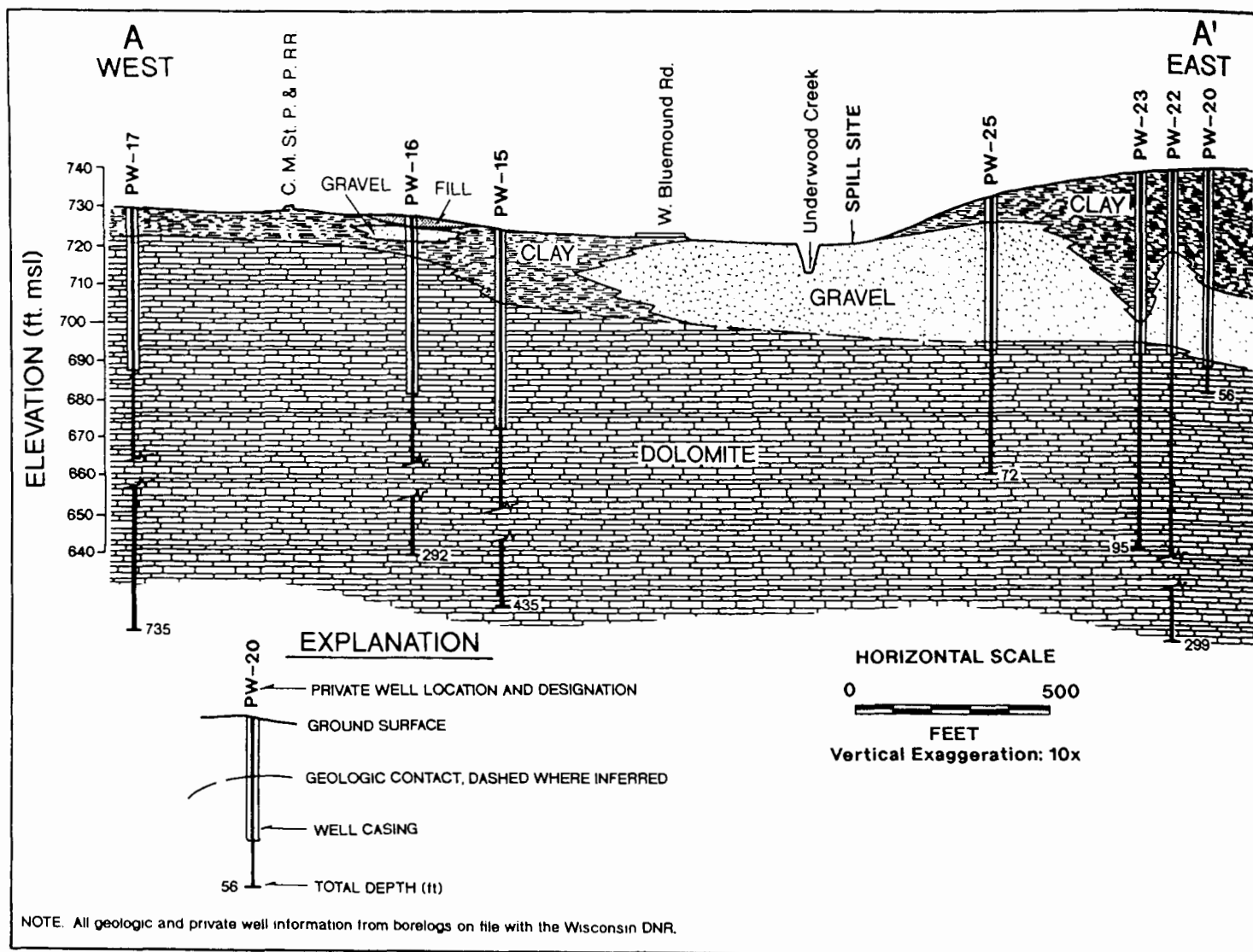
Figure 1
Regional Geologic Cross-Section A-A'

The site hydraulic gradient is relatively gentle, averaging approximately 0.035 feet per foot. The hydraulic conductivity at the site ranges from approximately 1×10^{-3} cm/sec to 1×10^{-5} cm/sec. Assuming a porosity of 25%, the calculated range of flow velocities across the site varies depending upon the hydraulic conductivity from 0.4 ft/day (146 ft/year) to 0.004 ft/day (1.46 ft/year).

Local Groundwater Use

All homes in the vicinity of the site have a municipal water supply available for use. Records indicate 41 private wells are located near the site. With the exception of five deep wells, all the private wells were constructed prior to 1963. Because these homes are supplied with a source of municipal water, the private wells are no longer used for potable water. Therefore, the risk to local residential water users is low. Some of the private wells may be used for watering lawns. All the private wells are cased from the ground surface into the bedrock.[3]

Soil Impacts

The horizontal and vertical extent of soil impacted by the diesel fuel leak was investigated by installing 36 soil borings at the site. The boreholes were advanced using the continuous split spoon sampling technique.

All soil samples were screened for volatiles in the field during drilling using an HNu Model PI-101 photoionization detector (PID) with an 11.7 eV probe. Soil samples with elevated PID readings were submitted for laboratory analysis of total petroleum hydrocarbon (TPH). Two samples were submitted from several boreholes to determine the vertical extent of the petroleum impacts. In general, soil impacts ranged from non-detectible levels of less than 10 parts per million (ppm) TPH to 24,000 ppm TPH.[1]

In Wisconsin, there are no regulations governing the concentration of petroleum products in soils. However, the Wisconsin DNR uses a guideline of 10 ppm TPH as its cleanup standard.[4] Based on this standard, the lateral extent of impacted soil is shown in Figure 4. The impacted soils generally form a 25- to 50-foot halo around the surficially stained area where the spilled product initially pooled. The impacted soil area extends approximately 300 feet long by 100 to 260 feet wide and covers an area from east of the pipeline rupture to the edge of Underwood Creek. The lateral wicking of the product into the unsaturated soils was enhanced by the extremely dry condition of the soils at the time of the release due to drought conditions occurring in the area during the summer of 1988.

The vertical extent of soil impacts indicated elevated TPH concentrations to depths of 12 feet.[1] The impacts below the water table are attributed to the forced migration associated with the pressure of the release. Figure 2 shows the lateral and vertical extent of soil impacts
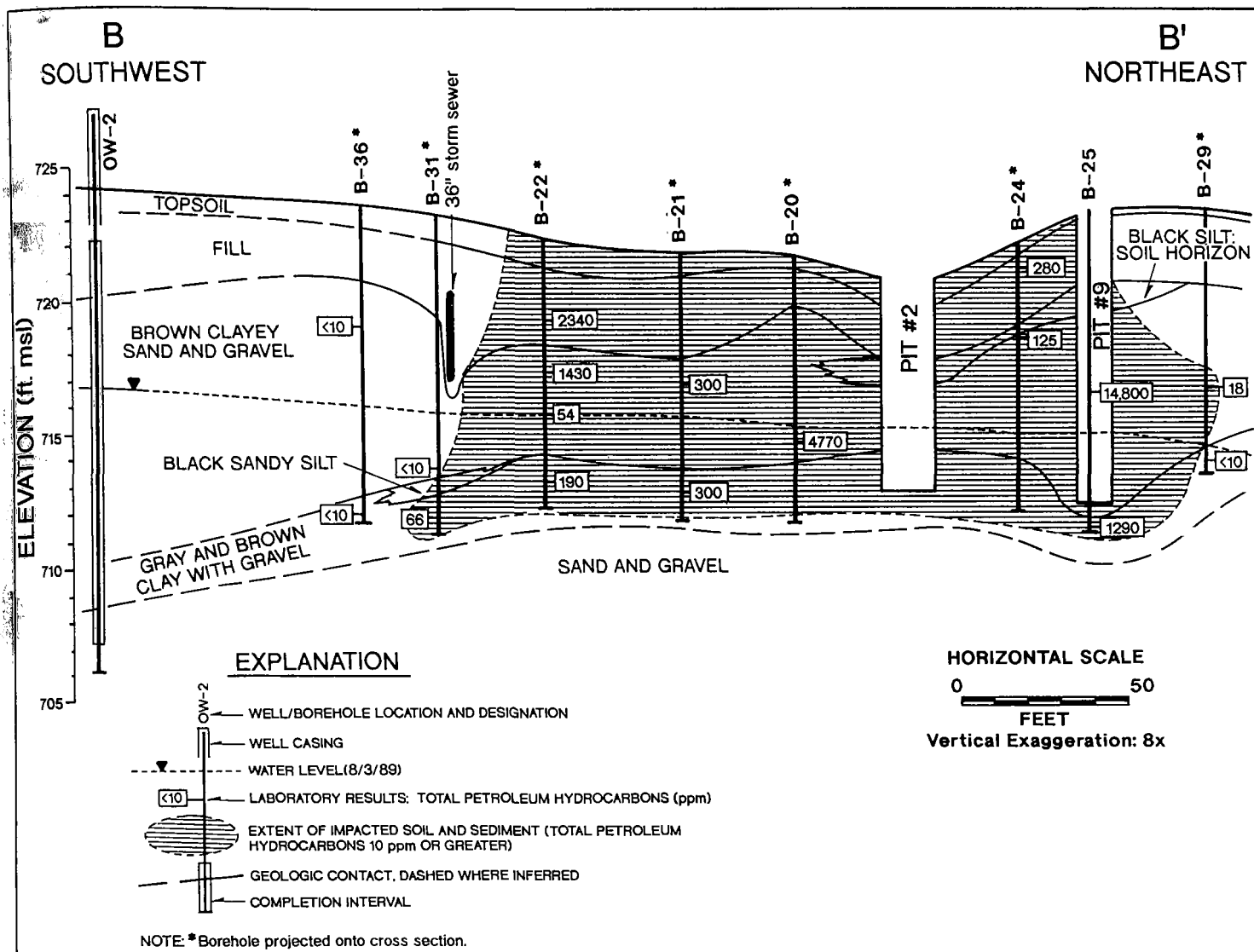
Figure 2
Local Geologic Cross-Section B-B'
with Extent of Impacted Soils

at the site along a southwest to northeast cross-section.

Groundwater Impacts

Groundwater quality was monitored by sampling groundwater observation wells which were installed around the perimeter of the impacted soil area. These wells were sampled on several occasions and analyzed for either benzene, ethylbenzene, toluene and xylene (BETX), or volatile organic compounds (VOCs) and base neutral/acid extractable compounds (BNAs). The laboratory results from all sampling events indicate no detections of any compounds in any of the monitoring wells.[5] Monitoring wells were not installed within the impacted area since they likely would be destroyed during soil remediation.

INTERIM ACTION

Based on the results of the site investigations, two recovery trenches were installed to prevent off-site migration of hydrocarbon compounds and to facilitate additional product recovery. In July 1988, two 150-foot long recovery trenches were installed across the impacted area (Figure 4). Each trench was excavated to a depth of 2 to 5 feet below the water table, backfilled with pea gravel, and capped with site soils. A 36-inch diameter steel slotted culvert was installed vertically in each trench to act as a sump for recovery of groundwater and free product. Groundwater was pumped from the base of each sump and discharged

under permit into the sanitary sewer system. The groundwater pumping removed impacted water and depressed the water table to expedite free product recovery. Free product was recovered using an oil skimmer and/or oil absorbent pads.

During the past 2 years of operation of this recovery system, approximately 7,300 gallons of free product have been recovered with approximately 85% of this total coming from Trench 2 which is located closest to the pipeline leak. During this period, approximately 2,000,000 gallons of water were discharged to the sanitary sewer. Monthly monitoring of this effluent indicates the water contains an average of less than 500 ppb of total organics consisting predominantly of benzene, ethylbenzene, toluene, xylene, naphthalene, hexachloroethane, bis(2-ethylhexyl) phthalate, fluorene, acenaphthene and 2,4-dinitrotoluene.[5]

EVALUATION OF SOIL REMEDIATION ALTERNATIVES

Due to the large amount of unrecovered product contained within the soils, the WDNR required remediation to the 10 ppm TPH level.[4] Several methods for remediation of impacted soils were evaluated by Hydro-Search, Inc. and included:

• Passive Remediation
• Excavation and Landfilling
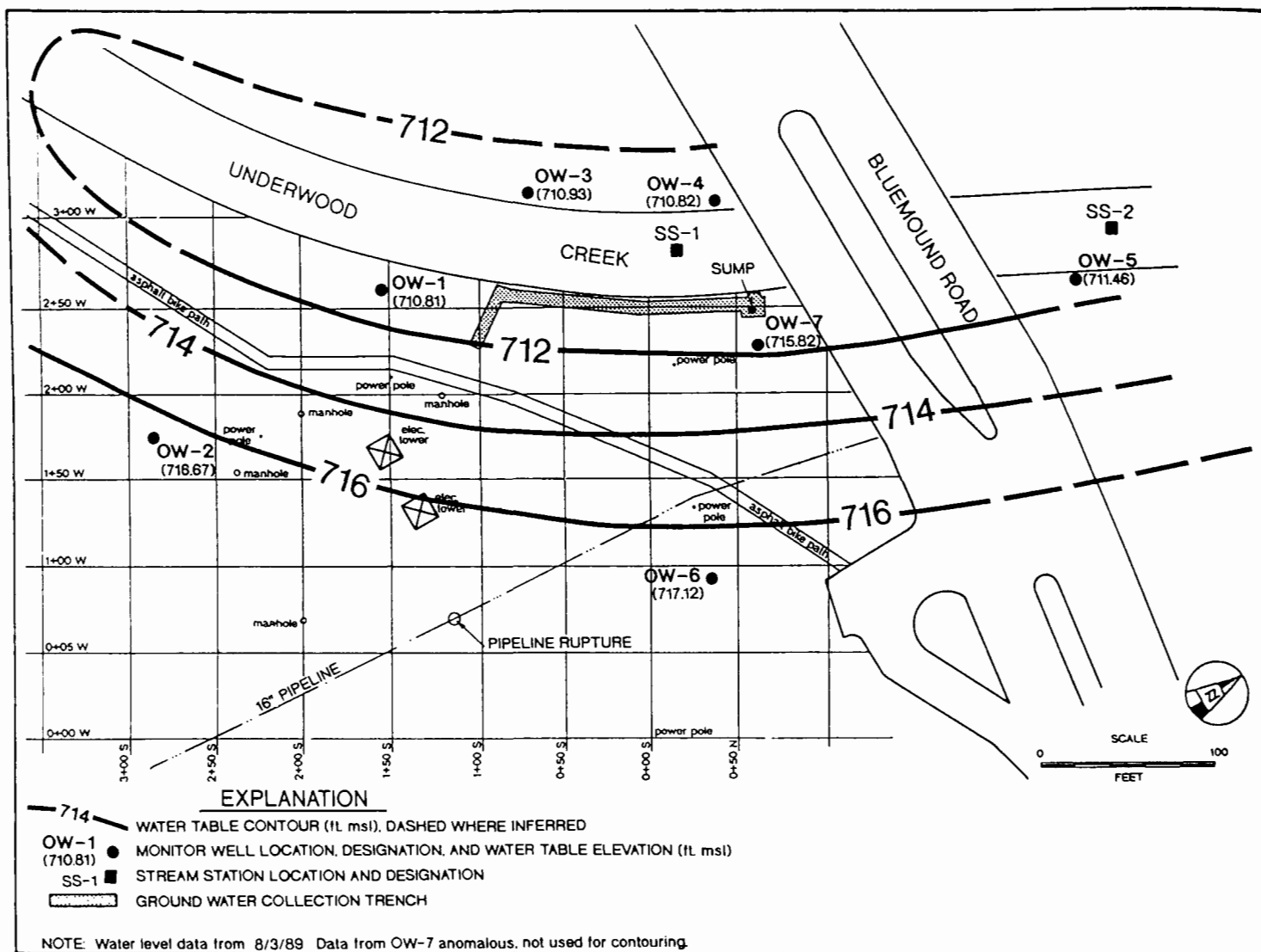
Figure 3
Water Table Surface

- Landspreading
- Vapor Extraction
- Bioremediation
- Enhanced In Situ Bioremediation
- Thermal Evaporation

These alternatives were evaluated for technical implementability and environmental effectiveness; permitting and monitoring requirements; and cost and duration of project.

In order to evaluate various cleanup methods, the following assumptions were employed:

- The volume of impacted soils requiring remediation is 10,000 cubic yards. The approximate dimensions of the impacted area, as determined by laboratory TPH analysis of less than 10 ppm, are 200 feet by 250 feet by 7 feet deep.
- The worst case average TPH concentration in the impacted soils is 5,000 ppm. This conservative value is more than double the average laboratory TPH concentration detected in the impacted soil samples.
- Remedial alternatives involving excavation would not be required to excavate beneath the high tension electrical towers, behind or beneath the concrete panels lining the creek or below the water table which occurs at a depth of between 5 and 7.5 feet.

In August 1988, Hydro-Search, Inc. submitted the feasibility study to the WDNR. A summary of the evaluation of these alternatives is presented in Table 1. The WDNR review of the feasibility study concluded the following:

- Passive Remediation: determined to be inappropriate and rejected in favor of more environmentally responsible options.
- Excavation and Landfilling: determined to be an acceptable means for cleaning up the site because it provides for source removal, thus eliminating many long-term site management concerns.
- Landspreading: determined to present a number of permitting, operating and monitoring obstacles which limit the applicability of the method. In addition, landspreading was not recommended for diesel fuel contaminated soils.
- Vapor Extraction: determined to be not appropriate based on the low volatility of diesel fuel.
- Bioremediation: determined to be not acceptable because operational requirements for space preclude the use of the immediate vicinity of the spill site.
- Enhanced In Situ Bioremediation: determined to be unacceptable based on lack of approval by the Water Supply Section for a waiver for the use of injection wells.
- Thermal Evaporation: determined to be the most acceptable means of remediating the site because it contains a number of desirable aspects such as:

  — It eliminates the source of soil, air, surface water and ground-

EXPLANATION

OW-1 O   MONITOR WELL LOCATION, DESIGNATION, AND TPH CONCENTRATION (ppm)

B-39 ✦   SOIL BOREHOLE LOCATION, DESIGNATION, AND TPH CONCENTRATION (ppm)

----------   LATERAL EXTENT OF SURFICIAL SOIL STAIN

—–10—   LATERAL EXTENT OF IMPACTED SUBSURFACE SOIL, DASHED WHERE INFERRED. LABORATORY RESULTS TPH 10 ppm OR GREATER

▓▓▓▓   GROUND WATER COLLECTION TRENCH

NOTE: (NA) indicates not analyzed.
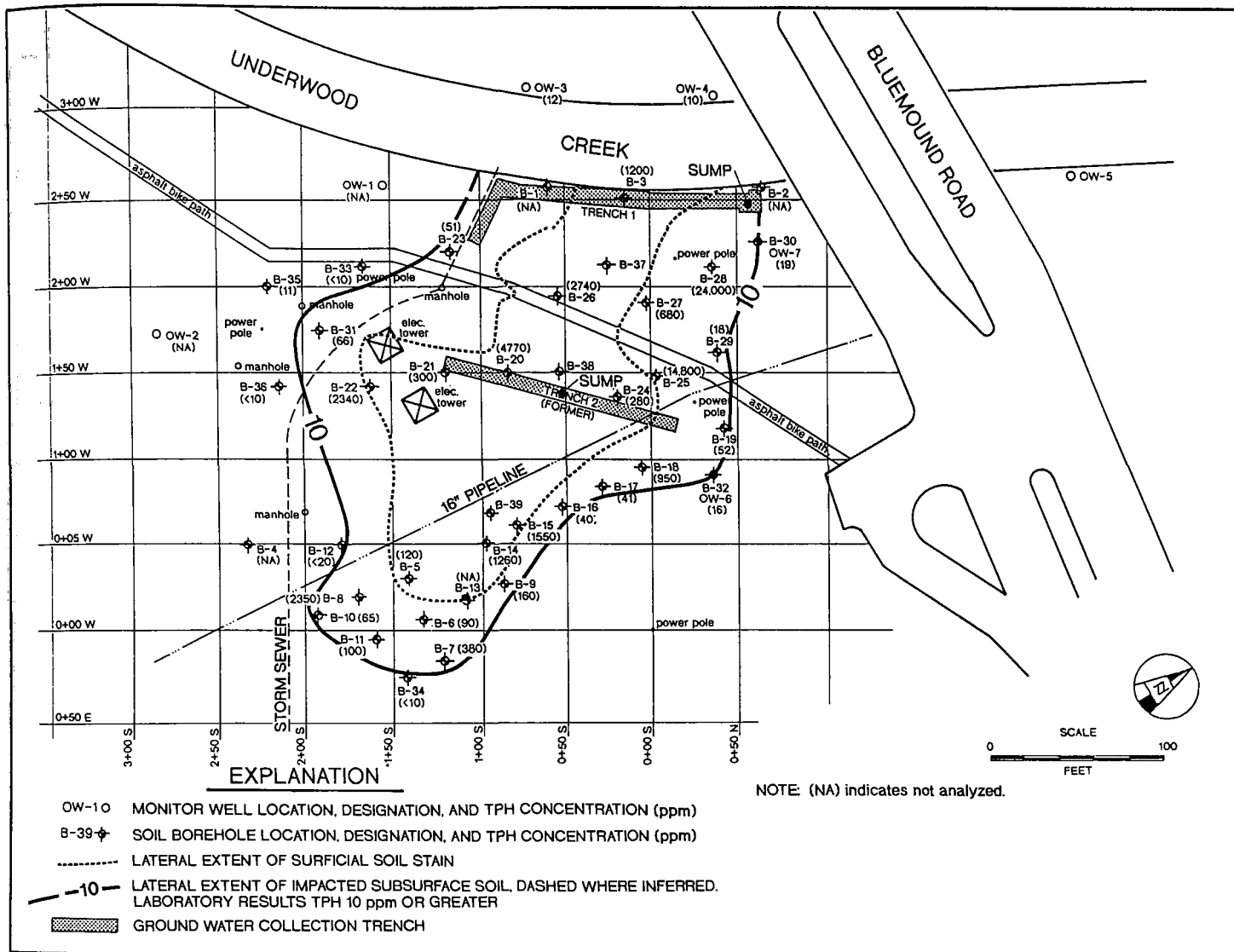
Figure 4
Lateral Extent of Impacted Soil

water contamination.

— It does not require a source of clean fill.
— It does not take up valuable landfill space.
— It does not generate a high volume of truck traffic to and from the site.
— It does not involve the use of injection wells for supplying nutrients to microbial populations.[4]

Based on these comments, the comparable costs of landfilling and thermal evaporation, and the potential for continued liability with land-filling, it was decided to remediate the soils using the thermal evaporation process, which was the first application of that technology in the State of Wisconsin.

SOIL REMEDIATION

Contracting and Permitting

Bid specifications were prepared by Hydro-Search, Inc. in July 1989, and submitted to several contractors who provide thermal evaporation process services. The contractor selected for the job was Clean Soils, Inc. of Minneapolis, Minnesota. Clean Soils was selected based on their experience, cost and the fact that they already had the required permits from the Air Management Section of the WDNR.

A soil remedial action plan was prepared by Hydro-Search, Inc. and submitted for WDNR approval in December 1989.[6,7] The plan con-

sisted of five general elements which included:

* soil excavation
* confirmational testing of excavation
* soil treatment and stockpiling
* confirmational testing of treated soils
* backfilling and restoration

The sequencing of these elements is presented schematically in the flow chart shown in Figure 5.

Prior to startup, arrangements had to be made and permits obtained from county and local officials regarding operational procedures and site restrictions. These included:

* Milwaukee County Parks and Recreation Board: permit specifying hours of operation, fencing restrictions, security arrangements, noise and dust restrictions, restoration requirements, and insurance requirements
* City of Wauwatosa: temporary occupancy permit specifying hours of operation, fencing restrictions, and emergency response arrangements
* Wauwatosa Fire Department: approved use of 18,000-gallon propane tank for treatment unit as well as fencing and signage requirements
* City of Wauwatosa Water Department: approved use of fire hydrant for dust control

Table 1
Comparison of Remedial Alternatives

REMEDIAL ALTERNATIVE	TIME	COST ESTIMATE		REGULATORY REQUIREMENTS	CONTINUING LIABILITY	COMMENTS
Passive Remediation	4-10 years	Site Characterization and Risk Assessment Soil Sampling and Ground-Water Monitoring	$ 25,000 - $ 50,000 $ 40,000 - $ 100,000 TOTAL: $ 65,000 - $ 150,000	Subject to DNR Approval	Yes	Potential ground-water impacts.
Excavation/ Landfilling/ Refilling	20 days	Landfilling Excavation/Fill Continuous Field Screening and Supervision	$ 120,000 $ 250,000 $ 15,000 TOTAL: $ 385,000 $38.50/cu.yd	Landfill Acceptance Forms Potential Noise Restrictions	Yes	Excavate Omega Hills Landfill Contractor costs may vary substantially
Landspreading	3-6 months	Excavation/Fill Tilling and Field Screening	$ 250,000 $ 20,000 TOTAL: $ 270,000 $27.00/cu.yd	Potential Air Emission Permit	No	Excavate Move impacted soils to another site.
Thermal	75 days	Excavation and Treatment Weekly Field Screening and Project Management	$ 560,000 $ 15,000 TOTAL: $ 575,000 $57.50/cu.yd	Potential Air Emission Permit: 90-120 days start-up delay Potential Noise Restrictions	No	Excavate
Vapor Extraction	6-12 months	Set-up and Operation $400,000 - $ 600,000 Project Manager $ 20,000 TOTAL: $420,000 - $ 620,000 $42-$62/cu.yd		Potential Air Emission Permit: 90-120 days start-up delay Potential Noise Restrictions wells	No	In-situ Cost dependent on final clean-up criteria and number of required
Bioremediation	6-8 months	Excavation $ 200,000 Set-up and Operation $500,000 $ 800,000 Project Manager $ 15,000 TOTAL: $715,000 - $1,015,000 $71.50-$101.50/cu.yd		Potential air Emission Permit: 90-120 days start-up delay	No	Excavate Cost dependent on final clean-up criteria and bacteria, nutritional requirements
Enhanced In-Situ Bio-remediation	9 months 2 years	Set-up and Operation Project Management	$ 500,000 $ 20,000 TOTAL: $ 520,000 $52/cu.yd	Requires DNR waiver of injection well restriction	No	In-situ Provides soil and water treatment. Cost dependent on final clean-up criteria, bacteria, nutritional requirements and number of required wells.

Note: All cost and item estimates are approximate based upon 10,000 cubic yards of impacted soils. Landfilling and thermal remediation costs are more fully determined than the other methods due to the nature of the respective methods.
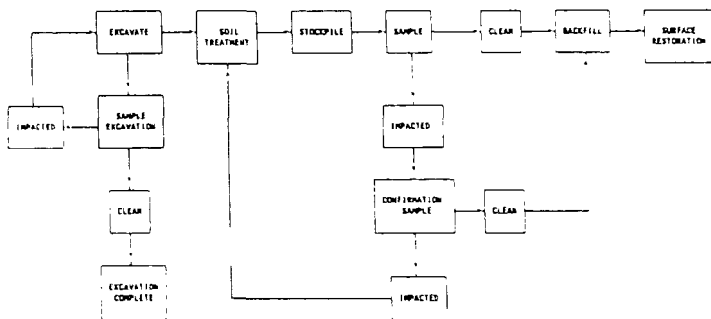
Figure 5
Soil Remedial Action Plan

- Wisconsin Electric Power Co.: approved set-back requirements to excavate around electric power towers and poles
- Metropolitan Milwaukee Sewage District: approved set-back requirement to excavate near concrete lined creek
- Digger's Hotline: clearance of on-site utilities

SOIL REMEDIATION PROCESS

The treatment of the soils was accomplished using the Clean Soils Thermal Desorber which was mobilized to the site in January 1990. A schematic of the system is shown in Figure 6.

Soils were excavated and transported to the processing unit using a back-hoe and front-end loader. The soils were first screened through two grates to remove rocks and debris larger than 2 inches in diameter and then fed by conveyor to the treatment unit. As the soils entered the treatment unit, they were cascaded by a 5-foot diameter rotating drum towards the main burner. Within the chamber, the soils were heated to approximately 450°F to vaporize the hydrocarbons. The resultant vapors were pulled through a baghouse to remove all dust-sized particulate matter. Combustion of the vapors occurred inside a propane-fired afterburner where the vapors were completely consumed by burning at temperatures of 1400 to 1470°F.

The treated soils exited the unit via a conveyor where they were stockpiled until confirmational analysis documented cleanup. Upon receipt of the laboratory analysis verifying that cleanup standards were met, the soils were backfilled into the excavation. Once the soil remediation was completed, the area was graded, covered with topsoil, seeded, landscaped and the bike path restored.

The soils were processed at a rate of between 15 and 30 tons per
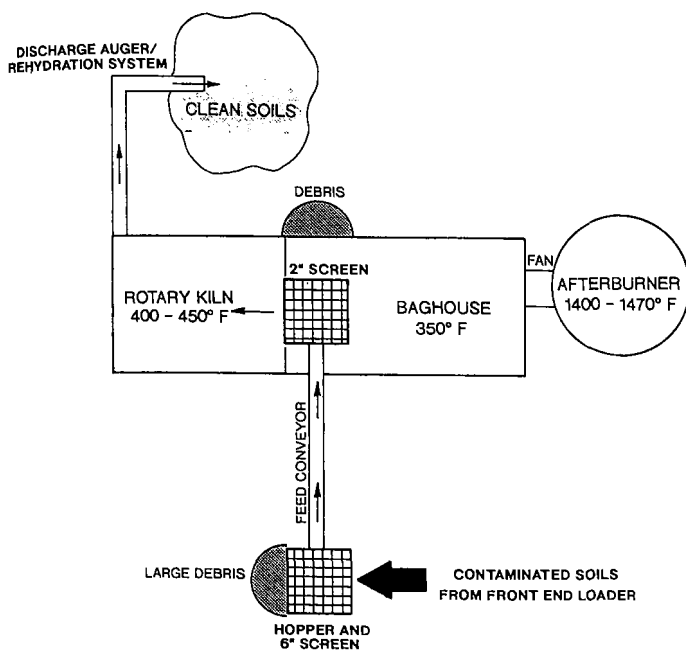
Figure 6
Thermal Desorption Treatment Unit Layout

hour. Processing rates were influenced by soil moisture content, diesel fuel concentration and soil type. Fine-grained soils with a high silt and/or clay content were processed at a slower rate than sandy or gravelly soils. Wet and highly impacted soils were also processed slowly to maintain the proper fuel/oxygen mixture in the afterburner for the combustion of the vapors. Weather, site ground conditions and equipment breakdowns also affected the rate of soil processing.

Soil processing was carried out from January through May of 1990. Over the total project duration of 132 days, actual soil processing was performed on 93 days. Complete system shutdown related to equipment failure, maintenance or inclement weather occurred on 39 days. Over the life of the project, daily soil processing rates varied from less than 20 tons to more than 400 tons per day. A total of 13,989 tons of soil were processed (10,000 cubic yards) in 93 days of actual soil processing for a daily average of 150 tons.

Over the last 6 weeks of the project, most of the mechanical difficulties associated with the equipment had been corrected, and the thermal desorption unit processed an average of more than 200 tons of soil per day.

GROUNDWATER REMEDIATION

A groundwater remediation plan was prepared by Hydro-Search, Inc. and submitted to the WDNR in July 1990 for approval.[5] The objectives of the remediation plan were to clean up groundwater to meet NR140 (Wisconsin Administrative Code) preventive action limits and to prevent off-site migration of impacted groundwater. The plan[5] called for:

* The recovery of groundwater from Trench 1 along Underwood Creek (Trench 2 was destroyed during soil remediation)
* Discharge of groundwater to the MMSD sanitary sewer
* Free product recovery from the sump in Trench 1 as necessary
* Performance monitoring of the system
* Periodic reporting on the system progress

Continued use of Trench 1 to capture on-site impacted groundwater was proposed based on its successful performance over the past 2 years. Although the trench has only been pumped on a part-time basis (8 to 10 hours a day) for the past 2 years, impacted groundwater has not

migrated off-site. Automation of the system will provide full-time operation. Discharge of groundwater to the sanitary sewer is the most cost-effective and least disruptive alternative for treating impacted groundwater at the site.

To implement the plan requires modifications to the existing trench system which are anticipated to take place in fall of 1990, and which include extending the trench 75 feet to the south to ensure adequate capture, deepening the sump construction, automating the pumping system to reduce the manpower requirements and winterizing the system to allow year-round operation. A plan and schematic of the proposed system are shown in Figures 7 and 8.

Operation of the system will be controlled by float-activated switches to maintain a 1.5-foot drawdown in the trench. Groundwater will be discharged to a sanitary sewer with the volume monitored by an in-line totalizing flow-meter.

Free product that collects in the sump will be pumped out with an oil skimmer or oil absorbent pads on an as-needed basis. Manual operation was chosen because the diminishing product recovery in the trench over the last 2 years indicates not much additional product will be recovered. Automated product recovery and containment would have included construction of a building to house the recovered product. Therefore, providing automated product recovery was not considered cost-effective.

Performance of the system will be monitored by the observation wells shown in Figure 7. These wells will monitor both the hydraulic capture of the system and water quality to ensure impacts do not migrate off-site. The system will operate until the hydrocarbon compounds in the groundwater are below the NR140 preventive action limits.

CONCLUSIONS

Within 24 months of the 115,000-gallon release, nearly all free product has been recovered, impacted groundwater has been controlled to prevent off-site migration and impacted soils have been remediated. Groundwater remediation is expected to continue for another 2 to 4 years, or until hydrocarbon compounds meet WDNR water quality criteria.

The cleanup's success is attributed to the emergency response efforts that resulted in the recovery of approximately 70,000 gallons of product, the interim action of installing trenches to intercept impacted groundwater and recover an additional 7,300 gallons of free product and the application of new thermal desorption technology which was mobilized to the site during a harsh Wisconsin winter and used to remediate 10,000 cubic yards of impacted soil in less than 5 months.

These accomplishments would not have been possible without the environmental consciousness of the pipeline owner/operator, the dedication of the response crews and contractors, the cooperation of the local agencies and officials, the understanding of the surrounding residents and the progressive attitude of the WDNR to allow the use of new and innovative technologies.

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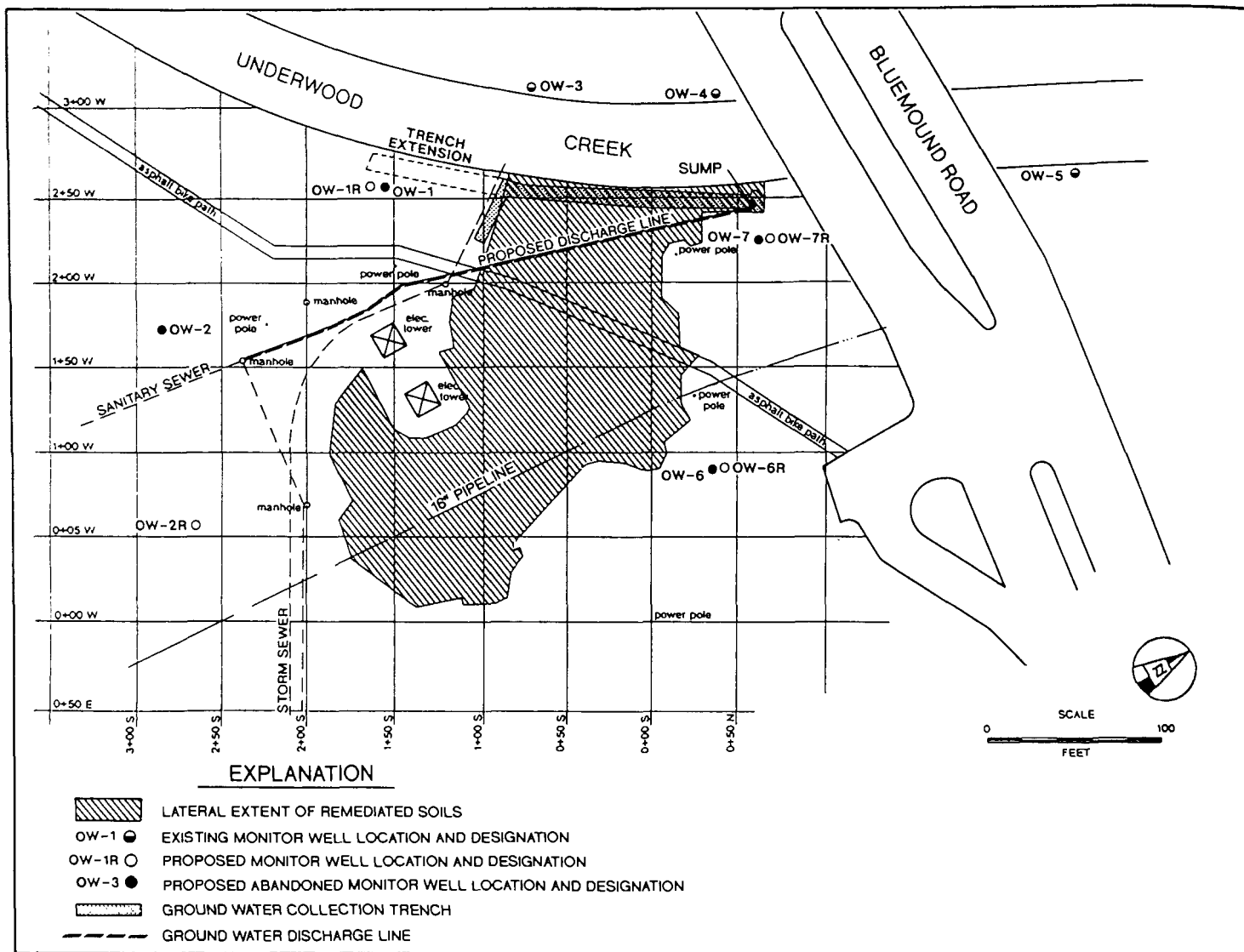
Figure 7
Groundwater Remediation Layout
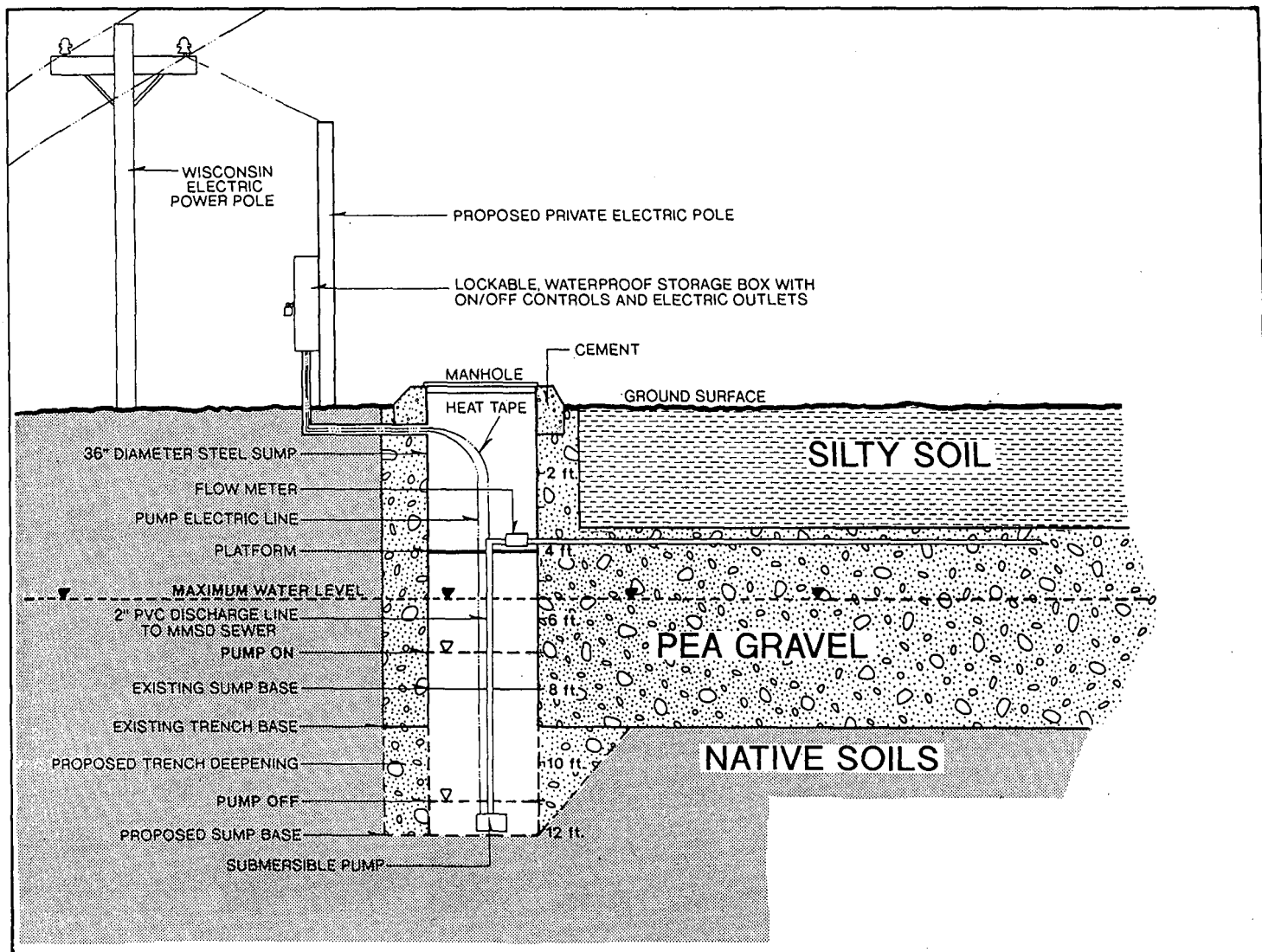
Figure 8
Groundwater Remediation Pump Detail

Assessment of the Emergency Response Actions and Environmental Impact of the January 2, 1988 Diesel Oil Spill Into the Monongahela River

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INTRODUCTION

This paper presents an assessment of the overall adequacy of the emergency response to the January 2, 1988, Ashland Oil spill into the Monongahela River near Pittsburgh, Pennsylvania. Additionally, we present an assessment of the environmental impacts of the spill. Information for the assessment has been gathered from meetings with public and private emergency response officials, public hearing records and government reports. Many of the recommendations made by emergency response officials involved in the Ashland incident have been included in this paper.

The assessment of the overall adequacy of the emergency response portion of this paper was adapted from a chapter of a report entitled "Economic and Policy Implications of the January 1988 Ashland Oil Tank Collapse in Allegheny County, Pennsylvania," which was a collaborative effort involving the staffs of both the Center for Social and Urban Research and the Center for Hazardous Materials Research at the University of Pittsburgh. The report was prepared for the Allegheny County Planning Department and funded through a grant provided to Allegheny County from the Pennsylvania Department of Commerce.

DESCRIPTION OF EMERGENCY RESPONSE ACTIVITIES

Successful protection of the public health throughout the emergency resulted from the outstanding efforts and cooperation of hundreds of response personnel, including individuals from Ashland Oil Inc. and its contractors, 17 regional offices of seven federal agencies, 11 state agencies from four states and numerous local emergency response agencies, fire departments and water suppliers.

The Center for Hazardous Materials Research (CHMR) has identified a number of events that are key to understanding and assessing the on-site emergency response. A detailed minute-by-minute summary of these events and a map of the accident site are provided in the full report on the economic and policy implications of this incident.

Initial response efforts focused on the terminal site in order to: (1) establish access control; (2) stop the flow of diesel fuel on-site; (3) plug leaks found in a damaged tank holding 1,000,000 gallons of gasoline; and (4) conduct a thorough assessment of the extent of the spill. The initial on-site assessment was severely hampered by cold weather, darkness and concern over the potentially volatile mixture of gasoline and diesel fuel. Dangerous conditions on the river (rapid currents, cold weather and darkness), moreover, severely restricted any possible response action on the water.

As a result, estimates of the large volume of fuel released and the severity of the impact of the spill on the river system and downstream water suppliers was not fully realized until early the next morning, January 3. Preliminary reports suggested that water intakes were low enough to avoid the oil or that river water could be adequately treated by the water plants. The dispersion of oil throughout the water column was not recognized until at least 12 to 18 hours after the release.

On January 3, 1988, approximately 14 hours after the release, the U.S. EPA On-Scene Coordinator arrived on-site and advised Ashland that the U.S. EPA determined that the response actions taken by Ashland were appropriate and that federal supervision of Ashland Oil's cleanup was equivalent in every respect to what the federal government would have done under the same circumstances.

Considering the initially rapid rate of release, standard response time for off-site emergency responders and circumstances common to incidents of this type, it is unlikely that the quantity of release could have been substantially reduced in the crucial first 2 hours.

It is important to note that the on-site company personnel responded within minutes of the accident by closing a valve controlling the discharge of oil from the facility API separator. This action effectively stopped the discharge of oil from this source and contained millions of gallons of oil within the facility's spill containment system.

On January 2, 1988, the flowrate and velocity of the Monongahela River were high. As river water moved over each dam, it dropped many feet in height — a circumstance which adversely affected oil recovery efforts because it caused the oil, water and suspended sediment to become increasingly mixed as each dam was passed. This mixing action caused the oil to contact and coat sediment particles suspended throughout the water column, which prevented much of the oil from floating back to the surface.

Approximately 205,000 gallons of diesel fuel (29% of the total 705,000 gallons released to the river) were recovered through skimming operations. The oil which remained in the river became completely mixed and emulsified in the water by the time the spill passed the Dashields Lock and Dam, approximately 38 miles downstream from Floreffe on the Ohio River. No substantial recovery occurred below this point. The cleanup operations, which ultimately spanned 38 miles, were severely hampered by extremely cold weather conditions. The risk of hypothermia for cleanup crews led to the decision to remove all personnel from working on the river on the fourth day after the spill.

The morning following the accident, state and local authorities directed their efforts toward concerns over water quality and drinking water supplies. By noon on January 3rd, these efforts began to constitute a separate, significant response activity, which the state and county authorities managed.

A disaster emergency was declared for Allegheny, Beaver and Butler Counties by the governor. Temporary interconnects were installed to link the City of Pittsburgh and West Penn Water systems. Work was started on numerous new permanent interconnects and other, older interconnects were opened. Substantial efforts were made to bring in equipment in order to distribute drinking water to affected communities.

West Penn Water Company, with assistance from the Pennsylvania Department of Environmental Resources (PADER), developed and pilot-tested a treatment that successfully removed oil from water supplies. This process was used by downriver water suppliers, making it possible for them to open river intakes days before they otherwise would have been able to do so. Water supplies in four states — Pennsylvania, Ohio, West Virginia and Kentucky — were affected as the spill flowed downriver. By the time the spill passed Cincinnati, oil concentrations in the Ohio River had decreased to the point where immediate concern with regard to drinking water had subsided.

Over the short-term, the diesel oil spill produced a few small to moderate impacts on organisms dependent on the river system in limited regions of the first 185 miles down-river. Natural processes associated with the spill and river system combined to mitigate and significantly restrict the impacts, except in a few localized areas. Significant long-term effects on the river system as a whole from the spill are not expected.

CONCLUSIONS AND RECOMMENDATIONS

The oil spill incident had a significant impact on the water companies which depend on the Monongahela and Ohio Rivers for their source of supply. The spill created water supply shortages in some areas requiring customers to conserve water; the spill actually led to the loss of water supply in one service area. In spite of these hardships, the outstanding efforts of all responding agencies, groups, individuals and Ashland Oil Company resulted in the successful protection of the public health throughout the emergency. Extensive emergency response actions prevented any contamination of operating public water systems.

The goal of the following recommendations is to improve preparedness among emergency responders in confronting incidents similar to the Ashland Oil spill. The recommendations benefit from CHMR's experience in emergency management and preparedness as well as from observations and suggestions offered by emergency response officials in public hearing records and government reports on the Ashland Oil spill.

Organization and Speed of the Response

The following list provides a summary of CHMR's conclusions and recommendations regarding the overall organization and speed of the response. Five key findings can be highlighted.

- Ashland took appropriate initial response actions, which included notifying the National Response Center and calling the necessary emergency response contractors.
- Although downstream water users were quickly notified of the incident, the severity of the potential impact on the river system and downstream water supplies was not fully realized until 12 to 18 hours after the spill.
- The fact that the severity of the potential off-site impact was not realized, combined with concern over volatile conditions on-site, cold weather, darkness and dangerous conditions on the river, hampered initial response actions and caused the initial priority of the response to be directed on-site.
- Although initial problems with the overall organization of the response caused some operational difficulties for response personnel during the first 24 to 36 hours, it is unlikely that these difficulties adversely affected the overall adequacy of the emergency response for minimizing losses to property, businesses and individuals.
- It is also unlikely that any other organization of the emergency response would have resulted in more effective protection of the public health or further minimized losses caused by the accident.

The overall organization and speed of the response thus were adequate to fully protect public health and minimize losses to property, businesses and individuals under the circumstances of this incident. However, some lessons can be learned which may improve the efficiency of future responses.

- In the future, the On-Scene Coordinator should initiate coordination activities earlier and start assigning responsibilities sooner. The RRT team should be activated as soon as possible and a decision

made as to whether its members should be brought together on-site. An "RRT Coordinator" should be designated to assist the OSC by facilitating communications among responding agencies.

- A responsible party representative (in this case, someone from Ashland Oil) in RRT conferences should directly provide the RRT with factual details regarding the responsible party's activities and ability to comply with RRT recommendations to the OSC.
- Important environmental data were not collected during the first few hours of the incident because emergency response personnel were preoccupied with responding to the emergency at hand. Facility Preparedness Prevention Contingency plans should identify individuals of the responsible party or its contractors whose sole responsibility is the collection of environmental data.
- In the initial days of the spill, the coordination and communications of river monitoring data suffered because no lead agency was assigned to oversee these activities. A lead agency should be designated to focus the coordination and communication of monitoring data and to assure standardization in the analysis of these data.

Adequacy of Equipment & Materials

The lack of immediately available containment and monitoring equipment hindered the emergency response. The need to locate and transport essential equipment caused delays.

However, as a result of the unique circumstances of this incident (e.g., the rapid release and discharge of most of the oil into the river with the first two hours, darkness, cold weather, rapid river currents and dispersion of oil throughout the water column), it is unlikely that another response could have been any more effective in significantly reducing the total quantity of oil discharged to the river or increasing the total quantity of oil recovered from the river.

Nevertheless, additional lessons can be learned. The following 11 points summarize CHMR's conclusions and recommendations regarding the adequacy of available equipment and materials as well as the preparedness of personnel for future contingencies.

- Containment dikes are an essential first line of defense to prevent the release of oil and hazardous substances from leaking tanks. It is unlikely, however, that dikes can be constructed to provide complete containment of all possible incidents such as sudden massive tank ruptures.
- Facility Preparedness Prevention Contingency plans should "look beyond the dike" and be prepared to install a "second line of defense" in the event a spill escapes the containment area. All drainage ways near containment dikes should be identified in PPC plans, a strategy should be developed for intercepting releases in the drainage ways and secondary structures should be maintained.
- A computerized geographic information system with the capability for displaying maps of the physical infrastructure of Allegheny County should be implemented to provide emergency responders as quickly as possible with necessary information for rapid responses.
- Facility PPC plans should be current and include information on locations of hazardous and environmentally sensitive materials stored on-site. PPC plans should be provided or made readily available to local emergency responders. Consideration should be given to keeping a current copy of this plan in a highly visible "lock box" located on the perimeter of the site.
- Inventories of locally available equipment should be prepared to assist emergency responders in quickly locating necessary items. Such inventories could be developed and augmented where necessary through a cooperative arrangement between local industries and government.
- Methods to monitor the dispersion and concentration of airborne contaminants which could emanate from a spill should be considered in local contingency plans. The availability of air-monitoring equipment (local stationary installations and mobile units) capable of providing real-time data needed to estimate community exposures should be assured and included in inventory lists.
- State or local contingency plans should maintain a list of local laboratories certified to perform necessary testing in an emergency. Development of a mobile laboratory capability by the responding agencies should be considered.

- The Ashland incident could have been far more devastating if public water supplies had been contaminated or water shortages had become more severe. Emergency planning agencies and water suppliers should work toward improving the availability of contingency water supplies with consideration given to the installation of permanent interconnect grids among neighboring water suppliers and expanded storage capacities for both raw and treated water.
- The ability of facilities such as hospitals, nursing homes, medical clinics and schools to respond to and maintain operations should be strengthened.
- Emergency planning agencies should maintain a current list of available bulk water haulers, facilities with tankers that can be used in refill operations and sources of plumbing expertise and supplies for distribution hookups.
- Each water supplier should maintain a list of service and equipment companies that can provide replacement pumps, chlorination equipment and chemical feed equipment to add water treatment chemicals in the event of an emergency.

Adequacy of Communication Among Emergency Responders

Problems were encountered due to insufficient communications equipment at the command post to support the large number of response agencies. Problems were encountered contacting RRT members during off-duty hours, and numbers to installed or rented phones were not available in a timely manner.

- A list of 24-hour telephone numbers for RRT members should be regularly updated and made available. Electronic mail systems operated by various agencies can be efficient mechanisms for communication among RRT members. An RRT E-mail distribution system should be established, and each RRT member should be assigned an electronic mailbox.
- Adequate telephone lines must be immediately installed at command posts in addition to having ample numbers of cellular phones available. Telephone numbers of newly-installed or rented portable phones must be gathered early and disseminated more aggressively during an emergency.
- The Ohio River Valley Water Sanitation Commission's electronic bulletin board was widely used and worked well for distributing river monitoring data. Procedures could be developed to use such a resource even more effectively.

Adequacy of Communications Between Responders and the Public

The water suppliers' public communications activities were generally excellent during the Ashland emergency, but some lessons nonetheless can be learned from the experience. The following conclusions and recommendations regarding proper procedures for communicating with the public during emergencies are offered for consideration based on the lessons learned from how information was provided to the public during the Ashland episode.

- At one point, prior to receiving official notice from the state, a local agency suggested that the need for water conservation was lessening. Criteria and authority for lifting water conservation orders should be made clear by the party establishing such an order, so there is advance agreement on when conservation can be discontinued.
- Information should be given to the media consistently and on a regular basis during emergencies, preferably through one spokesperson at the facility.
- Special attention must be paid to ensure that the media continually notify the public if the problem is one of quantity and not of contamination. Suppliers must communicate to the public that the use of interconnections, changes in water flow patterns and varying pressures may lead to taste and odor problems that can be misinter-

preted as contamination.
- The need for predetermined health advisory threshold levels for releases of a wide variety of hazardous substances to surface waters and the atmosphere and a system to warn the public about health-threatening conditions continues to be a concern.

Educational Training and Information Resources

Although the response to the Ashland Oil spill was effective in protecting public health, it is evident that more timely health effects data on spilled hazardous substances were needed along with assistance in interpreting their significance.

Recent federal requirements under the SARA are generating significant new information on the specific locations of hazardous materials produced or used by particular industries. Firefighters and other emergency responders should be properly equipped to respond to any emergency which could occur in their respective service areas.

CHMR's conclusions and recommendations regarding training and information resources, based on lessons learned from the Ashland Oil spill, include the following items.

- The federal Agency for Toxic Substances and Disease Registry (ATSDR) as well as state health departments could be better utilized to provide more timely health effects data and data interpretation.
- More training for fire fighters and other responders is recommended. The training programs need to emphasize rapid identification of hazardous substances involved in an emergency. The significant volumes of new SARA information on specific locations of hazardous materials used by particular industries must be assimilated into training updates for local emergency responders.
- Consideration should be given to the creation of computerized data base capabilities for local emergency responders. An appropriate mobile command vehicle might have access to this system.
- Sampling and analysis protocols for emergency responders should be developed.

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The "Petroleum Exclusion" Under CERCLA: A Defense To Liability

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ABSTRACT

When CERCLA was originally passed in 1980, the petroleum industry lobbied successfully to exclude the term "petroleum" from the definition of a CERCLA §101 (14) hazardous substance. Under CERCLA § 101 (33), petroleum is also excluded from the definition of a "pollutant or contaminant." Exclusion from the designation as a defined hazardous substance has provided a defense to liability under CERCLA § 107 when the release of petroleum occurs.

The scope of the petroleum exclusion under CERCLA has been a critical and recurring issue arising in the context of Superfund response activities. Specifically, oil that is contaminated by hazardous substances during the refining process is considered "petroleum" under CERCLA and thus excluded from CERCLA response authority and liability unless specifically listed under RCRA or some other statute. The U.S. EPA position is that contaminants present in used oil, or any other petroleum substance, do not fall within the petroleum exclusion. "Contaminants," as discussed here, are substances not normally found in refined petroleum fractions or present at levels which exceed those normally found in such fractions. If these contaminants are CERCLA hazardous substances, they are subject to CERCLA response authority and liability.

This paper discusses the parameters of the CERCLA "Petroleum Exclusion." It briefly examines selected state laws, RCRA, the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA) for treatment of petroleum and petroleum products. And, finally, this paper discusses new legislation regarding oil pollution liability and compensation.

INTRODUCTION

Crude oil, and the commercially derived fractions therefrom, represent by quantity the largest volume of hazardous substances in our environment today. However, the CERCLA as amended by SARA specifically excludes oil and its fractions as defined hazardous substances. This exclusion limits Superfund expenditures on sites contaminated by such substances and denies claims based on the strong liability scheme of CERCLA/SARA.

The following sections discuss the current environmental legislation on oil, the liability scheme within this legislation and new legislation related to releases of oil in the environment.

RELEASE OF CRUDE OIL AND DERIVATIVES UNDER CERCLA/SARA

When the release[1] of a hazardous substance occurs in the environment, statutory authority to address such a release can be found in CERCLA/SARA and analogous state laws. In establishing liability under CERCLA/SARA, a key factual element is classification of the substance released as "hazardous." The term hazardous substance is defined in

CERCLA § 101 (14), 42 U.S.C. §9601(14)(1990) to mean:

(A) any substance designated pursuant to section 311(b)(2)(A) of the Federal Water Pollution Control Act, (B) any element, compound, mixture, solution, or substance designated pursuant to section 102 of this Act, (C) any hazardous waste having the characteristics identified under or listed pursuant to section 3001 of the Solid Waste Disposal Act (but not including any waste the regulation of which under the Solid Waste Disposal Act has been suspended by Act of Congress), (D) any toxic pollutant listed under section 307(a) of the Federal Water Pollution Control Act, (E) any hazardous air pollutant listed under section 112 of the Clean Air Act, and (F) any imminently hazardous chemical substance or mixture with respect to which the Administrator has taken action pursuant to section 7 of the Toxic Substances Control Act. The term does not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of this paragraph, and the term does not include natural gas, natural gas liquids, liquefied natural gas, or synthetic gas usable for fuel (or mixtures of natural gas and such synthetic gas).

Liability can also be established under CERCLA/SARA to include release of those substances described as pollutants or contaminants under CERCLA §101(33), 42 +wS.C. §9601(33) and defined as follows:

...any element, substance, compound, or mixture, including disease-causing agents, which after release into the environment and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will or may reasonably be anticipated to cause death, disease, behavioral abnormalities, cancer, genetic mutation, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring; except that the term "pollutant or contaminant" shall not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of paragraph (14) and shall not include natural gas, liquefied natural gas, or synthetic gas of pipeline quality (or mixtures of natural gas and such synthetic gas).

If the substance being released into the environment does not come under the definition of "hazardous" or pollutant or contaminant, then CERCLA/SARA is not applicable. Note the last portion of each definition specifically excludes crude oil and derivatives therefrom as a defined hazardous substance pollutant or contaminant. With a few words, the U.S. Congress denied CERCLA liability to the most voluminous class of substances released in the environment today. And it did so with

poorly worked definitions which have resulted in a variety of attempts to describe the congressional "intent" of its exclusatory language.

In 1982, the U.S. EPA Office of General Counsel described the liability under CERCLA for diesel oil contamination of groundwater.[2] This memorandum discussion regarded classifying diesel oil as a hazardous substance due to the presence of hazardous substances such as benzene and toluene. General Counsel concluded that diesel oil and its hazardous constituents fall within the CERCLA petroleum exclusion, unless the constituents were found in elevated levels or added after the product was issued as diesel oil. This early memorandum helped define the question which recurs to this day, "When are crude oil and derivatives therefrom not subject to the CERCLA petroleum exclusion?"

In 1983, the General Counsel again issued an interpretive memorandum on the CERCLA petroleum exclusion.[3] This memorandum concerned releases of gasoline, which in its refined state always contains defined hazardous substances, pollutants or contaminants. The interpretation posed to the General Counsel was that only raw gasoline, without any additives, comes under the petroleum exclusion. The General Counsel determined that such an interpretation would enervate the intent of CERCLA. As with diesel oil, the conclusion was that blended gasoline, as it is issued in a refined state, comes within the petroleum exclusion. Again, the addition of hazardous substances, pollutants or contaminants to blended gasoline after refining may nullify the applicability of the petroleum exclusion.

Subsequent case law upheld the interpretation offered by the U.S. EPA General Counsel in the 1982 and 1983 memoranda. In the 1984 case *U.S. v Wade*,[4] the court held that fuel oil came within the petroleum exclusion, regardless of the hazardous components found to normally occur therein. A 1986 case, *Marmon Group, Inc. v. Rexnord, Inc.*,[5] came to a similar conclusion. In that case the substance at issue was "cutting oil." Based on the facts, the court held that this specific cutting oil came within the petroleum exclusion.

As an apparent result of receiving numerous interpretive inquiries on the petroleum exclusion from the U.S. EPA Regional Counsel, the General Counsel in 1987 issued yet another memorandum on the subject.[6] In this memorandum, the General Counsel gave a history of the U.S. EPA's position regarding the CERCLA petroleum exclusion. At issue was the applicability of the exclusion to "used oil." The General Counsel's conclusion was that oil, having been used and combined with hazardous substances, pollutants and contaminants, did not come under the petroleum exclusion.[7] The General Counsel further noted, "moreover, under this interpretation not all releases of used oil will be subject to CERCLA since used oil does not necessarily contain non-indigenous hazardous substances or hazardous substances in elevated levels. Although used oil is generally "contaminated" by definition, *see e.g.*, RCRA Section 1005 (36), the impurities added by use may not be CERCLA hazardous substances."

The 1987 the U.S. EPA memorandum was followed by a case whose facts were similar to the memorandum discussion. In *State of Washington v. Time Oil Co.*,[8] the defendant was held liable for the release of hazardous substances which contaminated groundwater supplies. In this opinion, the court discussed used oil that was present and stated,

". . .some of the contaminants found on the Time Oil property were found in amounts in excess of the amounts that would have occurred in petroleum during the oil refining process. Other substances found on the property would not have occurred due to the refining process. The "petroleum exclusion," CERCLA §104(a)(2), will not operate to exclude Time Oil from liability."

Time Oil at 687 F. Supp. 532.

The *Time Oil* case was followed by the most recent definitive opinion on the petroleum exclusion. In *Wilshire Westwood, Assoc. v. Atlantic Richfield*,[10] the Ninth Circuit court was asked to interpret the CERCLA petroleum exclusion as it applies to unrefined and refined gasoline. The facts of this case were similar in form to the 1983 U.S. EPA memorandum discussed above.[11] In this case, a number of CERCLA hazardous substances were found to exist in the gasoline that had been released into the environment. These hazardous substances were those normally occurring or added to gasoline in the refining process. In finding

that gasoline comes within the petroleum exclusion, the court concluded, "the petroleum exclusion in CERCLA does not apply to unrefined and refined gasoline even though certain of its indigenous components and certain additives during the refining process have themselves been designated as hazardous substances within the meaning of CERCLA."[12] The court, in this opinion, relied in part on the 1987 U.S. EPA memorandum discussed above.[13] It is unclear how the U.S. EPA interpretation could carry such great weight when the word "petroleum" is not defined in CERCLA.[14]

STATE CERCLA-TYPE STATUTES AND THE PETROLEUM EXCLUSION

Under the federal CERCLA statute, the petroleum exclusion covers not only crude oil, but also a large number of crude oil derivatives. While CERCLA is expansive in jurisdiction, this statute does not preclude several states from developing legislation wherein the release of petroleum and its derivatives is actionable.[15]

A list of states with CERCLA-type legislation where petroleum and its derivatives are classified as hazardous substances is beyond the scope of this paper. However, CERCLA-type statutes of Montana[16] and Washington[17] provide examples of state laws where petroleum is defined as an actionable substance.

PETROLEUM PRODUCTS SUBJECT TO REGULATION UNDER RCRA

While CERCLA may exclude petroleum products from the definition of hazardous substances, a recourse to liability for release of petroleum may be available under RCRA. As with CERCLA hazardous substances, petroleum or crude oil is not defined as a RCRA hazardous waste.[18]

If the constituents of the petroleum or oil product are considered a hazardous waste, then a release may be actionable under RCRA. And a finding that various components of petroleum may be considered a RCRA hazardous waste when combined with soil is more likely under the new Toxicity Leaching Characteristic Procedure.[19] For cleanup liability to be established under RCRA, the release must occur from a transportation, treatment, storage or disposal facility. The release is actionable both within and outside of the facility boundaries.[20]

Perhaps the greatest source of petroleum contamination comes from leaking underground storage tanks (USTs). In response to this obvious problem, Congress added Subtitle I to RCRA.[21] This subtitle provides requirements for new USTs, testing of in place USTs, and remedies for releases from USTs. To ensure that releases from USTs were remedied, Congress provided funds under SARA to assist in the financing of cleanup costs.[22] The scope of the term UST is defined in Subtitle I, as is the word "petroleum."[23]

RCRA UST legislation provides an avenue for cleanup liability when a release of petroleum or crude oil occurs from a regulated tank. While this legislation is a positive step in the direction of remediating all land-based releases of crude oil and petroleum, it is not as far reaching as CERCLA in its liability scheme.

PETROLEUM PRODUCTS SUBJECT TO REGULATION UNDER FWPCA

Should a release of crude oil or derivatives therefrom occur upon the navigable waters of the United States, then said release is actionable under the Federal Water Pollution Control Act (FWPCA).[24] The FWPCA has a specific section that details the scope of liability for releases of oil.[25]

PETROLEUM PRODUCTS SUBJECT TO REGULATION UNDER SDWA

The Safe Water Drinking Act (SDWA) has as its primary purpose the protection of public drinking water supplies from contamination.[26] For a substance to be actionable under the SDWA, it must exceed the Maximum Contaminant Level (MCL) for that substance. The SDWA does not identify an MCL for crude oil or petroleum. However, hazardous substances found in petroleum such as benzene or xylene have established MCLs.

The SDWA also established a permit program for the underground injection of wastes. The Underground Injection Control (UIC) Permit Program regulates those persons utilizing underground injection wells for waste disposal.[27] It appears injection of oil or petroleum wastes would be regulated or prohibited if such injection would endanger drinking water resources.

PETROLEUM PRODUCTS SUBJECT TO REGULATION UNDER THE OIL POLLUTION ACT OF 1990

At the time of submittal of this paper, proposed legislation entitled the "Oil Pollution Act of 1990" (OPA) had not become law. The most recent information available on this legislation was the conference committee report on the bill.[28] OPA concerns and coverage focuses on costal and marine environments. This legislation is obviously a reply to the recent oil spills in Alaska, the Gulf of Mexico, and along the east coast of the United States The term oil is defined as follows:[29]

"... "oil" means oil of any kind or in any form including, but not limited to, petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil, but does not include petroleum, including crude oil or any fraction thereof, which is specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of section 101(14) of the [CERCLA] (42 U.S.C. §9601(1990)) and which is subject to the provisions of that Act."

Liability for discharge of oil into the costal and marine environments covered by the OPA is the same as in the CWA.[30] One of the main distinctions of the OPA is the establishment of a fund for the removal costs incurred to cleanup the discharge.[31] The OPA appears in many ways to be a combination of CERCLA and the CWA. It does provide a true liability scheme for discharge of oil and derivatives therefrom. However, this liability is limited to those environs described by the OPA.

CONCLUSION

The petroleum exclusion is alive and well under CERCLA. When a defined hazardous substance exists within crude oil or petroleum in levels exceeding the norm, CERCLA's strong liability scheme is unavailable. There are a number of valid public policy arguments to support the petroleum exclusion, but public policy should not be allowed to interfere with our need for great care in exploration, transportation, use and disposal of crude oil and its derivatives. These substances are truly hazardous and any release should be immediately addressed and remediated by the person responsible parties.

It appears that petroleum and oil will be treated as other hazardous substances when discharged in our costal and marine environments. And under the new Toxic Characteristic Leaching Procedures (TCLP), RCRA corrective authority may be available for cleanup of a wider variety of oil and petroleum wastes. But there remain a number of land-based sites in the United States where releases of crude oil and petroleum are not actionable under federal law. On a number of these sites the responsible party will initiate cleanup. On those sites without a identifiable or financially viable responsible party, the Hazardous Substance Trust Fund is unavailable unless the release of a hazardous substance can be identified.

Public policy intends to represent the collective good of the population at large. It is incongruous that the public and private industry support the Hazardous Substance Trust Fund and yet a burdensome exclusion stands in the way of using this fund for its intended purpose: the cleanup of "hazardous substances" in our environment.

REFERENCES

1. Release is defined in CERCLA §101(22), 42 U.S.C. §9601(22) as:

... any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles containing any hazardous substance or pollutant or contaminant), but excludes (A) any release which results in exposure to persons solely within a workplace with respect to a claim which such persons may assert against the employer of such persons, (B) emissions from the engine exhaust of a motor vehicle, rolling stock, aircraft, vessel, or pipeline pumping station engine, (C) release of source, byproduct, or special nuclear material from a nuclear incident, as those terms are defined in the Atomic Energy Act of 1954, if such release is subject to requirements with respect to financial protection established by the Nuclear Regulatory Commission under section 170 of such Act, or, for the purposes of section 104 of this title or any other response action, any release of source byproduct, or special nuclear material from any processing site designated under section 102(a)(1) or 302(a) of the Uranium Mill Tailings Radiation Control Act of 1978, and (D) the normal application of fertilizer.

2. Perry, R.M., Applicability of CERCLA to Contamination of Groundwater by Diesel Oil, U.S. EPA Memorandum, Washington, DC, December 2, 1982.
3. Barnes, A.J., Applicability of the CERCLA Petroleum Exemption to Gasoline Spills, U.S. EPA Memorandum, Washington, DC,August 12, 1983.
4. *United States v. Wade*, 14 E.L.R. 20440 (April 1984)
5. *The Marmon Group, Inc., v. Rexnord Inc.*, No. 85C 7838 (N.D. Ill. June 16, 1986) *rev'd on other grounds*, 822 F.2d 31 (7th Cir. 1987).
6. Blake, F.S., Scope of the CERCLA Petroleum Exclusion Under Sections 101(14) and 104(a)(2), U.S. U.S. EPA Memorandum No. 9838.1, July 31, 1987.
7. Note that the response to a release of such used oil can only address the cleanup of those hazardous substances found within the used oil, and not the originally constituted oil.
8. *State of Washington v. Time Oil Co.*, 687 F. Supp 529 (W.D. Wash. 1988).
9. *Id.* at pg. 532.
10. *Wilshire Westwood Assoc. v. Atlantic Richfield Corp.*, 881 F. 2nd 801 (9th Cir. 1989). For an excellent article on this decision see, Baller, J. " The Petroleum Exclusion-Stronger Than Ever After *Wilshire Westwood*." *Southwestern Law J.* 915 (1990).
11. See footnote 5 *supra*.
12. *Wilshire Westwood*, 881 F.2d at 810.
13. See U. S. U.S. EPA Memorandum cited in footnote 6 *supra*.
14. Further, the adulteration of naturally occurring crude oil with hazardous substances, pollutants and contaminants and yet excluding the end product from CERCLA is incongruous. The level of authority given to the U.S. EPA General Counsel memoranda may be questionable in light of *U.S. v. Zimmer Paper Products, Inc.*, 20 ELR 20556 (December 1989)
15. *Newsweek*, "E pluribus, plures," pgs. 70-72, November 13, 1989. And see generally Landreth, L.W. and K.M. Ward, "Natural Resource Damages: Recovery Under State Law Compared with Federal Laws" *20 ELR* 10134, 10137 (April 1990).
16. Mont. Code Ann. tit 75, Ch. 10, pt. 701(6), (a)-(d). (1989)
17. Wash. Rev. Code Ann, tit. 70, Ch. 70.105 D (1989)
18. 40 CFR Part 261
19. 55 Fed. Reg. 11798 (March 29, 1990).
20. 42 U.S.C. §§3004(v) and 7003. Note that 3004(v) only applies to owners and operators of a facility.
21. 42 U.S.C. subchapter IX.
22. 26 U.S.C. §9508
23. 42 U.S.C. §9001. The definition of petroleum is stated in §9001(8) as: ...petroleum, including crude oil or any fraction thereof which is liquid at standard conditions of temperature and pressure (60 °F and 14.7 psia).
24. 33 U.S.C. §1251 et. seq. Note that §1321 details areas in addition to navigable waters where a release is actionable.
25. 33 U.S.C. §1321
26. 42 U.S.C. §300f et. seq.
27. 42 U.S.C. §300h
28. Conference Report on H.R. 1465. Congressional Record - House H6232 August 1, 1990.
29. *Id.* at H6234, §1001(23).
30. *Id.* at H6234, §1001(17).
31. *Id.* at H6238, §1013.

The Development and Status of the U.S. EPA's Emergency Response Notification System

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ABSTRACT

A major objective of the U.S. EPA's Emergency Response Program is to evaluate and, if necessary, respond to releases of oil and hazardous substances that pose a threat or potential threat to public health and/or the environment. To manage this function appropriately, the U.S. EPA in coordination with other members of the emergency response community including the National Response Center (NRC) and the U.S. Coast Guard (USCG), developed a nationwide system to receive and process notifications of releases.

This nationwide system consists of notification data collection and reporting processes that meet the legislative and regulatory requirements of the Clean Water Act (CWA), section 311; CERCLA of 1980, sections 103 and 104; SARA; and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), sections 300.125, 300.300 and 300.405.

Central to collecting, processing and reporting release notifications among the NRC, U.S. EPA and USCG is a national computer data base called, the Emergency Response Notification System (ERNS). The data base is maintained by the Department of Transportation's Transportation Systems Center (TSC) through an interagency agreement with the U.S. EPA. The data base contains release notification data reported each time a call is made to the NRC, U.S. EPA or USCG.

This paper focuses on the process used in the development and advancement of ERNS and on the trends of oil and hazardous substance releases collected by ERNS for the past three years.

INTRODUCTION

The Emergency Response Notification System (ERNS) supports two U.S. EPA Emergency Response Program processes: release notification and release verification. The notification process involves receiving and capturing data on all reported notifications of a release. The verification process involves making an initial release assessment, a response evaluation and then, if necessary, planning a removal action for the release.

The U.S. EPA portion of ERNS represents release notification reports collected by each of the 10 U.S. EPA Regions using a Regional ERNS data base. The Regional ERNS is a stand-alone Personal Computer (PC)- or Local Area Network (LAN)-based system which standardizes the process of collecting, documenting and analyzing data on releases of oil and hazardous substances specific to each Region.

Each time a call is made to the U.S. EPA to report a release of oil or a hazardous substance, the data are put into the Regional ERNS data base as shown in Figure 1. Regional notification and verification data are sent electronically to the National ERNS data base on a weekly basis. At the same time, NRC notification reports, that are referred to the U.S. EPA via phone for verification and response evaluation, are also sent electronically to the respective Regional ERNS data base.

By standardizing the collection, processing and reporting of oil and hazardous substance release notifications through the use of ERNS, the emergency response community has achieved consistent data collection, reduced operational differences among entities receiving notifications and streamlined data sharing among the numerous and widely dispersed members of the response community. The objective of this paper is to describe the process used to develop ERNS and some of the factors that led to its successful implementation.
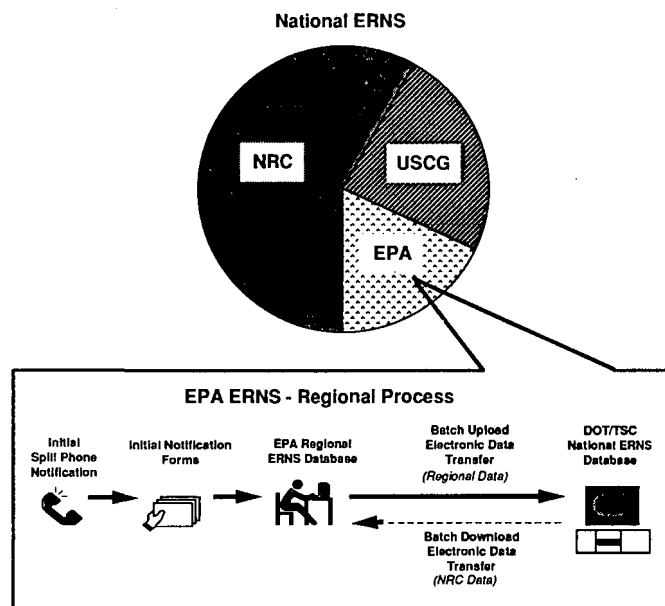
Figure 1
Emergency Response Notification System

ERNS DEVELOPMENTS
YESTERDAY, TODAY and TOMORROW

ERNS development began in 1986. The objective was to meet the functional and regulatory requirements for recording and maintaining data collected from the notifications of oil and hazardous substances. Since then, ERNS has expanded its objective to include the assessment of notification data for incident and program management analyses.

ERNS was developed and implemented in two phases as shown in

Figure 2: Phase I documented initial release notification information and Phase II expanded the focus of information flow to assessment and response.

PHASE I

Building ERNS Notification Data Collection Capabilities

Documented initial release notification data for:

* Initial incident evaluation
* Transmission to national ERNS
* Responding to information requests

PHASE II

Enhancing ERNS Capabilities To Support Release Verification

Focus information flow to assessment and response:

* Verifies initial information
* Characterizes incident sources/causes
* Documents incident disposition

PHASE II

Developing ERNS Into An Incident Analyses and Program Management Tool

Target initiatives on:

* Establishing program definitions for ERNS data
* Improving data quality through training and audit reports
* Expanding data access and usage

| 1986 | 1988 | 1990s |

Figure 2
ERNS Developments by Phase

A phased systems development approach was taken in order to: (1) provide ERNS users sufficient time to understand and test how ERNS capabilities would or would not meet specific data and work needs and (2) permit the ERNS development team to gain a thorough understanding of removal program data and operational requirements and produce results within a short time frame. The following paragraphs describe ERNS developments by phase.

Phase I: Building ERNS Notification Data Collection Capabilities in 1986

Prior to ERNS development, collection of notification data was a manual and paper-intensive process. At an April 1986 meeting with federal emergency response personnel including the NRC, USCG, TSC, U.S. EPA Emergency Response Division (ERD) Headquarters (HQ) personnel and U.S. EPA Regional On-Scene Coordinators (OSCs), 85 critical notification data elements were defined as the national data set. The U.S. EPA and TSC participants later became the U.S. EPA ERNS Work Group. The Work Group concept provided and continues to provide, a core team that ensures that ERNS user needs are addressed on all current and new system initiatives and that continual improvement is built into the operation and maintenance of the system.

To obtain the national data set for each notification, report forms were developed and completed by U.S. EPA Regions manually. A copy of the forms was sent to TSC for data entry into a National ERNS data base. While the pre-ERNS process met legislative and regulatory data collection requirements, data handling and processing problems were encountered. They included: (1) notification forms being completed and copied illegibly; (2) form contents varying by Region, thereby hampering data entry speed and causing inconsistent data collection and interpreta-

tion; (3) use of different abbreviations and acronyms which hampered data retrieval; and (4) poor notification reporting accountability for program planning and management.

To address several of these problems, ERNS Phase I development was initiated to automate the processes of capturing Regional notification data and sending the forms to TSC. The ERNS role in Phase I was to document notifications at the Regional level on standard notification report forms. Regional staff would then either mail a copy of the form to TSC or enter the data into ERNS which would transmit the data electronically to the National data base. In addition, Regions were requested to list Region-specific data elements. These data typically included data for response tracking and referral.

ERNS Phase I was developed for stand-alone PCs using dBASEIII and was pilot tested in U.S. EPA Regions II and VI. The pilot program served as a test for monitoring real-world performance of ERNS. Regional piloting also allowed direct system support by the ERNS development team. The ERNS development team concentrated on the two pilot Regions' systems to ensure smooth change integration and full system operability before implementation in the remaining Regions. ERNS Phase I became operational in October 1986.

Phase II: Enhancing ERNS Capabilities to Support Release Verification in 1988 and Developing ERNS Into An Incident Analyses and Program Management Tool in the 1990s

ERNS Phase II has focused and continues to focus, on improving the Emergency Response Program's ability to characterize actual incidents by providing information on the nature of the release for response evaluation. While basic notification data collected by ERNS Phase I helps an OSC decide whether a U.S. EPA response is warranted, Regions follow up on most, if not all, notifications to obtain more detailed information. This information is obtained by calling State/local contacts at the scene or by an OSC or an authorized contractor visiting the site. It is the information collected from these activities that provides the key data gaps during response determination.

In collecting after-the-fact or verification data, the emphasis is on collecting as much data as possible on the release and to ensure that the data are accurate and reliable enough to make a sound response determination. After-the-fact data provide a clearer, more complete picture of the accidental release. It provides key data that substantiate, verify or revise data collected during the initial release notification. It is this level of detail, accuracy and completeness that the U.S. EPA management needs in order to make sound planning and budgeting decisions and to report program activities accurately to Congress and the public.

ERNS Phase II focuses on enhancing system capabilities by collecting and modifying detailed after-the-fact data on a release and streamlining the NRC data transfer process. ERNS Phase II provides the capability to: (1) record additional data elements specific to verified incidents, along with the original notification data; (2) continually update the status of a verified incident; (3) receive notifications, originally received by the NRC, automatically through electronic transmissions from the National ERNS data base; (4) integrate user aids, such as chemical and location tables, in the data capture process; and (5) expand Regional access to ERNS by upgrading to a multiuser LAN environment.

Additional features such as password security, variable fiscal year data, cursor movements, restricted input fields, on-line help, popup screens, screen colors, archived spill records, free-form notepad, backup procedures and NRC data transfer are also included in ERNS. To ensure that ERNS Phase II features are appropriate for Regional ERNS operations, they are demonstrated at National ERNS conferences for maximum user suggestions and are tested in a pilot Region for real-world performance.

ERNS Phase II telecommunications enhancements and user aids reduce the data input workload in the U.S. EPA Regions significantly. The telecommunications enhancements enable each Region to keep their individual notification data base current with the National notification data base. ERNS Phase II ensures that the 10 distinct Regional systems operate in a parallel fashion with one another and merge effectively

with NRC and USCG data to create the centralized National ERNS data base. This merging of data bases saves resources and improves the completeness and quality of the data.

ERNS today encompasses all of these data capture and telecommunications capabilities. As ERNS users become increasingly skilled in using ERNS as a notification data collection tool, they also identify ways of applying ERNS data to response activities. ERNS' function is evolving from strictly an initial notification data collection system. ERNS is used increasingly to support incident and program management analysis, emergency preparedness and planning, U.S. EPA enforcement and responses to public and private information requests. To meet these dynamic needs, the U.S. EPA's ERD has begun several initiatives in fiscal year 1990 including: (1) establishing program definitions for ERNS data to ensure consistent interpretation and usage; (2) improving data quality for response determination; and (3) expanding data access for information queries and public use.

KEYS TO ERNS SUCCESS

ERNS success is attributed largely to the frequent and dynamic communication among the ERNS Work Group members and the close working relationships among the U.S. EPA, TSC, NRC and USCG. Regional communications cover topics such as assistance on ERNS operations and ad hoc reports; data quality assurance and data control issues; input and feedback on HQ activities; and working through and testing planned system enhancements and training activities. Communications with other federal agencies cover topics such as National ERNS data base integrity and data quality issues; information distribution to Congress and the public; and implications of other federal emergency response initiatives, such as the July 1990 promulgation of the final rule on "Reporting Continuous Release of Hazardous Substances."

This section describes the key factors that contributed to the successful development and implementation of ERNS. These factors include extensive user participation from the inception of ERNS; keeping ERNS simple and flexible; proactive development and implementation initiatives; and maintaining ERNS visibility to management and visibility to the emergency response community.

Extensive User Participation From The Inception Of ERNS

The ERNS Work Group established in 1986 has been and continues to be the round table discussion forum for addressing ERNS program requirements and user needs on all current and new initiatives. The Work Group consists of ERD HQ personnel, Regional OSCs and program staff who represent U.S. EPA Emergency Response Program users and the TSC and U.S. EPA ERNS development team who support the National and Regional ERNS data bases respectively. As illustrated in Figure 3, the ERNS Work Group is central to system management in addressing programmatic and system issues and coordinating and communicating ERNS activities within the U.S. EPA, with its federal counterparts, NRC and USCG and with the public.

A participatory development and implementation approach is used to ensure that ERNS contains usable and practical features for U.S. EPA Regional users. The overall approach consists of:

- Identifying requirements or improvement areas for ERNS
- Demonstrating a system improvement concept to the entire Work Group usually at the National ERNS conference
- Incorporating the new capability into ERNS if the feedback is favorable
- Conducting a Regional pilot test for real-world performance
- Refining the capability based on Regional pilot results
- Implementing the enhancements or improvements in the remaining Regions
- Operating, maintaining and monitoring the system.

All or parts of this approach have been used successfully for a variety of ERNS initiatives—from implementing system changes and improvements to developing training courses and procedural guidance.

Keeping ERNS Simple and Flexible

Many of ERNS users were and are first time PC users. The way ERNS

'looks and feels' is, therefore, important to its initial and continued use. With this in mind, ERNS was developed as a menu-driven system with tables which lead users through its operations. Additionally, the phased development approach and Regional pilot tests helped pace and tailor the introduction of new ERNS features and capabilities with users' knowledge and comfort with PCs and the system. The human/machine interactions also contributed to ERNS success. Human/machine interactions took into account how ERNS needed to 'look and feel' in order to ease any user discomforts with using a computer for the first time.
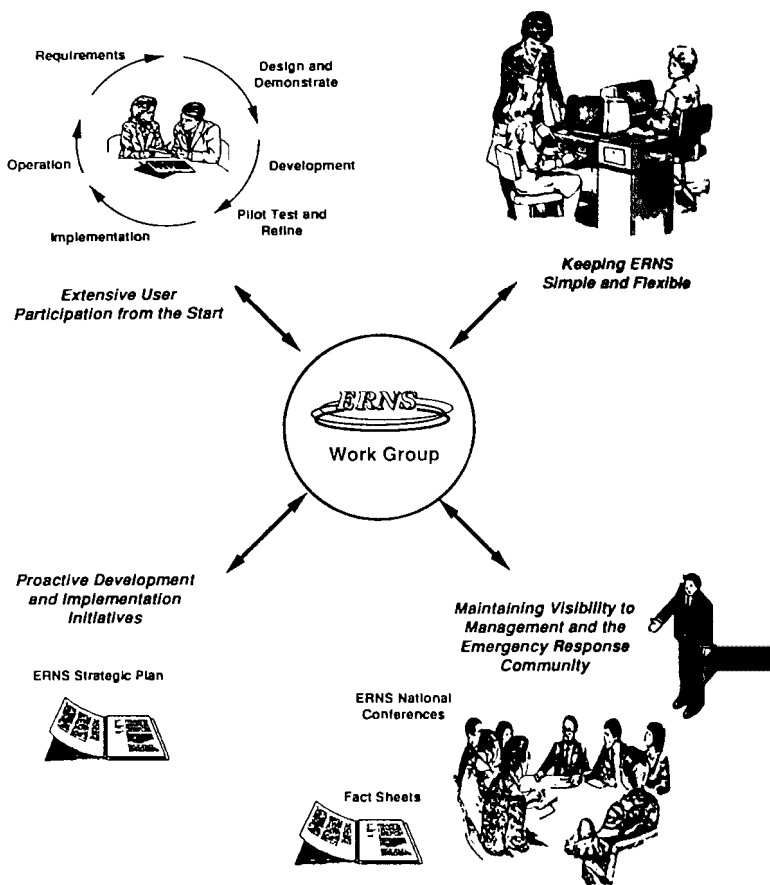
Figure 3
Keys to ERNS Success

Not only does ERNS need to be easy to use, but it also needs to be flexible to support evolving program and user needs and changes in PC technology. As users became more knowledgeable and confident in the system, ERNS usage began to grow and change. ERNS users grew to need more system capabilities as evidenced by the number of features added to ERNS in Phase II. ERNS maintains its simplicity to accommodate new users while providing expanded capabilities for more sophisticated users. In keeping with the Agency's direction in the use of PC LAN technology, ERNS was also upgraded from a single user system on a stand-alone PC to a multiuser system operating on a LAN. Today, ERNS initiatives include addressing an evolving and growing need by the Emergency Response Program and the public to use ERNS data for incident analysis in addition to the notification analysis performed today.

Proactive ERNS Development and Implementation Initiatives

Throughout development and implementation, ERNS Work Group members defined what ERNS should do and what ERNS needs to do. The ERNS development team designed and developed how ERNS would operate and worked closely with Regional OSCs and program staff in testing and refining ERNS operations and user interface.

Following ERNS Phase I implementation, the ERNS development team began providing technical support to ERNS Regional users. The Team provides user assistance more than the telephone; uses software which allows remote ERNS diagnostics, repair and assistance; and obtains user suggestions and feedback on ERNS operations and uses regularly. By having continual contact with Regional users, the ERNS development team has tracked recurring questions and problems and has suggested ERNS improvements based on first-hand knowledge of how ERNS is being used. This close working relationship keeps ERNS aligned with the emergency response support needed by the Regions.

Maintaining ERNS Visibility to Management and Visibility to the Emergency Response Community

Management support and ERNS visibility to the emergency response community were obtained through the U.S. EPA's Emergency Response Program management briefings, environmental conference presentations and public relations brochures. Fundamental to ERNS success is its well-established reputation and use by federal agencies and an increasing number of state and local agencies and commercial firms.

NOTIFICATION TRENDS IN OIL AND HAZARDOUS RELEASES

ERNS captures data on the initial notification of a release and on verified releases. With the 85 notification data elements, the following data are collected: the notification caller, the discharger and the released substance; the release location, date and time; the release source, medium and cause; the potential human health risks or imminent danger; and actions already underway to mitigate the reported release or release threat.

Since October 1986, more than 95,000 release notifications have been collected by ERNS, including 49,000 release notifications for oil releases. In the past two years, the total number of notifications has increased slightly with 29,874 reports in 1988 and 34,089 reports in 1989. Figure 4 shows the distribution of notifications received since 1987.
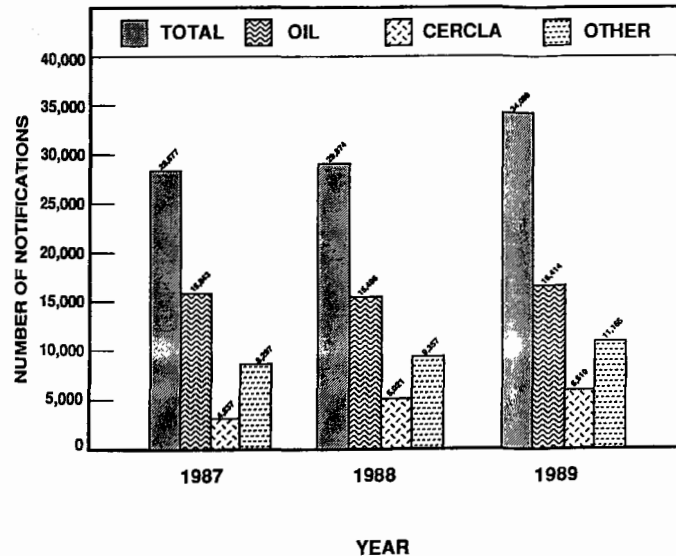
Figure 4
ERNS Trends: Total Oil, CERCLA, and Other
1986 Through 1989

As seen in Figure 4, the number of oil soil notifications in the last three years has remained stable, showing only an increase of 571 reports more than the three-year period. In contrast, reports of CERCLA substance releases have increased steadily with 2000 more reports in 1989 than in 1987. The increase in CERCLA substances release reports may be attributed to an actual increase in the number of releases, an increase in awareness of reporting requirements and/or compliance with

spill reporting requirements, as well as an improvement in data recording and record-keeping used by the federal government.

Since 1987, there have been more than 16,000 CERCLA release notifications. More than 75% of these reports identified the source of the reported release as a fixed facility-related incident. Highway and rail incidents comprise another 15% of the reported sources of CERCLA notifications. Figure 5 provides the complete distribution of reported release sources resulting in CERCLA notifications for the last three years.
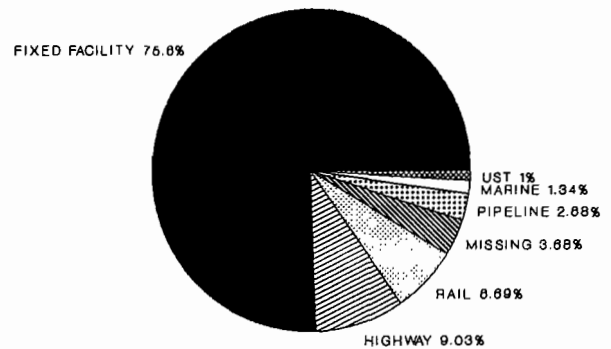
Figure 5
CERCLA Release Notifications by Source From
1987 to 1989

The five CERCLA substances most frequently reported released, for each of the last three years are shown in Figure 6. These most released chemicals include PCBs, chlorine, sulfuric acid, sodium hydroxide and anhydrous ammonia. PCBs have remained the most frequently reported CERCLA hazardous substance for all three years. Figure 6 shows an increase of more than 100% in the number of anhydrous ammonia
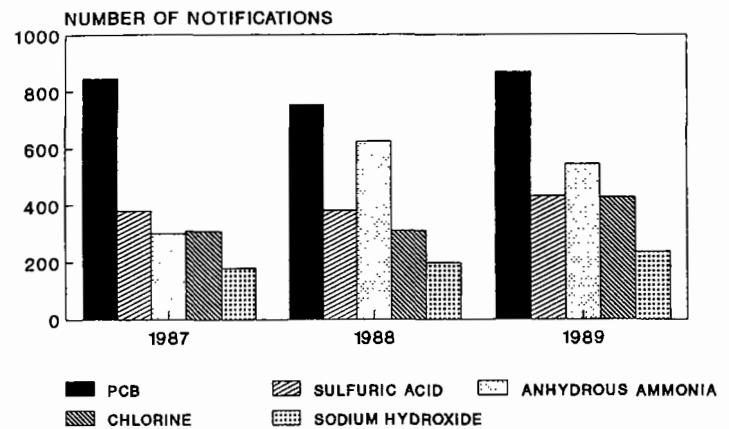
Figure 6
"ERNS Top 5"
CERCLA Hazardous Substances

release notifications in 1988 more than 1987. Although there was a slight decrease in the number of anhydrous ammonia reports in 1989, anhydrous ammonia remained the second most frequently reported CERCLA substance for that year.

More than 47,000 oil release notifications have been received since 1987. Incidents related to fixed facilities, such as refineries and oil wells, account for 49% of the oil reports; 25% have been marine related. Figure 7 provides the complete distribution of CERCLA notifications since 1987.

The most frequent oil substances released in 1987, 1988 and 1989 are shown in Figure 8. As the graph shows, crude oil reports increased

more than 40% from 1988 to 1989 and surpassed the number of diesel oil reports. These data reverse the trend established in 1987 and 1988
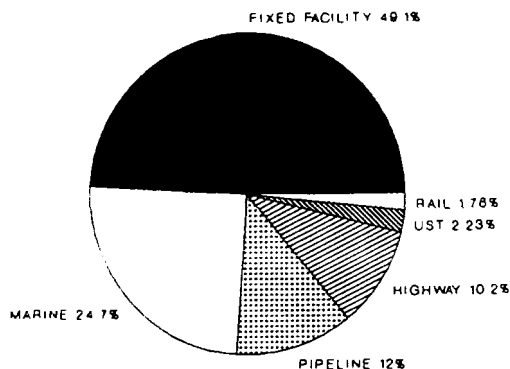
Figure 7
Oil Release Notifications by Source
From 1987 to 1989

when diesel oil releases were the most reported oil releases. The graph also shows a significant drop in the number of waste oil reports from approximately 1,100 in 1987 and 1988 to 670 in 1989.

CONCLUSIONS

ERNS is a critical tool in streamlining and standardizing the collection and dissemination of information on notifications of oil and hazardous substance releases. Its success is largely a result of the frequent and dynamic communications among members of the emergency response community including the U.S. EPA, NRC and USCG.
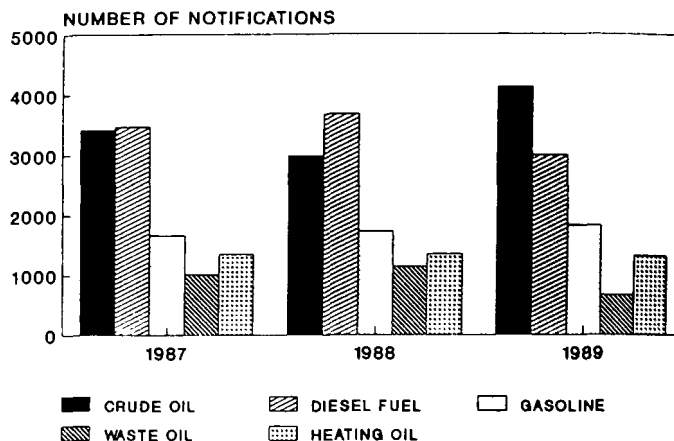
Figure 8
ERNS Top 5" Oil 1987 Through 1989

With a solid data base of release notification information, ERNS is now being developed to support incident and program management analysis, emergency preparedness and planning, U.S. EPA enforcement and responses to public and private information requests.

The NLM/ATSDR ANSWER™ Work Station with the TOMES Plus™ CD-ROM Information System for HAZMAT Incident Response

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ABSTRACT

The time-critical nature of emergencies involving hazardous materials demands a means of retrieving needed emergency response, medical, and toxicological information rapidly. Transportation-related hazardous materials emergencies often occur in locations where access to a telephone connection for on-line searching is unavailable and where surrounding terrain may complicate or preclude radio contact for dispatch-based information transfer.

The ANSWER™ Workstation was produced by the National Library of Medicine (NLM) in conjunction with the Agency for Toxic Substances and Disease Registry (ATSDR) to address these issues. This work station is based on an IBM-compatible portable computer with a compact disc drive and internal modem. If telephone access is available, a gateway program called MICRO-CSIN allows for simplified on-line access to a wide variety of remote data bases. Pro-Com provides access to real-time weather information from the National Weather Service. A hard-disk data base contains information collected during previous emergency response situations. Other ANSWER Workstation features are an air dispersion plume modeling package, word-processing and FAX transmission capabilities. The ANSWER Software will also run on a desktop IBM-AT or compatible PC.

The TOMES Plus™ Information System (Toxicology, Occupational Medicine and Environmental Series) is the CD-ROM (Compact Disc-Read Only Memory) portion of the ANSWER Workstation, allowing over 500 megabytes of information to be provided on-site on a single compact disc only 4-3/4 inches in diameter and weighing only 1/2 ounce. A menu-driven search software allows even novice users to quickly retrieve required information on over 100,000 individual chemicals, accessed by chemical name, synonym, CAS number, NIOSH/RTECS number, UN/NA number, STCC number, RCRA Hazardous Waste Number, etc.

The TOMES Plus system currently contains the following data bases of particular interest to hazardous materials incident responders: HAZARDTEXT™, DOT Emergency Response Guides, HSDB (the Hazardous Substances Data Bank produced by NLM), CHRIS (the Chemical Hazards Response Information System produced by the US Coast Guard), OHM/TADS (the Oil and Hazardous Materials/Technical Assistance Data System produced by the U.S. EPA) and RTECS (the Registry of Toxic Effects of Chemical Substances produced by NIOSH). Additional data bases on the TOMES Plus disc provide information on medical evaluation and treatment, risk assessment, toxicology and reproductive hazards. Under development in 1990 are SARATEXT™ for SARA Title III Extremely Hazardous Substances medical evaluation and treatment reporting and REPROTEXT™ with rating scales and monographs on the chronic toxicity and reproductive hazards of chemicals.

The ANSWER Workstation is currently being used by several State health departments and hazardous materials response agencies.

INTRODUCTION

Emergencies involving hazardous materials may occur anywhere and any time. Some crucial aspects of successful HAZMAT incident response involve rapid procurement of adequate data on hazards, toxicity and proper response actions; plotting the anticipated spread of released airborne contaminants to determine possible areas for evacuation; transmission of data and current incident status to other agencies or facilities that may become involved in the response; and collection of incident-specific data for later evaluation and utilization when similar situations occur in the future.

Because radio or telephone line communications may be difficult to achieve, particularly during the initial response phase, as much information as possible should be moved directly to the incident site. The concept of a portable work station, able to be carried on airplanes as hand baggage (fitting in overhead compartments or under a seat) and weighing less than 30 pounds, has been developed by the National Library of Medicine (NLM) in conjunction with the Agency for Toxic Substances and Disease Registry (ATSDR). The prototype product, the ANSWER™ Work station (ATSDR/NLM's Work station for Emergency Response), encompassing a variety of features required for HAZMAT incident response and including a CD-ROM data base (the TOMES Plus™ Information System from Micromedex, Inc.) is currently being beta-tested by a number of state health and HAZMAT response agencies.

ANSWER WORKSTATION FEATURES

The Event Description File (EDF) is a hard-disk data base enabling emergency response personnel to maintain and query a wide range of information on previous HAZMAT response events. HAZMAT responders can retrieve actual experience and results from either their own or a nationally collated and shared data base of the results of similar incident responses. Each individual HAZMAT response incident and the results of various interventions can be recorded in the EDF, retrieved by the responding organization and may also be shared nationally with other similar agencies. The EDF can also be used to prepare reports required for local, state or national agencies, or the National Fire Protection Association (NFPA).

Should information regarding a particular incident need to be shared on an urgent basis with other response agencies, the FAX feature of the ANSWER Workstation can be used to transmit hard copy and files to fire departments, hospitals, other governmental agencies, etc. Both transmission of information and review of FAX files received from remote sites can be accomplished. Hard copy can be printed on-site as required.

The Health/Hazard module of the ANSWER Workstation is the CD-ROM-based TOMES Plus™ Information System developed and provided by Micromedex, Inc. of Denver, Colorado. CD-ROM data bases which can be accessed through the ANSWER Workstation are described below. Any portion of the TOMES Plus Information System can be printed out in hard copy or sent to the hard disk for local editing or remote transmission with the ANSWER Workstation FAXing feature. After telephone line connection is established, the MICRO-CSIN feature of the ANSWER Workstation allows simple access to a very wide range of on-line data bases for retrieval of further information about hazardous substances. MICRO-CSIN is a gateway program which minimizes the training required to successfully query remote on-line data bases for retrieval of fact, numeric and chemical identification data from eight component vendor systems. TYMENET and Telenet can be used with MICRO-CSIN through the Communication Parameters feature. The menu-driven software package Grateful Med, which greatly simplifies searching NLM's MEDLARS data base, can also be used with the ANSWER Workstation.

The ANSWER Workstation WEATHER feature uses Pro-Com to obtain the most recent weather observations from 1,000 National Weather System reporting stations throughout the United States and Canada from the Weather Information System developed by the WSI Corporation. The most applicable plume modeling program for ANSWER Workstation users is currently being studied. As soon as a plume model is available, data such as current wind direction and speed, relative humidity, dew point, etc. can be retrieved with the WEATHER feature and used in the plume modeling program.

The ANSWER Workstation also incorporates word processing and management functions to allow information editing, development of local "call lists" of crucial personnel, inter- and intraagency locally-defined communications functions and more. ANSWER Workstation Project Information is available from Specialized Information Services at the National Library of Medicine, Bethesda, Maryland. User Support Staff are available at the Training & Management Systems Division of the Oak Ridge Associated Universities, Oak Ridge, Tennessee.

TOMES PLUS CD-ROM DATA BASES

The TOMES Plus™ Information System (Toxicology, Occupational Medicine and Environmental Series) developed and produced by Micromedex, Inc. of Denver, Colorado, is the CD-ROM (Compact Disc-Read Only Memory) portion of the ANSWER Workstation. The TOMES Plus system provides more than 500 megabytes of information available on-site on a single compact disc only 4-3/4 inches in diameter and weighing only 1/2, ounce and is accessible with either a half-height CD-ROM disc drive which can be internally mounted in certain portable personal computers, or an external CD-ROM disc drive connected to a desktop PC. The unique TOMES Plus system menu-driven search software allows even novice users to quickly retrieve required information on more than 100,000 individual chemicals, accessed by a wide variety of identifiers, including: chemical name, synonyms, CAS number, NIOSH/RTECS number, UN/NA number, STCC number, RCRA Hazardous Waste Number, etc. After initial query, a resident function allows retrieval of all NIOSH/RTECS (and other source) synonyms and identifiers to confirm that the correct chemical is being researched.

The TOMES Plus system currently contains a wide variety of data bases which are of particular utility for hazardous materials incident responders:

- HAZARDTEXT™ (produced by Micromedex, Inc.) containing a review of EMT-paramedic level clinical effects, patient evaluation

and treatment data, range of toxicity including pertinent workplace and environmental exposure standards and recommendations, a thorough review of common handbooks and other primary and secondary sources of information for fire control, hazards of combustion products, environmental hazards, chemical reactivities, physical and chemical properties and recommendations for the choice of chemical protective equipment

- Frequently-consulted DOT Emergency Response Guides (from the Department of Transportation); the entire HSDB (the Hazardous Substances Data Bank produced by NLM) with detailed information on the production, common uses, manufacturing, physical/chemical properties and hazard, environmental and potential health effects of more than 4,200 individual chemical substances
- CHRIS (the Chemical Hazards Response Information System produced by the US Coast Guard) with fire, health, environmental and other hazard data on over 1,200 chemicals
- OHM/TADS (the Oil and Hazardous Materials/Technical Assistance Data System produced by the U.S. EPA) with information on the environmental and health hazards of over 1,000 chemical substances and recommendations for cleanup or amelioration of spills or other releases
- RTECS (the Registry of Toxic Effects of Chemical Substances produced by NIOSH) containing information on the irritant, acute toxicity, genotoxicity, tumorigenicity and reproductive hazards of over 100,000 individual chemical substances

Additional data bases on the TOMES Plus disc:

- MEDITEXT™ (produced by Micromedex, Inc.), which provides physician-level detailed information on the medical evaluation and treatment of patients exposed to hazardous chemicals for use by both emergency responders and emergency department or other hospital-based medical personnel
- U.S. EPA's IRIS (Integrated Risk Information System) data base for performing risk assessments following releases into air or drinking water
- REPRORISK™ series of data bases for the assessment of potential chronic exposure and reproductive hazards of hazardous chemical exposure

New TOMES Plus data bases being developed by Micromedex, Inc. during 1990 are SARATEXT™ for SARA Title III Extremely Hazardous Substances medical evaluation and treatment reporting and REPROTEXT™ with rating scales and monographs on the chronic toxicity and reproductive hazards of chemicals.

BETA-TEST SITES

The ANSWER Workstation with the TOMES Plus Information System is currently undergoing beta-testing. Fifteen initial installation sites have been chosen, including five State health agencies, a city-county health department, three poison control centers, a county fire department, three locations of the ATSDR, the National Library of Medicine and the Oak Ridge Associated Universities (where training development is in progress).

CONCLUSION

Continuing development of both the informatics and utilities content and features of the ANSWER Workstation and the TOMES Plus Information System have promise to make this combination portable/remote HAZMAT incident response tool an indispensable information and communications resource for HAZMAT incident response, community planning and risk assessment.

1990 Exhibitors

**3M Environmental
Protection Products** 0905-0907
3M Center, Building 223-6S-04
St. Paul, MN 55144-1000
612/736-5335

3M Company - Environmental Protection Products - 3M Foams. 3M Foams have proven their suppression effectiveness during hazardous material clean-up that involves release of volatile organic compounds (VOCs), air toxics, odors, and dust. These water-based foams conform to the terrain and last hours, days, and even weeks, depending on the site requirements.

A.E.T.C. 2411/2413
Gold Mine Rd.
Flanders, NJ 07836
201/347-7111

A.E.T.C. has been providing fully integrated hazardous and chemical waste management services since 1976. A.E.T.C. specializes in the management of reactives and package laboratory chemicals, as well as production wastes, PCB destruction, household hazardous waste, and a full range of site remediation services from our thirteen locations.

**A.O. Smith Harvestore
Products, Inc.** 1903
345 Harvestore Dr.
DeKalb, IL 60115
815/756-1551

A.O. Smith Harvestore Products, Inc. will be exhibiting its Aquastore® Tank products line. These tanks, with capacities up to 2 million gallons, are factory coated with fused silica glass on the inside and outside for corrosion control. The tank is field-erected by bolting and the joints are sealed.

ABB Environmental Services Inc. 0223
261 Commercial St.
Portland, ME 04112
207/775-5401

Environmental Consulting, monitoring and

chemical analysis; hazardous waste site investigations, remedial design, construction and clean-up; thermal and non-thermal waste treatment systems.

AIM USA 0218
P.O. Box 720540
Houston, TX 77272-0540
713/240-5020

AIM develops and manufactures microcomputerized portable toxic/combustible/oxygen air monitoring instruments. AIM is able to quickly develop hardware and software solutions for many special gas detection needs. AIM instruments are used by over 70 USA military installations, environmental remediation firms, all types of industries and many major hazardous material response teams.

**ALCOA SEPARATIONS
TECHNOLOGY, INC.** 2008/2010
Subsidiary of Aluminum Company
of America
181 Thorn Hill Rd.
Warrendale, PA 15086-7527
412/772-0086

Innovative technologies for the recovery/treatment of groundwater and the treatment of sanitary and hazardous landfill leachates are on display by Alcoa Separations Technology, Inc., Subsidiary of Aluminum Company of America. Comprehensive treatment/recovery equipment, services and technologies are highlighted and information regarding the various treatment approaches are available.

ALL-PAK, INC. 1608
2260 Roswell Dr.
Pittsburgh, PA 15205
412/922-7525

U.N. Performance Tested/DOT Exempt Packaging, EPA Pre-cleaned Sample Bottles, Overpack Drums - metal/plastic, Lab Packs, Teflon-lined Caps, Safety Coated Bottles, Complete Line of Glass, Plastic and Metal Containers.

ARAMSCO 0320
1655 Imperial Way
Thorofare, NJ 08086
609/848-5330

ARAMSCO specializes in safety products for the hazardous environment, introducing the Blastrac - a portable shotblast cleaning system for emoving contaminants such as PCB, asbestos, radiation from concrete or metal floors.

AVS Video Productions 0613
8548 N. Dale Mabry, 2nd Floor
Tampa, FL 33614-1600
813/935-1898

Turnkey video production - scripting through duplication of finished programs; OSHA certified camera crews shoot broadcast quality footage of remedial investigations, Superfund cleanups, SITE demonstrations and experimental facilities; post production capabilities include state-of-the-art 3D animation to illustrate the operation of innovative equipment and chemical processes.

AWD Technologies, Inc. 2119
15200 Omega Dr.
Rockville, MD 20850
301/869-4800

AWD Technologies, Inc., a wholly owned subsidiary of The Dow Chemical Company, provides full-service groundwater, soil, and site remediation. Services include site investigation, planning and engineering design, construction, operation and maintenance, and overall project management.

Acres International Corporation 0501
140 John James Audubon Pkwy.
Amherst, NY 14228-1180
716/689-3737

Acres provides waste management expertise to a wide variety of industrial firms, utilities, and government agencies (federal, state and local). Site investigations, permitting and regulatory compliance evaluations, remedial investigations and feasibility studies, conceptual and detail de-

sign, and construction supervision are among the comprehensive services offered. Acres offers a multidisciplined and experienced team of geologists, hydrogeologists, chemists, biologists, geotechnical, chemical, civil and hydraulic engineers and support staff to successfully complete a variety of waste management projects.

Agency for Toxic Substances and Disease Registry 2407
1600 Clifton Rd., N.E. (MS F-38)
Atlanta, GA 30333
404/639-0708

The Agency for Toxic Substances and Disease Registry (ATSDR) is part of the Public Health Service and is based in Atlanta, Georgia. It was created by Congress to implement the health-related sections of laws that protect the public from hazardous substances.

Alliance Technologies Corporation 0301
213 Burlington Rd.
Bedford, MA 01730
617/275-9000

Alliance specializes on the investigative, diagnostic phases of environmental projects. The services we offer include: emission source characterization and quantification, health and ecological risk assessments, pollution control technology evaluation and design, site assessments and subsurface investigations, environmental audits for facilities, permitting and advanced modeling, health and safety plans, database design and management, and waste minimization and pollution prevention.

Alternative Systems, Inc. 2009
225 S. Cabrillo Hwy., Suite 124-C
Half Moon Bay, CA 94019
415/726-5700

TINIA is the most comprehensive hazardous materials liability management software designed for industry, State and Local, and Federal government. TINIA is written in a fourth generation language utilizing state of the art technology, integrated imaging, telephony, geographic information mapping, and systems integration. TINIA is platform independent. TINIA is a commitment to the environment.

American Colloid Company 2021
1500 West Shure Dr.
Arlington Heights, IL 60004
708/392-4600

American Colloid Company is the world's largest producer of bentonite clay and related products. ACC's Environmental Division manufactures Volclay bentonite for landfill lining, Bentomat seepage control liner and Sorbond waste solidification/fixation agents. The Water/Mineral Division will be showing the PureGold product line of Groundwater Monitoring products, which include environmentally safe bentonite grout, drilling fluid and tablets.

American Health & Safety, Inc. 0309
6250 Nesbitt Rd.
Madison, WI 53719
608/273-4000

American Health & Safety, Inc. is a nationwide

industrial safety supply house featuring a full line of on-the-job safety products. We have over 5,000 line items which are distributed throughout the safety industry, including asbestos, laboratory and food industries. American Health & Safety specializes in the hazardous materials and toxic waste disposal fields. We will be displaying gloves, respirators, coveralls, boots, safety glasses, tape, shovels, instrumentation and first aid used heavily in the hazardous materials industry.

American Industrial Marine Services 0224
1550 E. Patapsco Ave.
Baltimore, MD 21226
201/756-4200

American Industrial Marine Services LDC
1550 E. Patapsco Ave.
Baltimore, MD 21226
301/355-7600

American Industrial Marine Services specializes in Hazardous Waste Transportation, Tank Cleaning and Removal; Remedial Services; Emergency Spill Response; Decontamination Services; Industrial Maintenance, and Equipment and Materials Sales. Offices are located in NJ, MD, PA and NY. Call 1/800/762-4201 for more information.

American International Companies 0317
2005 Market St., Suite 2800
Philadelphia, PA 19103
215/981-7117

Meeting the insurance needs of industry by providing Environmental Impairment Liability, General Liability, Business Automobile Coverage, and Property Insurance, for companies in the environmental field, through experienced underwriting, comprehensive risk management, and dedicated claims handling.

American Laboratories & Research 0409
P.O. Box 15609
Hattiesburg, MS 39404
601/264-9320

Amoco Fabrics and Fibers Company 1710
900 Circle 75 Pkwy., Suite 300
Atlanta, GA 30339
404/956-9025

Amoco Fabrics and Fiber Company is the only manufacturer of both woven and nonwoven geotextiles. Nonwoven polypropylene fabrics ranging in weight from 3 to 20 ounces per square yard. Applications for geotextiles include geomembrane cushion, filtration, stabilization, erosion control, separation and reinforcement. Call (404) 984-4433 for information.

AnalytiKEM, Inc. 1008
28 Springdale Rd.
Cherry Hill, NJ 08003
609/751-1122

AnalytiKEM is a full services analytical laboratory network with facilities located in Cherry Hill, NJ, Rock Hill, SC, Houston, TX, and Wilmington, MA. AnalytiKEM's expertise includes environ-

mental analysis for NJ/ECRA and other real estate assessments, cleanup, Full RCRA characterization, NPDES permit compliance, groundwater monitoring and compatibility testing. AnalytiKEM utilizes state-of-the-art instrumentation including GC/MS and provides field sampling services.

Andco Environmental Processes, Inc. 0401
595 Commerce Dr.
Amherst, NY 14228
716/691-2100

Wastewater treatment systems to remove heavy metals, fluorides, phenol, and other organics from industrial wastewater, contaminated groundwater, and leachate. Also a portable heavy metal pilot unit.

Andersen Instruments, Inc. 0712
4801 Fulton Industrial Blvd.
Atlanta, GA 30336
404/691-1910

Andersen Instruments, Inc., is one of the world's foremost manufacturers of environmental monitoring and occupational health diagnostic instrumentation. Andersen equipment is known for protocol compliance, ease of use, and accuracy. Specifically featured will be EPA-approved remote air samplers, particulate impactors and ambient toxic gas analyzers. Call (800) 241-6898 for more information.

Aqua Tech Environmental Consultants, Inc. 2017/2019
181 South Main St., P.O. Box 436
Marion, OH 43302
800/783-5991

Aqua Tech Environmental Consultants, Inc. proves accurate and precise analytical data on a timely basis, at competitive prices, to industrial, governmental and private clients. Aqua Tech's services include complete capabilities for organic and inorganic analysis, bioassay/biomonitoring, sampling, and mobile laboratory analysis. Call (614) 382-5991 for more information.

Aqua-Chem, Inc. LDC
210 W. Capitol Dr., Box 421
Milwaukee, WI 53201
414/962-0100

Aquastream LDC
1115 North First St.
Garland, TX 75040
214/276-5690

Aquastream has recently expanded its innovative water well equipment product line to include a lab-certified pre-packed "Gravelwall Monitor Screen." The unique environmental well screen (available in stainless, PVC or Teflon), features a silica gravel-pack which is bonded directly to the screen itself, thus insuring uniform filtration with reduced drilling costs.

Art's Manufacturing & Supply 1112
105 Harrison at Oregon trail
American Falls, ID 83211
800/635-7330

AMS will be exhibiting their full line of soil

sampling equipment. AMS will be displaying for the first time, the new "PAT" dual valve liquid sampler. AMS will also be showing a video of the new AMS dual reel portable boom system for groundwater monitoring wells.

Associated Design & Manufacturing Co.   1114
814 N. Henry St.
Alexandria, VA 22314
703/549-5999

Associated Design provides suitable laboratory equipment for TCLP and liquid relase testing of solid waste. Featured products include the zero headspace extractor (ZHE) for collection of volatile contaminants, two bench-top filtration units, the new liquid relase test device, and large-capacity rotary agitators which hold bottles separatory funnels or ZHEs. Design and fabrication services are available. New products will be introduced at this conference.

ATLANTIC RESEARCH - ARC/ARCTECH   0110
1375 Piccard Dr.
Rockville, MD 20850
301/670-2000

ATLANTIC RESEACRH ARC/ARCTECH provides remedial technologies and consulting/ engineering services including: LARC Light Activated Reduction of Chemicals for PCB and Pesticide Destruction; OZO-DETOX - Ozonation for Destruction of Coal Tars and PAHs; COMPOSTING - Bioremediation of Organic Compounds and Explosives; INFORMATION/DATA MANAGEMENT; MONITORING/MODELING; SITE ASSESSMENT/SAFETY and TRAINING/EDUCATION.

B&V Waste Science and Technology Corp.   1505
4370 W. 109th St., Box 7960
Overland Park, KS 66211
913/339-2900

A Black & Veatch Company, BVWST provides complete hazardous waste management services, including RI/FS, design plans and specs, implementation oversight, RCRA services, regulatory and permit support, and litigation assistance. Other specialties include waste treatment, PCB transformer replacement, public health evaluations, facility closure services, environmental audits, and community right-to-know planning.

BAKER/TSA, Inc.   0808
420 Rouser Rd., Airport Office Dr., Bldg.3
Coraopolis, PA 15108
412/269-6000

Performance of: remedial investigation/feasibility studies; site assessments; risk assessments, remedial/closure design and management; RCRA permitting and compliance programs; industrial hygiene and asbestos management; economic analyses, waste utilization and market studies; tank management; waste minimization programs; water and wastewater treatment; environmental auditing; and air quality services.

BCM Engineers   2100
One Plymouth Meeting
Plymouth Meeting, PA 19462
215/825-3800

Quality engineering since 1890. Services include hazardous waste management and control; groundwater studies, geophysical surveys, remedial design engineering, Superfund site investigations, facility permitting, closure plans, real estate contamination assessments, asbestos surveys, and full-service laboratory.

BGI Incorporated   1811
58 Guinan St.
Waltham, MA 02154
617/891-9380

Manufacturer/distributor of air sampling equipment, negative air pressure monitors, and calibration equipment. Also available is a complete line of personal gas monitors, Draeger grab sampling/ dosimeter tubes and respiratory equipment. In addition, gas sampling bags of tedlar and teflon and gas bag filling pumps.

BNA Communications Inc.   LDC
9439 Key West Ave.
Rockville, MD 20850
301/948-0540

BNA Communications Inc. will display brochures on our new eight-module safety training program, WORKING IN THE HAZARD ZONE, plus brochures on our HANDLING HAZARDOUS WASTE program, and our safety catalog in the Literature Distribution Center.

BNA, INC.   2218/2220
1231 25th St., N.W.
Washington, DC 20037
202/452-4200

BNA Publishes regulatory, legal and working guides providing the latest information concerning the manufacture, transportation, safe handling and disposal of hazardous materials.

BOOZ, ALLEN & HAMILTON Inc.   1109
4330 East West Hwy.
Bethesda, MD 20814
301/951-2200

Booz, Allen & Hamilton Inc. is a leading technology and management consulting firm that has earned an outstanding reputation in environmental services through years of direct involvement developing and implementing key programs for government and industry world-wide. The firm has worked with the Superfund and RCRA programs since their inception and offers comprehensive mission and program-related expertise. Technology and management services include: risk management; audits and technical evaluations; regulatory enforcement and policy support; records management; information system development; and program planning, implementation, and evaluation.

Barnebey & Sutcliffe Corporation   0903
835 N. Cassady Ave.
Columbus, OH 43219
614/258-9501

We manufacture activated carbons made from coconut shell, coal and wood. Granular, pelletized and powder forms available. Carbon regeneration service is offered by our factory in Columbus, Ohio. We offer custom package systems for solvent recovery, VOC emission control and wastewater treatment applications.

Beazer Environmental Services, Inc.   LDC
436 Seventh Ave.
Pittsburgh, PA 15219
412/227-2198

Beazer Environmental Services, Inc., offers a full range of environmental construction and remediation services to customers on a world-wide basis. We can provide complete engineering and design, project management and construction services for groundwater and wastewater treatment plants, RCRA/CERCLA closures, and bioremediation projects.

Bergen Barrel & Drum Company   1815/1915
43-45 O'Brien St.
Kearny, NJ 07032
201/998-3500

An innovative line of polyethylene drums, both open and closed head, tanks and environmental products specifically designed for the hazardous waste industry. Various sized drums and tanks along with pallets, overpacks and other products will be displayed.

Betz Laboratories   1913
9669 Grogans Mill Rd.
The Woodlands, TX 77380
713/367-6201

Betz Analytical Services offers complete environmental testing. We provide accurate timely data using the latest, automated instrumentation. Our facilities located in Houston and Philadelphia follow strict QA/QC programs to meet your testing needs. We participate in the EPA Contract Laboratory Program (CLP).

Bioscience Management, Inc.   0319
1530 Valley Center Pkwy.
Bethlehem, PA 18017
215/974-9693

Your best single stop for bioremedial supplies and services for cleaning up soil, sludge, groundwater and wastewater. We manufacture and market automated laboratory treatability and waste characterization instruments, microbial cultures, packaged groundwater biotreatment units and biostimulation chemicals. We furnish treatability studies, process engineering, site monitoring and trouble shooting, and turnkey bioremedial programs.

Biospherics Incorporated   1512
12051 Indian Creek Ct.
Beltsville, MD 20705
301/369-3878

Biospherics Incorporated has serviced asbestos

related and industrial hygiene needs for years, therefore, knowledgeable of technical and operational requirements of such programs. Comprehensive services are provided including consulting, visual and physical inspections, bulk sampling, analysis, training, program management/development, risk assessment and abatement prioritization, lead paint and PCB investigation and remediation.

Brown and Caldwell Consultants   1124
3480 Buskirk Ave.
Pleasant Hill, CA 94523-4342
415/937-9010

Brown and Caldwell Consultants is a nationwide multidisciplinary environmental consulting firm, providing complete project services for hazardous waste, water, wastewater, and solid waste. Services include RI/FS, regulatory compliance, permitting, design, engineering, remediation, air and water quality, laboratory services, project and construction management.

Burlington Northern Railroad   LDC
3700 Continental Plaza, 777 Main St.
Fort Worth, TX 76102
817/878-2168

Burlington Northern Railroad Company operates the largest railroad system in the United States. Its main lines runs through 25 states and 2 Canadian Provinces. It moves raw materials and finished products to over 4,000 communities nationwide. In addition, it serves ports in the Pacific Northwest and the Gulf of Mexico.

**CALGON CARBON
CORPORATION**   1105
P.O. Box 717
Pittsburgh, PA 15230
412/787-6700

Calgon Carbon Corporation supplies activated carbon products, systems and services, and airstrippers to remove soluble and volatile organic chemical compounds from contaminated groundwater, surface water or wastewater.

**CDM/Federal Programs
Corporation**   2016
13135 Lee Jackson Memorial Hwy.
Suite 200
Fairfax, VA 22033
703/968-0900

CDM Federal Programs Corporation provides environmental consulting services to the federal government, including: environmental assessments, site investigations, sampling and analysis, feasibility studies, risk assessments, environmental impact statements, groundwater modeling, GIS and CADD computer modeling, health and safety plans, community relations planning, operations/maintenance and underground storage tank remediation services.

CEA Instruments, Inc.   0306
16 Chestnut St.
Emerson, NJ 07630
201/967-5660

CEA Instruments, a leading supplier of hazardous gas detection instrumentation since 1972, will be exhibiting a new portable Landfill Gas Analyzer

for CO_2 and CH_4, portable and wall mounted CO_2 analyzers, and other units for monitoring toxic gases, combustible gases and oxygen levels in portable, single and multichannel fixed systems.

**CEIMIC
CORPORATION**   2215/2217/2219
100 Dean Knauss Dr.
Narragansett, RI 02882
401/782-8900

Ceimic, an employee-owned full-service environmental laboratory, provides analytical support nationwide to both industry and government. Ceimic specializes in rapid turnaround services and our ability to produce quality data is evidenced by participation in EPA's Contract Laboratory Program (CLP), DOD's HAZWRAP and NEESA programs, and multi-state certifications. The laboratory facility and instrumentation are state-of-the-art and they are complemented by a staff of over 60 environmental professionals.

CH2M HILL, INC.   0510/0512
P.O. Box 4400
Reston, VA 22090
703/471-1441

CH2M HILL provides waste management services - including design, construction, investigation, and planning - to industry and government. We are the largest environmental engineering firm in the United States, with 4,500 employees in 60 offices worldwide. Over a third of our business is managing hazardous, radioactive, and solid waste.

The CHEMTOX^R System   2117
P.O. Box 1848
Brentwood, TN 37024-1848
615/373-5040

The CHEMTOX^R System provides software (The CHEMTOX Database, MSDS ACCESS^R, and DocuWaste™ for Hazardous Waste) for retrieval and documentation of chemical data needed for safety and health environmental, emergency response, and transportation decisions. It will produce needed management reports, record inventories, employee exposures, create material safety data sheets, departmental reports, and track chemical processes and waste through disposal. Updated quarterly, users are provided the most current chemical and physical data. All records are variable length and accept any alphanumeric character combination. CHEMTOX and MSDS ACCESS are registered in the U.S. Trademark & Patent Office. DocuWaste is a trademark of Resource Consultants, Inc.

**COMPUCHEM
LABORATORIES, INC.**   2110/2112
3308 Chapel Hill/Nelson Hwy.
Research Triangle Park, NC 27709
919/549-8263

CompuChem Laboratories, Inc., a full service organic and inorganic laboratory, specializes in CERCLA, RCRA, DIOXIN, PRIORITY POLLUTANT and WASTE CHARACTERIZATION ANALYSES following the new TCLP regulations. In 1990 CompuChem has expanded its analytical services to include low level RADIOLOGICAL and MIXED WASTE ANALYSES. CompuChem's Environmental Site Profile (ESP),

a proprietary data management system, provides on-line access to test results which can be downloaded to your personal computer. For forensic quality data and expedited turn-around times, visit the staff of CompuChem Laboratories at booths 2110 and 2112.

Camp Dresser & McKee, Inc.   2014
One Cambridge Center
Cambridge, MA 02142
617/621-8181

Camp Dresser & McKee, Inc., (CDM) provides environmental engineering and consulting services to government and industry for the management of hazardous and solid wastes, wastewater, and water resources. Waste management services include remedial design, site assessments, environmental audits, RCRA compliance, treatment facility design and operation, and groundwater modeling and restoration.

Canadian Hazardous Materials Mgmt.   LDC
12 Salem Ave., Suite 200
Toronto, Ontario, Canada M6H 3C2
416/536-5974

**Canonie Environmental
Services Corp.**   1017
800 Canonie Dr.
Porter, IN 46304
219/926-8651

Comprehensive design and construction services for the remediation of sites contaminated by hazardous wastes. Principal services include, but are not limited to, soil remediation (thermal treatment and in situ), groundwater restoration, landfill and lagoon closure, removal actions, slurry walls and facility decommissioning. Complimentary services include engineering design and analytical services.

Carbonair Services, Inc.   2419
8530 35th St., South
Minneapolis, MN 55343
612/935-1844

Carbonair Services, Inc. provides technology and treatment plants for the decontamination of water, soil and air. Services provided include carbon adsorption, airstripping, inorganic and biological pretreatment, soil venting, and other decontamination technologies. Carbonair can provide whatever level of assistance needed to complete the project. Systems may be purchased or rented.

Caswell, Eichler and Hill, Inc.   LDC
One Harbour Pl., Suite 300
Portsmouth, NH 03801
603/431-4899

CEH is a full-service hydrogeological consulting firm with extensive experience and capability in contaminated industrial site characterization and remediation and water supply development. We are a firm of professionals specializing in geology, hydrology, geophysics and remediation engineering, who provide expert consulting services to private industry, governmental agencies and large contractors. Our services focus on solving the complex problems associated with the use, protection, management and cleanup of ground and surface water resources.

ChemCycle Corporation 1311
129 South St.
Boston, MA 02111
617/451-0922

ChemCycle Corporation is an engineering and design consulting firm that specializes in solving industrial hazardous waste and environmental problems. We offer services in process engineering, environmental controls, waste minimization, site assessments, compliance audits, permitting, site remediation and construction management.

Chemfix Environmental Services 0106
2424 Edenborn Ave., Suite 620
Metairie, LA 70001
504/831-3600

Chemfix Environmental Services offers the patented Chemfix^R process for treatment of sludges and high solids wastes. Complete mobile services are offered, as well as fixed plant facilities. CES services include site assessment, waste stream characterization and permitting support.

Chemical Waste 2207/2209
Management, Inc. 2211/2213
3001 Butterfield Rd.
Oak Brook, IL 60521
708/218-1500

Chemical Waste Management, Inc., is America's complete Hazardous Waste Manager. Our full range of services includes: Water Reduction Services, Resource Recovery, Site Remediation, Treatment, Transportation, Disposal, Incineration, Secure Landfill, Asbestos Abatement and Advanced Technologies for On-Site Soil Remediation and Wastewater Treatment and Recovery. Call Toll-free: 1-800-843-3604 for more information.

Clark Boardman Company, Ltd. LDC
375 Hudson St.
New York, NY 10014
212/929-7500

Clark Boardman Company is proud to offer its acclaimed Environmental Law Library. Designed to save hours of research time for busy practitioners and industry professionals, the library provides detailed analysis of the law - and expert guidance. We understand that ensuring compliance with today's environmental laws is your first priority.

Clayton Environmental
Consultants, Inc. 0101
1252 Quarry Ln., P.O. Box 9019
Pleasanton, CA 94566
415/426-2600

Since 1954, a recognized leader in the field of environmental consulting with broad-based capabilities in the areas of environmental engineering, industrial hygiene, asbestos management, indoor air quality, and laboratory analysis. Clayton has 11 offices and six laboratories throughout the U.S., Canada and the United Kingdom. The Michigan facility is an EPA CLP laboratory.

Clean Air Engineering Inc. 1616-1617
500 West Wood St.
Palatine, IL 60067
708/991-3300

Clean Air Engineering: Clean Air Engineering is

a full service environmental consulting firm, offering its industrial and municipal clients a wide range of services. These include air quality monitoring (EPA Methods 1-25, Multi-metals, VOST/MM5), trial burn assistance, mobile analytical laboratory services, environmental audits, flow modeling, environmental software design, temporary environmental professionals, design engineering, instrumentation rental and training seminars. CAE Instrument Rental: The leader in portable HazMat instrumentation, including PIDs, FIDs, O$_2$/LELs, Sample Pumps, Aerosol Monitors, Met Equipment, PUFs, etc. All available for short or long term rental featuring our "10 Day Week." Introducing a new product this year, the ADC LFG 10 for landfill gas analysis. Those of you who know who you are, stop by and say hi. Those of you who don't, come on by and get acquainted.

Clean Sites, Inc. 0910
1199 North Fairfax St., #400
Alexandria, VA 22314
703/739-1209

Clean Sites is a non-profit organization founded in 1984 to accelerate hazardous waste cleanup. We help parties at sites with: cost allocation; dispute resolution; technical assistance; quality assurance; and managing site studies and cleanups. We also work with government agencies to develop effective hazardous waste programs and conduct independent policy analyses.

Clem Corporation
(James Clem Corp.) 0216
444 North Michigan Ave., Suite 1619
Chicago, IL 60611
312/321-6255

The James Clem Corporation manufactures CLAYMAX®, an impermeable clay liner made with the world's highest quality sodium bentonite. It combines the durability of a woven geotextile fabric with the impermeability of a pound per square foot of sodium bentonite. The liner can be used as a primary or secondary liner in landfills and landfill caps, tank farm secondary spill containment and various applications in the mining industry.

Consolidated Rail Corporation 2513
Room 919 - One Liberty Place
Philadelphia, PA 19103-7399
215/851-7281

Conrail is one of the largest freight railroad systems in the Northeast-Midwest quarter of the United States, operating over a network of approximately 13,100 route miles. Conrail is a licensed and registered transporter of hazardous waste and sixty percent of all Superfund sites are located within its territory. Conrail works closely with connecting rail carriers, trucking, and equipment companies to offer reliable transportation services.

Corroon & Black Env'l
Insurance Svs. 2221
6510 Grand Teton Place, #102
Madison, WI 53719
608/833-2887

Cousins Environmental Services 0414
1800 Matzinger Rd.
Toledo, OH 43612
419/726-1500

A complete environmental contractor. Specializing in contaminated site remediation, we have extensive experience in bioremediation of soil contaminated with both hazardous and non-hazardous materials. In addition, we have designed and operated biological systems for pretreatment of industrial waste. Cousins' staff of over 100 are experienced in UST removal, site assessments, and specialized waste treatment and removal.

Curtis & Tompkins, Ltd. 0710
2323 Fifth St.
Berkeley, CA 94710
415/486-0900

Curtis & Tompkins Laboratories. Analytical services since 1878. Environmental, Industrial Hygiene and Air Analyses. For analytical services, look to Curtis & Tomkins - the complete laboratory offering customized reports, data management, and electronic data transfer to ensure complete, accurate and timely results for your projects.

DartAmerica 1212
61 Railroad St.
P.O. Box 89
Canfield, OH 44406
216/533-9841

A group of companies dedicated to the transportation of hazardous waste and general commodities in 48 states utilizing dumps, roll-offs, vans, flatbeds, pneumatic and liquid tank equipment, and LTL van service.

DataChem Laboratories 2214
960 West LeVoy Dr.
Salt Lake City, UT 84123
801/266-7700

Serving the analytical chemistry support sectors since 1971, DataChem Laboratories is now one of North America's largest and most experienced providers of laboratory services. The highly specialized tests performed by DataChem Laboratories are designed to assist clients in the evaluation of industrial hygiene and environmental issues.

Davy Environmental 0503
2430 Camino Ramon
San Ramon, CA 94583
415/866-1166

Davy Environmental draws upon Davy's worldwide technologies and project execution capabilities to provide comprehensive consulting, engineering, design and construction management services. These services include: remedial investigations/feasibility studies; treatment systems design; remediation of contaminated soils, water and air; waste encapsulation, isolation and incineration; and facility closure monitoring.

Dexsil Corporation 0102
1 Hamden Park Dr.
Hamden, CT 06517
203/288-3509

Dexsil Corporation provides environmental field

testing kits that detect environmental contaminants. Dexsil's field test kits are quick, easy to use, and afford the user an economical advantage over costly and time-consuming laboratory services. Dexsil's test kits detect total halogens (chlorine) in waste oils, total organic halogens in oil/water mixtures, and PCBs in transformer oil and soil.

Donohue & Associates, Inc. 1513
4738 North 40th St.
Sheboygan, WI 53083
414/458-8711 x2222

Donohue is an ARCS contractor with a nationwide staff of over 1,000 and a 1990 ENR ranking of 72. Our environmental scientists and engineers are specialists in waste management, disposal and cleanup. Donohue's hazardous waste services include RCRA investigations and compliance monitoring, RI/FS studies, and engineering of remedial cleanup actions.

Du Pont Company 2104/2106
1007 Market St., EA, NA-228
Wilmington, DE 19898
302/774-7248

Du Pont Safety and Environmental Resources will exhibit its Environmental Remediation Service which provides the treatment of contaminated soil and groundwater. In addition, the Du Pont Waste Management offering will be exhibited, providing state-of-the-art, in-compliance treatment and disposal services and environmental consulting to industry.

Dunn Geoscience Corporation 1415
12 Metro Park Rd.
Albany, NY 12205
518/458-1313

Full Service Environmental Consultants: Complete staff of hydrogeologists, geologists, environmental specialists and engineers, toxicologists, and regulatory experts provides a range of services including RI/FS and RCRA Corrective Actions, Remedial Design and Construction Management, Toxicology/Public Health Assessments, Hazardous Waste Planning and Management, Hydrogeologic Investigatory Services and Property Transfer Environmental Site Assessments.

Dynamac Corporation 0812
Dynamac #2 Bldg.
11140 Rockville Pike, Third Floor
Rockville, MD 20852
301/230-6117

Dynamac is a full service environmental firm. We are specialists in integrating expertise in environmental regulations and technology with the latest in information management techniques. Our services include preliminary site and risk assessments, RI/FS and remedial design activities, management of removal and remedial action efforts, program management, as well as community relations and public outreach activities.

Dynamic Graphics 1501
7201 Wisconsin Ave., Suite 640
Bethesda, MD 20814
301/656-3060

Dynamic Graphics provides advanced software

tools for the modeling, analysis and display of 2-dimensional and 3-dimensional phenomena in the earth, water and air. Applications include plume modeling and monitoring, particle dispersion, site characterization and remedial evaluations. Geoscience disciplinary fields include geology, hydrology, geochemistry and meteorology.

EA Engineering, Science & Technology, Inc. 0612
11019 McCormick Rd.
Hunt Valley, MD 21031
301/584-7000

EA is a nationwide, multidisciplinary professional services consulting firm providing a wide range of engineering, scientific, analytical and remediation capabilities to address existing and potential threats to the environment and to human health and safety. EA develops solutions for waste management, energy conservation and emissions control, and indoor air quality.

EBASCO Environmental 0504/0506/0603/0605
160 Chubb Ave.
Lyndhurst, NJ 07071
212/839-2744

Ebasco Environmental, a division of Ebasco Services Incorporated, provides a wide range of environmental and waste remediation services to industry and government clients. Services include remedial assessments/investigations, feasibility studies, remedial designs and corrective actions; a broad range of environmental and risk assessment and remediation consulting services; design and construction of quality management and control systems; and comprehensive licensing and permitting services.

ECOFLO, Inc. 2208
8520-M Corridor Rd.
Savage, MD 20763
301/498-4550

ECOFLO provides answers to client-specific waste management needs from our extensive offering of services, including: Waste Characterization; Collection, Transportation and Treatment/Disposal of Most Wastes; Lab Pack Services; Remediation and Cleanup Services; Waste Minimization Advice. ECOFLO serves the Mid-Atlantic region from offices in Maryland and North Carolina.

ECOVA Corporation 2310
3820 159th Ave., N.E.
Redmond, WA 98052
206/883-1900

ECOVA solves hazardous waste problems with technologies for on-site remediation: Bioremediation, In Situ Treatment, Soil Washing, Incineration. ECOVA has cleaned up more than 800,000 cubic yards of soil and millions of gallons of water using bioremediation. Integrated science, technology, and engineering expertise provides successful technology dvelopment and field remediation.

EIMCO Process Equipment Co. 1804/1806/1808/1810
P.O. Box 300
Salt Lake City, UT 84110
801/526-2000

EIMCO supplies a complete line of liquid-solids separation and dewatering equipment, including cost-effective bioremediation for treating hazardous wastes. Bioremediation offers lower energy costs than conventional systems, and is able to biodegrade organic slurries of 30-50 WT. % solids concentration.

EMPIRE SOILS INVESTIGATIONS, INC. 1015
140 Telegraph Rd., P.O. Box 250
Middleport, NY 14105
716/735-3502

Empire Soils Investigations, Inc., along with its laboratory division, Huntington Analytical Services, and its wholly owned subsidiary, Asteco, Inc., provides the following services: contract drilling and installation of groundwater monitoring wells, geotechnical testing including contaminated soils, geotechnical engineering, chemical analytical testing, asbestos inspection and testing, and materials engineering and testing.

ENCYCLE/TEXAS, INC. 0802/0804
5500 Up River Rd.
Corpus Christi, TX 78407
512/289-0035

Encycle/Texas is a Part B permitted waste recycling facility with the capabilities of processing as well as recovering heavy metals from solids, liquids, sludges, waste streams. Also, we process acids, bases, sulfides and hexavalent chromium.

ENRECO, Inc. 1611-1613
P.O. Box 9838
Amarillo, TX 79105
806/379-6424

ENRECO, Inc. uses a combination of basic chemistry and specialized equipment to stabilize the hazardous constituents within a waste matrix. ENRECO consists of four operating groups; Laboratories, Engineering, Technologies, and Operations. The four groups provide a wealth of experience which is used to design innovative, yet economical, remedial plans, navigate through the regulatory maze, and complete the construction in a timely and proficient manner.

ENSCO, Inc. 0410-0412, 0509-0511
333 Executive Ct.
Little Rock, AR 72205
813/289-5600

ENSCO provides integrated hazardous waste management services to private industry, public utilities, and government entities. These services include chemical analysis, collection, transportation, processing, and incineration of hazardous waste.

ENTROPY Environmentalists, Inc. 1125
P.O. Box 12291
Research Triangle Park, NC 27709
919/781-3550

ENTROPY Environmentalists, Inc., provides the

most comprehensive air emissions testing services nation-wide. In business since 1972, ENTROPY is the specialist for Trial Burns, VOCs, RCRA/TSCA, SARA, CEM, Particulates, POHCs, and Criteria Pollutant testing. Call Pete Watson for further information at (919) 781-3550.

ENVIROCARE OF UTAH, INC.　　　LDC
215 South State, Suite 1160
Salt Lake City, UT 84111
801/532-1330

ENVIROCARE is the country's first licensed disposal facility for naturally occurring radioactive material (NORM). ENVIROCARE has recently received a permit to dispose of hazardous (RCRA) radioactive waste. Our facility location and design are the result of long-term environmental planning. Transportation options for shipment to ENVIROCARE include rail and highway.

ENVIRONMENT TODAY　　　0113
1905 Powers Ferry Rd. #120
Marietta, GA 30067
404/988-9558

ENVIRONMENT TODAY - the Newsmagazine of Environmental and Pollution Control.

Environmental Audit, Inc.　　　0701
717 Constitution Dr.
Hankin Bldg., Ste. 101
Exton, PA 19341
215/458-1122

Environmental Audit, Inc. is an environmental information and education company. EAI provides parties to real estate transactions and their consultants with EPA and state environmental agency records organized on a database for use with real estate assessments and audits. EAI also provides education and training for use of these records.

ENVIRONMENTAL PROTECTION Magazine　　　1809
225 N. New Rd.
Waco, TX 76710
817/776-9000

ENVIRONMENTAL PROTECTION magazine reaches more than 90,000 buyers of environmental and pollution control products and services. OCCUPATIONAL HEALTH & SAFETY reaches more than 80,000 buyers of occupational health, safety and hygiene products and services.

ENVIRONMENTAL PROTECTION SYSTEMS　　　1812
3800 Concorde Pkwy., Suite 2100
Chantilly, VA 22021
703/631-2411　　　.

Environmental Protection Systems (EPS) is a rapidly growing engineering, industrial hygiene and analytical firm that has been providing environmental consulting services to government and industry for over 17 years. With eight offices nationwide, EPA has developed an outstanding reputation for providing quality engineering in hazardous waste assessments and site investigations; RI/FS development; spill response planning and mitigation; real estate audits; facility permitting and design; asbestos management and abatement supervision and analytical services.

ERCE　　　1813
3211 Jermantown Rd.
Fairfax, VA 22030
703/246-0440

ERCE is a professional and technical services company that offers environmental, infrastructure and energy consulting and engineering services to industrial and commercial companies, electric utilities and governmental agencies. Engineering, design and environmental science services are supported by four EPA-accredited analytical laboratories strategically located throughout the U.S.

ERM Group, The　　　2018-2020
855 Springdale Dr.
Exton, PA 19341
215/524-3500 ˙

The ERM Group, a full-service environmental consulting firm with more than 50 offices worldwide, provides the following services: site remediation; hydrogeology; hazardous/solid waste management; management consulting; industrial/municipal water and wastewater treatment; underground tank management; environmental science; air pollution control; computer sciences; construction management; and health, safety and toxicology.

Eagle-Picher/Environmental Services　　　1119
36 B.J. Tunnell Blvd. East
Miami, OK 74354
918/540-1507

Precleaned and certified, glass and plastic sample containers to EPA specifications. Documentation of quality control and chain of custody with each container. Complete line of clear or amber glass and high density polyethylene in a variety of styles and sizes. Also offering various ampule preservatives. Free sample reference guide. For more information, call our toll-free number: 800-331-7425.

Earth Resources Consultants, Inc.　　　2417
1227 Marshall Farms Rd.
Ocoee, FL 34761
407/877-0877

Earth Resourses Consultants (ERC) is a full-service hazardous materials management firm specializing in the containment, treatment, and removal of all types of hazardous materials. ERC has a highly trained professional and technical staff experienced in the design and implementation of innovative solutions to today's waste problems. ERC's capabilities include but are not limited to soil, groundwater, facilities, containerized wastes and pressurized gas cylinders.

Earth Technology Corporation, The　　　1605/1607
100 W. Broadway, Ste. 5000
Long Beach, CA 90802
213/495-4449

As one of the nation's leading environmental, earth sciences and geotechnical consulting firms, The Earth Technology Corporation's primary business activities include: Waste Management and Environmental Services, Critical Facilities Siting, Related Advanced Technology and Testing Services, and Asbestos and Air Quality Management. Founded in 1970, our staff of 500 expert hydrogeologists, geologists, engineers, environ-

mental scientists, chemists and managers in 15 offices nationwide work to deliver superior technical solutions for government and private industry. Visit booths 1605 and 1607 for more specific capability information.

EcoTek LSI　　　2114
3342 International Park Dr.
Atlanta, GA 30316
404/244-0827

Full service environmental laboratory with multiple state certifications. EPA CLP participant. 8,000 ft^2 chemical laboratory, 16,000 ft^2 radiological laboratory. EcoTek LSI provides analyses of full organics and inorganics, and some R & D. EcoTek LSI's radiological laboratory provides analyses on hazardous wastes, mixed wastes, drinking water, solid wastes, and other toxic materials.

Ecology and Environment, Inc.　　　2103/2105
　　　2107/2109
Buffalo Corporate Center
368 Pleasantview Dr.
Lancaster, NY 14086
716/684-8060

Ecology and Environment, Inc., provides the complete range of scientific and engineering consulting services required by generators, storers, transporters, and disposers of hazardous, toxic, infectious, radioactive and solid wastes. The firm has offices from coast-to-coast and is represented around the globe. A broad spectrum of environmental assessment and pollution control services are also provided including emergency spill response, asbestos removal management, hazards and risks analysis, and analytical laboratory and testing services.

Ejector Systems, Inc.　　　0902/0904/0906/0908
910 National Ave.
Addision, IL 60101
708/543-2214

Ejector Systems, Inc., manufactures pumping and treatment systems for contaminated groundwater and leachate.

Engineering News-Record (ENR)　　　1711
1221 Avenue of the Americas
New York, NY 10020
212/512-3132

Engineering News-Record (ENR), McGraw-Hill's building and construction newsweekly, reports on every segment of the marketplace: buildings, transportation projects, water and power, the environment, and more. Over 416,000 decision-makers rely on ENR for the business and technical news they need to compete in the world's largest industry.

Engineering-Science　　　2204/2206
75 North Fair Oaks Ave.
Pasadena, CA 91103
818/440-6101

Engineering-Science (ES) is a full service, national and international environmental engineering firm providing complete services in hazardous waste management. With offices in 27 domestic locations, ES is active in supporting industrial and military clients in all phases of site/remedial investigations, feasibility studies, remedial action

plan preparation, site cleanup/closure and post-closure activities.

**Enviro-Tech Management
Consulting** 1713
7120 Wyoming N.E.
Albuquerque, NM 87109   505/828-9885

Enviro-Tech is a full service management consulting firm that specializes in acquisitions, mergers, source funding, certified business valuation and search & recruitment primarily for the environmental industry. Give us your requirements for a corporate candidate and let us put our highly qualified personnel to work. (Offices nationwide) For information call 1-800-873-4280.

The EnviroMed Companies, Inc. 0602
414 West California Ave.
Ruston, LA 71270
318/255-0060

The EnviroMed Companies, Inc. (EMC), is a multidisciplinary environmental engineering, consulting and testing firm founded in 1974. EMC Personnel include engineers, geologists, chemists, biologists, toxicologists and industrial hygienists who provide turnkey solutions to groundwater, hazardous waste, effluent discharge and industrial hygiene problems. EMS routinely designs and installs hazardous waste/groundwater remediation systems. EMC owns three full-service laboratories operating GC/MS, GC, ICP, AA, HPLC and other state-of-the-art instrumentation. Call NATIONWIDE 1-800-256-4362.

Environmental Careers 0311
760 Whalers Way, Suite 100-A
Fort Collins, CO 80525
303/229-0029

ENVIRONMENTAL CAREERS magazine is dedicated to the human resources needs of the environmental industry. Each issue features advertising for environmental employment opportunities and training programs, a professional education calendar, and timely career and training articles written by industry experts. Also on display are ENVIRONMENTAL LAB and ASBESTOS ISSUES magazines.

**Environmental Chemical
Associates, Inc.** 0226
5118 Highway 33 & 34
Farmingdale, NJ 07727
201/938-3010

Waste Management Services: Waste Characterization, Laboratory Analysis, Facility Approval, Transportation, Documentation, Disposal. Technologies available include Recycling, Fuels Blending, Incineration, Treatment, Stabilization, Secure Landfill. Services also include: Lab Packing, Site Remediation and Consulting.

**Environmental
Company, Inc., The** 1606
P.O. Box 5127
1230 Cedars Court, Suite 100
Charlottesville, VA 22905
804/295-4446

The Environmental Company (TEC) is a multi-disciplinary environmental consulting company providing services to DOD, civilian agencies, and private clients. TEC offers the full range of environmental disciplines: engineering, environmental, physical science, asbestos, health and safety, as well as construction management in support of environmental projects.

**Environmental Compliance
Services, Inc.** 0302
One East Uwchlan Ave., Suite 300
Exton, PA 19341
215/269-6731

ECS is an organization dedicated to assisting environmental companies with their insurance, safety, and compliance needs through the unique combination of in-house expertise in environmental regulation, risk management, and insurance underwriting. ECS is the only company in the country to provide an exclusive program of insurance for companies facing an environmental exposure.

Environmental Directory, The 2415
60 E. Chestnut, Suite 415
Chicago, IL 60611
708/671-5853

The Environmental Directory is a nationwide company which publishes Regional Environmental Directories. The Environmental Directory is a Single-source Directory of hundreds of companies offering a variety of Environmental Products and Services ranging from Air Consultants to Waste Minimization. Directories are currently available for the Midwest, Eastern Seaboard, Southern California, Northern California, Southwest, Pittsburgh, and the Pacific Northwest, with more to come.

**Environmental
Instruments, Inc.** 0313/0315
2170 Commerce Ave., Unit S
Concord, CA 94520
415/686-4474

Environmental Instruments Co. (EI) sells and rents equipment specifically designed to meet the needs of the environmental industry - specializing in innovative equipment for water, soil and air treatment, sampling and monitoring. We will be demonstrating our vapor extraction blower and vapor treatment system, a catalytic incinerator, new photo-ionization detector and new flame-ionization detector. For more information, call our toll-free number: (800) 648-9355.

**Environmental Science &
Engineering, Inc.** 2118/2120
P.O. Box 1703
Gainesville, FL 32602-1703
904/332-3318

ESE offers comprehensive in-house services in Toxic and Hazardous Materials Control; Environmental Engineering; Analytical Services; Industrial Hygiene/Safety; Geosciences; Surface and Groundwater Monitoring; Air Resources; Asbestos Management; Biosciences; Risk Assessment; Underground Storage Tank Management; Environmental Audits; Planning and Permitting; and Public/Community Relations.

Environmental Technology, Inc. 0608
3705 Saunders Ave.
Richmond, VA 23227
804/358-5400

HazWaste Industries Incorporated and its operating subsidies (Environmental Technology, Environmental Risk Sciences, Bionomics and HazLabs) provide a full range of environmental services: Site Investigations, Inspections and Audits; Risk Assessments; Feasibility and Treatability Studies; UST Closures; Facility Decontamination and On-Site Treatment; Site Remediation, Emergency Response and Removal; and Long-Term Monitoring. HazWaste provides complete, quality and cost-effective solutions to its clients' environmental problems.

Envirosafe Services, Inc. 2122/2123
P.O. Box 167571
Oregon, OH 43616-7571
419/255-5100

Envirosafe Services, Inc. provides cost effective, proven waste management services to generators of hazardous and industrial waste materials. Federal Part B awarded waste management facilities in Idaho and Ohio conveniently service the entire nation via truck or rail transportation. Envirosafe specializes in secure disposal, chemical stabilization and PCB management services. Envirosafe offers economical, environmentally sound waste management for a wide variety of hazardous and industrial waste materials.

Envirotrol, Inc. 0711
P.O. Box 61, 432 Green St.
Oregon, OH 43616-7571

Envirotrol is a nationwide full service activated carbon company. We provide carbon reactivation, and adsorption systems for wastewater, groundwater, air purification, solvent recovery, and process applications. We also offer virgin carbon, bulk transportation. We serve hazardous, non-hazardous, liquid, and vapor phase applications.

Exxon Chemical Company 1303
P.O. Box 4321
Houston, TX 77210-4321
713/460-6826

Exxon Chemical Company offers a complete line of products and application expertise specifically for waste-water treatment. Of particular interest are Diklor® chlorine dioxide products for organic contaminate destruction of phenols, mercaptans and sulfides.

Fenn-Vac, Inc. 2022
P.O. Box 62679
North Charleston, SC 29419-2679
803/552-8306

Fenn-Vac, Inc., offers Tank Cleaning and Decontamination; Tank Removal and Disposal; Lagoon Closure; Filter Press Dewatering Systems; Transfer, Transport and Disposal of Bulk Liquids/Sludge; Excavation and Removal of Waste Solids; Surface and Subsurface Product Recovery; Treatment of Contaminated Groundwater; Permitted

Hazardous Waste Transporter; Emergency Response Actions; Remediation of Hazardous Waste Sites; and Total Capability in Hazardous and Non-Hazardous Environments.

First Environmental Laboratories   0111
#2 Stewart Ct.
Denville, NJ 07834
201/328-3900

First Environmental Laboratories - complete analytical services for soil, air, water - NPDES, RCRA, drinking water, Superfund TLC - 19,000 square foot facility - state of the art instrumentation used by professional, experienced staff.

Fluor Daniel, Inc.   1014/1016
3333 Michelson Dr.
Irvine, CA 92730
714/975-6000

Fluor Daniel offers a broad range of environmental services including new facility support (permitting air emissions, wastewater treatment), regulatory compliance (audits, UST), and remediation services (RI/FS, Remedial Design, Remedial Action), which is backed by full engineering, construction, project management and maintenance experience.

Forestry Suppliers, Inc.   1315
P.O. Box 8397
Jackson, MS 39284-8397
601/354-3565

Environmental equipment catalog company displaying soil recovery augers and probes, groundwater/surface water sampling and testing equipment, safety wear for workers exposed to hazardous wastes, surveying/engineering instruments and supplies - and more! Sign up for our free 420-page catalog.

**Foster Wheeler
Enviresponse, Inc.**   2203-2205
8 Peach Tree Hill Rd.
Livingston, NJ 07039
201/535-2378

Foster Wheeler Enviresponse, Inc. is a full services environmental engineering, consulting, and remediation company. Principal services include regulatory compliance know-how, environmental technical assistance, remedial design capabilities and remedial action. The company has an outstanding and well-trained professional staff experienced in site investigations, environmental audits, permitting, risk assessments, remedial investigations, feasibility studies, technology evaluations, sampling, closure plans, wastewater treatment, air pollution control, and remedial designs as well as site cleanups.

**Four Seasons Industrial
Services, Inc.**   2509/2511
4920 Old Pineville Rd.
Charlotte, NC 28217
704/527-1293

Full service environmental construction company with capabilities in industrial services, tank services, on-site treatment systems, emergency re-

sponse, remedial services and transport tanker cleaning. To offer these capabilities, the company has developed the following technologies: groundwater treatment utilizing air strippers; contaminated soil treatment using vacuum extraction; bio-remediation; stabilization; design and construction of secondary tank containment systems and thermal volatilization and destruction of VOC-contaminated non-hazardous soils.

The Foxboro Company   2404/2406
Foxboro, MA 02035
508/543-8750

Instrumentation for providing quantitative and qualitative information on hazardous waste and spill site contaminants. The Foxboro CENTURY Organic Vapor Analyzer (OVA) can be used to detect areas of high vapor concentration, identify and determine concentration levels of various organic compounds and provide rapid, reliable screening/analysis of volatile hydrocarbons in groundwater samples. The newest Foxboro MIRAN portable Gas Analyzer, the MIRAN 203, is an economical choice for applications where only one gas is being detected and measured. This new lightweight analyzer permits the user to measure any number of gases by simply inserting a different calibration set.

FRANKLIN MILLER INC.   LDC
60 Okner Pkwy.
Livingston, NJ 07039
201/535-9200

**GREENHORNE &
O'MARA, INC.**   2500
9001 Edmonston Rd.
Greenbelt, MD 20770
301/982-2800 x442

Greenhorne & O'Mara, Inc. provides hazardous waste management services to industry and government. Our experienced staff (most OSHA/ AHERA-certified) know the requirements of RCRA, CERCLA, SARA, TOSCA, NEPA, CWA, and CAA. Services include site characterization, property transfer assessments, asbestos management, groundwater assessments, facility audits, RI/FSs, remedial design, waste minimization, and surveying.

Galaher Settlements Company   1209
260 Franklin St., Ste. 1510
Boston, MA 02110
617/439-6260

Pioneering the use of structured settlements in environmental cases, Galaher Settlements reinforces its position as a leading national firm specializing in the development of creative periodic payment programs individually tailored to the present and future needs of all parties. Contact our specialists today - there is no charge for our service.

Galson Remediation   0115-0117
6627 Joy Rd.
East Syracuse, NY 13057
315/463-5160

Gaslon Remediation Corporation (GRC) specializes in the development and application of chemical destruction of PCB's, dioxins, PCP, pesticides,

and other hazardous wastes in soils and sludges. Processes for cleaning soils and sludges are now at full scale commercial operation levels. Gaslon Laboratories offers complete and professional analytical services for the full range of environmental samples, including hazardous wastes, priority pollutants, toxic metals and organics in soil, groundwater and wastewater, air toxics, leachates, drinking water, and emission samples. Gaslon Laboratories has extensive analytical experience under environmental regulations such as RCRA, CERCLA, the Clean Air Act, and the Clean Water Act. We perform all pertinent analyses according to the EPA Contract Lab Program (CLP) protocols as a standard service.

Gartner Lee, Inc.   1302
105 Main St.
Niagara Falls, NY 14303
716/285-5448

Environmental consulting - offering services in environmental and engineering geophysics, packer testing and contaminant hydrogeology. Geophysical services include high resolution EM, magnetics, radar, borehole geophysics, seismic refraction and reflection. Hydrogeology services include site investigations, geochemistry, modeling, monitoring and water supply. Perform RI/FS, ECRA studies, Phase I and II surveys.

General Physics Corporation   0209
6700 Alexander Bell Dr.
Columbia, MD 21046
301/290-2300

General Physics Environmental Services offers laboratory and pilot treatability testing for many industrial waste and remediation technologies. GP combines the resources of environmental engineering with our in-house EPA CLP testing. GP provides a full range of industrial hygiene services. GP provides innovative, value-driven services that accurately address the needs of our customers.

Geo-Con, Inc.   0204/0206
P.O. Box 17380
Pittsburgh, PA 15235
412/856-7700

Geo-Con, Inc. is a national remedial construction company specializing in on-site hazardous waste treatment. Capabilities of the company include: Turn-key project execution; In-situ solidification and stabilization; Containment systems such as vertical barriers, capping and liners; RCRA landfill construction and retrofit; Deep soil and Shallow soil mixing; Groundwater collection and treatment; VOC removal from soil; Bioremediation; Plant decontamination and Decommissioning and construction Management.

GeoGroup, Inc.   1106-1108
9029 Shady Grove Ct.
Gaithersburg, MD 20877
301/258-7491

Geo Group, Inc. provides a range of quality soil, rock and environmental monitoring services. Part of our range includes Water Level Indicators, Bailer Samples and Temperature Meters. We also provide innovative Data Logging Systems and Portable Readout Units using infra red techniques to monitor gas emissions from landfill sites.

Geophysical Survey Systems, Inc.　0601
13 Klein Dr.
P.O. Box 97
North Salem, NH 03073-0097
603/893-1109

Radar: Ground penetrating, subsurface interface radar (SIR) systems used to non-destructively scan the subsurface for buried tanks, pipes, and drums; locate and delineate landfills and trenches; and identify water table, bedrock and other geological features.

Geoprobe Systems　2420
607 Barney St.
Salina, KS 67401
913/825-1842

Geoprobe Systems manufactures innovative equipment for soil gas, soil core, and shallow groundwater sampling using small diameter driven probes. This equipment includes the hydraulically powered Geoprobe 8-M probe machine which has found extensive use in site investigation work. Geoprobe manufactures a complete line of probing tools.

Geosafe Corporation　2102
303 Parkplace, Suite 126
Kirkland, WA 98033
206/822-4000

Geosafe Corporation offers in situ vitrification (ISV) services for remediation of contaminated soil and sludge sites. The ISV process destroys hazardous organics through pyrolysis and simultaneously immobilizes hazardous inorganics in a delistable, vitrified residual. This cost-effective process offers significant advantages over conventional soil treatment processes.

Geoscience Consultants, Ltd.　1914
500 Copper N.W., Suite 200
Albuquerque, NM 87102
505/842-0001

Geoscience Consultants, Ltd. (GCL) is a minority-owned small business (8(a) Certified) and is a full-service environmental design and engineering consulting firm. GCL provides the following services: UST Management; Air Quality Assessment or Permitting; Remedial Engineering, Investigations, and Actions; Waste Minimization and Compliance Reviews; Groundwater Remediation; Regulatory Negotiation; Risk Assessments; and Health and Safety Training.

**GILARDE ENVIRONMENTAL
OF FLORIDA, INC.**　LDC
1201 U.S. Hwy. One, Suite 435
North Palm Beach, FL 33408
407/624-9770

GILARDE ENVIRONMENTAL OF FLORIDA, INC. offers full service environmental management to private industry, utilities and governmental entities. GILARDE specializes in: project management, remedial action, hazardous waste transportation/disposal, biohazardous/medical waste removal/destruction, emergency response management and landfill construction/closure, utilizing its own fleet of heavy equipment and trained operators.

Golder Associates, Inc.　LDC
3730 Chamblee Tucker Rd.
Atlanta, GA 30340
404/496-1893

Golder Associates is an international group of employee-owned consulting engineering companies providing regular support to clients in the fields of hazardous, solid, nuclear and mixed waste management, transportation, power generation, water resources management, mining, and commercial development. The group of companies currently maintains 37 offices in the United States, Canada, the United Kingdom, Sweden, Australia, Germany and Italy. The worldwide staff consists of over 950 personnel including more than 600 professional engineers and geologists.

Griffin Remediation Services, Inc.　0610
500 Winding Brook Dr.
Glastonbury, CT 06033
203/657-4277

Griffin Remediation Services, Inc. (GRS) is a full-service remediation company with specialty expertise in the design and implementation of comprehensive solutions to groundwater-oriented environmental problems. An affiliate of Griffin Dewatering Corp., GRS utilizes over 50 years of groundwater control experience. From their 21 locations throughout North America, Griffin employs innovative technologies focused on the containment, recovery, treatment and/or disposal of hazardous and nonhazardous groundwater pollutants. Services include: remedial dewatering; trenching; slurry, bio-polymer, interceptor, leachate collection; landfill gas vents; deepwells; wellpoints; monitoring wells; soil vents; air stripping; and pump sale/rentals.

Groundwater Technology Inc.　1001
220 Norwood Park South
Norwood, MA 02062
617/769-7600

A full service environmental company specializing in petroleum hydrocarbon site investigation and remediation including in situ and aboveground bioremediation, vapor extraction, chemical neutralization, soil gas surveys, air quality monitoring, well drilling, real estate audits, risk assessments, GTEL Analytical Laboratories, and ORS Environmental Equipment including Thermal and Catalytic Scavenger Vapor Abatement Systems, product recovery pumps, bioreactors, and airstripping towers.

**GRUNDFOS PUMPS
CORPORATION**　0211
2555 Clovis Ave.
Clovis, CA 93612
209/292-8000

GRUNDFOS PUMPS CORPORATION is the manufacturer of the REDI-FLO ENVIRONMENTAL PUMP. The REDI-FLO is constructed of stainless steel and Teflon and is designed to pump contaminated groundwater from a 4-inch well or larger. REDI-FLO pumps can provide flow rates up to 32 gallons per minute and to heads of 680 feet. For more information, contact GRUNDFOS at (209) 292-8000.

Gundle Lining Systems, Inc.　0505
19103 Gundle Rd.
Houston, TX 77073
713/443-8564

Gundle Lining Systems, Inc. Houston, Texas, is recognized as the world leader in the manufacture and installation of high density polyethylene lining systems. Gundle manufactures HDPE (Gundline HD) synthetic liner in over 34 ft. seamless widths from 30 to 140 mils thick. The company offers a full product range that can be adapted to any operational need. In addition, Gundle illustrates its commitment to excellence with innovations such as the patented extrusion welding machine and the new automatic wedge welder. Product innovations from Gundle include: Gundnet, drainage net; Gundline HDT, a textured HDPE liner; and Hyperlastic, a very low density polyethylene liner.

H2M Group　1908
575 Broad Hollow Rd.
Melville, NY 11747
516/756-8000

H2M is a multi-disciplined consulting firm. With over 57 years of experience, H2M specializes in civil, environmental and structural engineering, architecture, planning and environmental science. The firm's full scope of professional services encompasses wastewater pollution control, civil/site engineering, community planning, water supply/resources management, solid and hazardous waste management, environmental impact analysis, as well as environmental laboratory services.

**HARDING LAWSON
ASSOCIATES**　0413/0415
1155 Connecticut Ave., N.W., #500
Washington, DC 20036
202/429-6675

HARDING LAWSON ASSOCIATES (HLA) provides engineering, environmental, and construction services for hazardous and solid waste management. Ranked 59th in top 500 design firms and 12th in hazardous waste by Engineering News Record; ranked one of nation's best small companies by Business Week and Forbes; and awarded two national and one State engineering excellence awards for innovative site remediation.

**HAZCO
Services, Inc.**　2303-2307 & 2304-2308
2006 Springboro West Rd.
Dayton, OH 45439
513/293-2700

Personal protective equipment, instrumentation rental and repair services, sampling equipment, decontamination trailers and software solutions for the hazardous waste cleanup market.

**HAZMAT Training, Information
and Services, Inc.**　1006
(Hazmat TISI)
6480 Dobbin Rd.
Columbia, MD 21045
301/964-0940

HAZMAT Training, Information and Services, Inc. (Hazmat TISI), is a training company whose offerings include the development and delivery of

courses that meet the hazardous waste operations and emergency response training requirments of 29 CFR 1910.120 and/or NFPA Standard 472, etc. In addition to open-enrollment courses offered at their Columbia, Maryland, location, they deliver tailored, on-site programs. For more information, call our toll-free number: (800) 777-TISI (8474).

HMCRI 2011
9300 Columbia Blvd.
Silver Spring, MD 20910-1702
301-587-9390

Hazardous Materials Control Research Institute (HMCRI) is a public, nonprofit membership organization. Its mission is to promote the establishment and maintenance of a reasonable balance between expanding industrial productivity and an acceptable environment. This major goal is being met by providing national and regional conferences, numerous publications and texts, seminars, advanced degree possibilities, exhibitions on a large scale showing equipment and products, and many other informational dissemination programs. HMCRI's membership program, unique to the industry, now exceeds 5,000 active participants. A definite and distinctive forum is now available for these individuals and future members to exchange information and experiences dealing with hazardous waste and the protection of the environment. JOIN HMCRI TODAY! Become active in the ONLY hazardous waste membership organization.

HMM Associates, Inc. 2201
196 Baker Ave.
Concord, MA 01742
508/371-4000

HMM Associates is an environmental engineering, consulting and planning firm with headquarters in Concord, Massachusetts. HMM provides a full range of hazardous waste/materials services including: Superfund RI/FSs, remedial design and construction oversight; personnel protection and safety training; and environmental compliance audits and management. HMM is a Summit Environmental Group company.

HNU Systems, Inc. 2421/2422/2423
160 Charlemont St.
Newton Highlands, MA 02161
617/964-6690

Model HW101 Hazardous Waste Analyzer; IS101 - Intrinsically Safe Analyzer; PI101 - Photoionization Analyzer (and portables); 301DP - Dedicated Programmable Gas Chromatograph; 311 - Portable Gas Chromatograph; 321 - Compact temperature programmed gc; 331 - Compact dedicated capillary gc; SEFA-P - Portable x-ray fluorescence analyzer; 75 Meter - Portable ph/mv temperature meter; 76 Meter - Microprocessor ph/ion meter; ISE - Ion Selective Electrodes.

HWAC 0514
1015 Fifteenth St., N.W., #802
Washington, D.C. 20005
202/347-7474

HWAC - An Association of Engineering and Science Firms Practicing in Hazardous Waste Management (formerly the Hazardous Waste Action Coalition) is a national trade association representing engineering and science firms involved in

hazardous waste management. HWAC represents more than 115 member firms who employ 60,000 people across the nation who are responsible for approximately 90 percent of the available consulting capacity of cleanup of hazardous waste sites in the United States. Since its formation in 1985, HWAC has worked to improve business and professional conditions for engineering and science firms.

HYDRO-SEARCH, INC. 0615
175 N. Corporate Dr., Suite 100
Brookfield, WI 53045
414/792-1282

Services in Hydrogeology, Engineering, and Project Management for: Remedial Investigations/Feasibility Studies (RI/FS); Preparation of Work Plans; Managing On-Site Activities; Designing and Implementing Remedial Action Programs; Technical Guidance for Responsible Parties; Oversee EPA Contractors; Review Groundwater Monitoring Plans and Reports; Underground Storage Tank Management; Landfill Siting and Design; Water Resource Management; Mine Tailings and Water Management.

Hanson Engineers Incorporated 1405
1525 S. 6th St.
Springfield, IL 62703
217/788-2450

Hanson Engineers, Inc., provides a full range of environmental-waste management services nationally to industry, government and consultants. Services include: site assessment; RI/FS; design/oversight of remedial action; hydrogeologic/geophysical services; UST management; property audits; RCRA permitting; site characterization for hazardous, mixed and LL nuclear waste; soil gas surveys; geotechnical laboratory for contaminated soils.

Hart Crowser, Inc. LDC
1910 Fairview Ave., E.
Seattle, WA 98102
206/324-9530

Hayward Baker Inc. 1021
1875 Mayfield Rd.
Odenton, MD 21113
301/566-6110

Hayward Baker Environmental, a national specialty contractor, provides a range of solutions including: Containment Barriers; Contaminated Groundwater Collection; Sludge Solidification and Stabilization; Landfill Closures and Stabilization; and other On Site Remediation Services. With over 40 years of experience, we have the resources to meet time, quality control and safety constraints.

HazMat Environmental Group, Inc. 1401
60 Commerce Dr.
Buffalo, NY 14218
716/827-7200

HazMat Environmental Group, Inc., is a firm specializing in hazardous waste/hazardous materials management. Our services are offered throughout the United States. The services we offer include transportation, technical consulting, and personnel training. HazMat operates offices in Buffalo, NY and Cincinnati, OH.

HazMat World Magazine 0411
800 Roosevelt Rd., Bldg. C, #206
Glenellyn, IL 60137
708/858-1888

A publication edited for individuals responsible for specifying and purchasing products, systems, equipment and services used for hazardous materials and waste management from generation through packaging, handling, transportation, processing or ultimate disposal. Information and forms for free subscriptions will be available for qualified individuals.

Hazen Research, Inc. 1004
4601 Indiana St.
Golden, CO 80403
303/279-4501

Hazen Research, Inc. provides a full range of waste treatment services including characterization, reduction, remediation and minimization, treatability studies, leaching and extraction processes, soil washing, and thermal processes. Specializing in treatment of metal-bearing wastes, Hazen's other services include custom engineering, pilot plant services, process development, analytical services, and market/feasibility studies.

Heritage Environmental Services Inc. 2401/2402
2728 Colonial Ave., #100
Roanoke, VA 24015
703/344-1750

Heritage is a full-service environmental company with national service. Some of the services provided include complete laboratory services, treatment and disposal, transportation, remediation and engineering, and lab pack.

Hewlett-Packard 1011-1013
Route 41, Box 1100
Avondale, PA 19311-1100

Hewlett-Packard will display systems for EPA environmental analysis and methods. They include: a GC/MS system for hazardous waste analysis, an HPLC-based Pesticide Analysis System, and a Supercritical Fluid Extractor for sample preparation. All feature automation and instrument control.

Hill International, Inc. 2502/2504
One Levitt Parkway
Willingboro, NJ 08046
609/871-5800

Hill International, the world's leader in construction claims and construction consulting, will be introducing the ENVIRONMENTAL CLAIMS CENTER. The Center is a professional services organization combining the skills of attorneys, engineers, and environmental specialists along with contracts and construction experts. The Center assists clients with Superfund enforcement actions and cost recovery.

Howard Smith Screen Company 1709
P.O. Box 666
Houston, TX 77001
713/869-5771

Howard Smith Screen Company is a manufacturer of well screens and accessories for the environmental, water well and oil industries.

Hoyt Corporation   0303
251 Forge Rd.
Westport, MA 02790
508/636-8811

Hoyt Corporation of Westport, MA will be displaying their full line of Solvent Vapor Recovery/ Air Pollution Control Equipment, Distillation Equipment, Odor Control Equipment, and Liquid Purification Equipment.

Hydro Group, Inc.   1118
97 Chimney Rock Rd.
Bridgewater, NJ 08807
201/563-1400

Hydro Group, Inc. is a unique full-service company that can combine engineering and construction capabilities for all phases of groundwater remediation from groundwater exploration through well installation and treatment systems to startup. Treatment equipment manufactured by Hydro Group, Inc. includes air stripping towers, clarifiers, pressure filters, aerators and GAC units.

Hygienetics, Inc.   0807
150 Causeway St.
Boston, MA 02114
617/723-4664

Hygienetics, Inc. is an industrial hygiene and environmental consulting firm specializing in asbestos management, hazardous materials management, and indoor air quality assessment. Our worldwide offices - in Boston (Headquarters); Hartford, New York City, Washington, D.C., Chicago, Los Angeles, San Francisco, Honolulu and Frankfurt, West Germany - assure quick and cost-effective service.

I-Chem Research   1703-1705
23787-F Eichler St.
Hayward, CA 94545
415/782-3905

A complete line of glass and polyethylene sample bottles, jars and vials supplied with Teflon-lined closures attached and available chemically precleaned and laboratory-certified to meet EPA specifications. Also available are: custom cleaned sample containers, protective shipping materials, convenient sampling kits, and preservatives in ampules.

ICF Kaiser Engineers   1214
1800 Harrison St.
Oakland, CA 94612
415/268-6000

ICF Kaiser Engineers provides engineering and construction services to clients involved with environmental, transportation, industrial, advanced technology, energy, and other infrastructure projects around the world. ICF Kaiser Engineers' 1600 professionals work on hundreds of projects including planning and managing the cleanup of Boston Harbor. We are one of the nation's top five companies in hazardous waste engineering.

ICM Laboratories   0416
1152 Route 10
Randolph, NJ 07869
201/584-0330

Full service laboratory specializing in environmental analysis. Laboratory services include

analysis for compliance with ECRA, RCRA, NJDES, hazardous waste classification, CERCLA and TCLP. Monitoring well sampling also available.

In-Situ, Inc.   1002
P.O. Box I, 210 South 3rd St.
Laramie, WY 82070
307/742-8213

In-Situ's HERMIT Data Logging Systems provide reliable field instrumentation for water resource evaluations, including aquifer testing and short- and long-term monitoring in many types of water bodies. The instrumentation is widely respected for its ability to operate unattended in extreme weather conditions over extended periods of time without compromising accuracy. In-Situ also offers a number of Hydrologic Software programs for both PC and mainframe computers. In-Situ's Leak Detection Systems use a patented sensing technology for monitoring underground storage tank installations that provides intrinsically safe and reliable leak detection. Three different models are available.

Industrial & Environmental Analysts, Inc.   0310
3000 Weston Pkwy.
Cary, NC 27513
919/677-0090

IEA, Inc. is an environmental testing and sampling corporation. IEA offers unparalleled performance under the EPA Contract Laboratory Program (CLP). Analytical services include TCL/ TAL, TPH by GC and IR, TCLP, asbestos by TEM, metals by AA, ICP and ICP/MS, SEM and full wet chemistry. In addition, IEA offers sampling services in groundwater, air, wastewater and soils, adhering to strict EPA protocols.

Inquip Associates   0713
1300 Old Chainbridge Rd., #3
McLean, VA 22101
703/442-0142

Inquip Associates, Inc. is a geotechnical contractor whose history dates back to the 1950's. Inquip's main activity has related to the installation of soil-bentonite cutoff barriers and liners. Recently, it has expanded to include other geotechnical techniques, especially environmental projects, using the latest technical advances in the field.

Institute of Gas Technology   1706/1708
3424 South State St.
Chicago, IL 60616
312/567-3794

IGT is a not-for-profit educational, energy and environmental research and development organization established in Chicago, Illinois in 1941. IGT's environmental capabilities include waste incineration and detoxification, and catalytic and biological decontamination of hazardous and industrial waste, soils and sludges, and groundwater. IGT programs range from fundamental investigations through bench-scale and pilot plant process development to field testing.

Integrated Chemistries, Incorporated   1609
1970 Oakcrest Ave. Suite 215
St. Paul, MN 55113
612/636-2380

An environmental specialty chemical company that develops and markets chemical processes that create more effective ways to remediate and analyze hazardous waste. Our CAPSUR system has effectively remediated nonporous surfaces contaminated with Polychlorinated Biphenyls and Pentachlorophenol. The CAPSUR system is cost-effective and offers significant advances over conventional surface cleaning methods.

Intergraph Corporation   1123
2051 Mercator Dr.
Reston, VA 22091
703/264-5600

Intergraph Corporation is the largest CAD/CAM/ CAE systems vendor in North America and the leading supplier of interactive computer graphics systems to the federal government. A Fortune 500 company, Intergraph provides UNIX workstations and servers as well as fully integrated software in environmentally oriented applications such as mapping/GIS, AEC and facilities management.

International Technology Corporation   0203
23456 Hawthorne Blvd.
Torrance, CA 90505
213/378-9933

International Technology Corporation (IT) is an environmental management company with multiple technologies and human resources to solve a wide variety of problems involving hazardous chemical and nuclear materials. The Company provides a comprehensive range of services and products to industry and governmental agencies in four business areas: Environmental Engineering and Services, Analytical Services, Remediation Projects and Services and Pollution Control Systems.

Interox America   0225
3333 Richmond Ave.
Houston, TX 77098
713/522-4155

Hydrogen peroxide and FB^R Sodium Percarbonate - the oxidants of choice for wastewater treatment. Control odors and oxidize organic compounds, cyanides, chlorine and reduced sulfur compounds without toxic by-products.

J.J. Keller & Associates, Inc.   2418/LDC
8361 U.S. Highway 45
Neenah, WI 54957-0368
414/722-2848

J.J. Keller & Associates, Inc. currently researches, writes, edits, and prints over 60 technical publications serving the CPI and transportation industry. Keller also offers chemical handling and regulatory training kits, videos, and handbooks as well as hazardous materials management software. Featured at Superfund '90 will be Keller's Hazardous Waste Management Guide; Chemical Regulatory CrossReference; HAZWOPER Manual and Training Kits; OSHA Compliance Man-

ual; Chemical Training Booklets; Hazardous Materials Guide; Chemical Crisis Management Guide; Haz Mat II Software, and Reg-A-Dex Software.

Jacobs Engineering Group Inc. 2108
251 South Lake Ave.
Pasadena, CA 91101
818/449-2171

Jacobs is one of the largest professional service firms in the U.S. providing engineering, design and consulting services; construction and construction management; and process plant maintenance. The Company provides its services nationwide and internationally for selected industries including environmental and hazardous waste; facilities for aerospace, high technology and other applications; and process plants for chemical, petrochemical and pharmaceutical industries, the energy and refining industries, and the mineral and fertilizer industries.

James T. Warring Sons, Inc. 2212
4545 S St.
Capitol Heights, MD 20743
301/322-5400

All types and sizes of containers - new and reconditioned - fiber, steel, plastic. Our hazardous waste containers are DOT approved and range in size from 5 to 110 gallons. We accept orders from one to truck loads and we ship anywhere. You order a container - we don't have it - it's special - we will get it for you. No order is too small for James T. Warring Sons, Inc. Let us help you contain your hazardous waste. Also provided is empty drum removal with custom shredding and crushing done on your site.

KV Associates 1414
281 Main St.
Falmouth, MA 02541-9811
508/540-0561

KV Associates is a manufacturer of investigation products for soil, gas and water; and soil sampling of remediation products for soil venting and volatile destruction using shield screens and catalitic converter systems and flowmeters for determining rate and direction of groundwater flow.

Kimmins Thermal Corporation 0806
256 Third St.
Niagara Falls, NY 14303
716/282-7252

Kimmins Thermal Corporation, a Subsidiary of Kimmins Environmental Service Corporation (NYSE:KVN), provides full-service hazardous waste remediation contracting. Services range from packaging, transportation, and disposal services to on-site incineration. Disposal services include: radioactive and mixed wastes, gas cylinders, and explosive/shock sensitive materials. Services available nationally.

LTC International, Inc. 0912
101-G Executive Dr.
Sterling, VA 22170
800/822-2332

LTC International offers a full line of dust-free, high production vacuum blasting machines. This equipment is suitable for removal of many toxic substances, such as lead paint, while reducing waste generated by 95% over conventional open blasting!

LWD, Inc. 1010
P.O. Box 327
Calvert City, KY 42029
502/395-8313

LWD, Inc. is a full service waste management company specializing in the rotary kiln incineration of hazardous and non-hazardous materials. We are a licensed transporter of such materials and operate a HDPE non-hazardous industrial waste "special" landfill. A field service division performs site remediation and industrial cleaning to customer specifications.

Laboratory Resources 2416
363 Old Hook Rd.
Westwood, NJ 07675   201/666-6644

Laboratory Resources is a full service analytical testing laboratory capable of analyzing air, water, soil, hazardous waste, asbestos, industrial hygiene and a host of other matrices. The distinguishing nature of the company includes responsiveness to the customer, fast turnaround and unparalleled quality service. Call (800) 729-1397 for more information.

**Laborers-AGC Education
& Training Fund** 2116
P.O. Box 37, Rte. 97 & Murdock Rd.
Pomfret Center, CT 06259
203/974-0800

The Laborers-AGC Education and Training Fund is a labor/management trusteed organization that develops and implements training programs for over 70 training centers located throughout the United States and Canada (32). Courses offered include: Line Foreman Safety Training, Pipe Laying, Blasting, Laser Beams, Asbestos Abatement, and Hazardous Waste Worker Training.

Laidlaw Environmental   0215/0217
Services, Inc.   0219/0221
P.O. Box 210799
Columbia, SC 29221
803/798-2993

Laidlaw Environmental Services is the new name for GSX Chemical Services, Tricil and their affiliated companies. From more than 50 locations throughout the U.S. and Canada, Laidlaw Environmental Services offers a longstanding record of performance, financial stability, and the organizational flexibility to tailor service solutions to your specific environmental concerns. Combined strengths. Combined resources. Laidlaw Environmental Services...the ONLY name you need to know to manage your industrial and hazardous wastes.

Lancaster Laboratories, Inc. 1005
2425 New Holland Pike
Lancaster, PA 17601
717/656-2301

An independently owned and operated testing laboratory located in Lancaster, Pennsylvania. With a staff of more than 370 scientists, technicians, and support personnel housed in a 78,000

sq. ft. facility, we provide a wide range of environmental, industrial hygiene, food, and pharamaceutical testing services. We also provide ExpressLAB and sample pickup services.

Law Environmental, Inc. 2503/2505
114 Town Park Dr.
Kennesaw, GA 30144
404/590-4605

With more than fifty years of experience in the environmental consulting field, Law focuses on giving you creative and proactive solutions to environmental regulatory compliance issues. We offer you services in the following areas: Underground Storage Tanks; RCRA Hazardous Wastes; CERCLA/SARA Superfund; Solid Waste Management; Hydrology/Water Resources; Commercial Property Transfers; Industrial Property Transfers; Air Quality; Wetlands.

**Layne-Western
Company, Inc.** 2004/2006
1900 Shawnee Mission Pkwy.
Mission Woods, KS 66205
913/362-0510

Layne-Western Company, Inc. brings technical knowledge and practical experience to the specialized fields of investigative drilling, remedial action and environmental monitoring. From offices located coast-to-coast, Layne provides clients with a pool of talented professionals and a high commitment to professionalism, safety and quality.

**Lockheed Analytical
Laboratory** 2517/2519
1050 E. Flamingo Rd.
Las Vegas, NV 89119
702/734-3303

Built to meet the environmental chemistry needs of industry and government, Lockheed's world-class laboratory in Las Vegas, Nevada, offers a broad range of superior analytical chemistry services...services that ensure the success of even your most difficult environmental projects.

Lopat Enterprises Inc. 2101
1750 Bloomsbury Ave.
Wanamassa, NJ 07712
908/922-6600

Lopat's K-20/LSC is used in the control and remediation of all hazardous leachable toxic metals mandated by the USEPA, state and local authorities in incinerator ash, soil, soil-like solids or semi-solid wastes. K-20/LSC treated wastes will meet TCLP, CAM WET, MEP or EP TOX requirements. K-20/TCC is used in the control of PCB's and other chlorinated and organic compounds in soil-like particulate matter and on various cementitious surfaces.

**Los Alamos Technical
Associates, Inc.** 1507
6501 Americas Parkway NE, Suite 900
Albuquerque, NM 87110
505/884-3800

Los Alamos Technical Associates, Inc. (LATA), provides engineering and scientific services to government and industry in the areas of waste

management (hazardous, radioactive, mixed-waste); NEPA compliance planning and documentation; and nuclear process equipment and facility design. Over 300 personnel representing 40 technical disciplines. Most staff hold DOE Q clearances.

MAC Corporation/
Saturn Shredders 1117
201 East Shady Grove Rd.
Grand Prairie, TX 75050
214/790-7800

Manufacturers, designers, and fabricators of reduction systems to address the needs of PCB, haz-waste, low-rad waste, and steel-drummed chem-waste processors. If incineration or other treatment requires preparing the infeed through shredding, opening, separating, disengaging or reducing the size of same, our expertise will positively contribute to your decision-making process.

MICROMEDEX, Inc. 1306
600 Grant St. 6th Floor
Denver, CO 80203-3527
303/831-1400

Referenced source on medical and hazard information regarding thousands of chemicals used in the industrial setting; in-depth coverage of clinical effects, range of toxicity, workplace standards, and response to hazardous incidents. Designed for use by health and safety directors, occupational medicine professionals, and industrial hygienists.

MPC Environmental 2015
8631 W. Jefferson
Detroit, MI 48209
313/849-2333

MPC Environmental is a full service Environmental Contractor. Services include: 24 hour Emergency Response Capability, High Capacity Portable Pumping Systems (3,000 GPM), Site Cleanups, PCB Decontamination/Removal/Transportation, Hazardous Materials Cleanup/Transportation and Groundwater Remediation Services. GET TO KNOW US BEFORE ALL HELL BREAKS LOOSE!

MSA (Mine Safety
Appliances Co.) 0304
P.O. Box 426
Pittsburgh, PA 15230
412/967-3000

MSA will display a full line of personal protective equipment including products for respiratory protection and environmental monitoring.

MSP Technical Services, Inc. 1313
110 James Drive West, Suite 218
St. Rose, LA 70087
504/465-3300

To provide technically advanced, innovative products and services for the Waste Management Industry, while achieving the highest level of customer-driven, quality service at the lowest possible cost with an organization of highly trained people committed to health, safety and the environment for its employees and the community.

MWR, Inc. 2121
615 W. Shepherd St., POB 10
Charlotte, MI 48813
517/543-8155

Remedial services emphasizing a patented soil vapor extraction process.

Map Express LDC
P.O. Box 280445
Lakewood, CO 80228
800/627-0039

Map Express provides the full-service link between you, the professional community, and the resources of the U.S. Geological Survey and other agencies, supplying the map products your company needs today. Overnight shipping, toll-free 24-hour order line, personalized customer service, corporate deposit accounts, and a special research department are among the services we offer.

Marcel Dekker, Inc. LDC
270 Madison Ave.
New York, NY 10016
212/696-9000

Publishing firm of all types of Hazardous Waste texts, reference books and manuals.

Maxwell Laboratories,
S-CUBED Division 1402
P.O. Box 1620
La Jolla, CA 92038
619/453-0060

Chemical Analysis Services: CLP Organic Analyses; RCRA Analyses; Methods 1618, 1624, 1625 Analyses for OWRS Samples; Inorganic Analytes. Quality Assurance Support - BDAT, SITE, OPP Projects: QA Project Plan Reviews; Final Report Reviews; Field Audits; QA Training. Analytical Methods Development and Research. Environmental Engineering: Site Investigation/ Field Sampling and Monitoring; Treatability Studies; Solidification/Stabilization.

Medlab Environmental
Testing, Inc. 0402
P.O. Box 2045
Wilmington, DE 19899
302/655-5227

Medlab offers: full service environmental testing laboratory; free courier service; sampling; and analysis for hazardous waste, asbestos, wastewater and soils, drinking water and radon, and industrial hygiene; multi-state certifications. NVLAP accredited, NIOSH PAT participant.

Metcalf & Eddy 1126/1128
30 Harvard Mill Square
Wakefield, MA 01880
617/246-5200

Metcalf & Eddy protects the environment. Using a complete range of environmental services and capabilities, we assure that the nation's water resources and waste-generating activities are properly managed. Unique in the environmental field, Metcalf & Eddy offers you a single source for the development, design, construction management, and operation of water, wastewater,

sludge, hazardous and solid waste management systems. Few other firms offer their clients financial planning and management alternatives, such as total project delivery, contract operations, and program management. Industries, municipalities, and governmental agencies around the world have benefitted from Metcalf & Eddy's unique blend of technical, operation, and management expertise provided by a highly experienced staff of 2,200 technical and management specialists. Licensed, highly skilled personnel use a large and specialized assembly of equipment to clean up and transport hazardous waste.

Michigan Waste Report, Inc. LDC
400 Ann Street, N.W., Suite 204
Grand Rapids, MI 49504-2054
616/363-3262

Publishers for: MICHIGAN WASTE REPORT - Bi-weekly Newsletter, 21 Issues plus Directories, $325/yr. 3 SPECIAL ANNUAL DIRECTORIES REPORTS (sold separately) Haz. Waste, Env. Mgt., Solid Waste, $43.60 each. ACT 64 LEGAL MGT. SYSTEM MANUAL, MI Haz. Waste Laws & Regulations, $395. RESOURCE EXCHANGE & NEWS MAGAZINE Waste Exchange & Recycled Material Markets, 6 Issues, $48/yr. ENVI-ROX ON-LINE COMPUTER SERVICE Environmental Information & Waste Exchange Listings.

Millipore Corporation 0202
80 Ashby Rd.
Bedford, MA 01730
617/275-9200 x2337

Millipore will exhibit its line of products for the analysis of hazardous materials including the Zero Head Space Extractor designed specifically for evaluating waste according to the TLCP. Millipore also offers a Rotary Agitator, dispensing pressure vessels and a complete line of membrane filters.

Morrison Knudsen Corporation 1101
P.O. Box 73
Boise, ID 83729
208/386-6172

"One Sea, One Sky, One World Environment, One Company: MORRISON KNUDSEN" - serving private- and public-sector clients worldwide through site investigation, feasibility studies, engineering, and construction for: Industrial waste treatment and pollution control; Municipal waste management; High- and low-level radioactive waste disposal; Waste treatment, storage, and disposal (TSD) facilities.

NUS Corporation 2322-2323
Park West 2, Cliff Mine Rd.
Pittsburgh, PA 15275
412/788-1080

For 30 years, NUS Corporation has provided the environmental and engineering expertise to solve industry and government waste problems with cost-effective solutions. Our staff of 1950 multidisciplinary professionals offers a full range of services including environmental assessment, environmental engineering, remedial design engineering, hydrogeologic and geologic services,

risk assessment, regulatory assistance, environmental health and safety and analytical services.

Nappi Trucking Corporation 1514
P.O. Box 510, Hwy. #34
Matawan, NJ 07747
201/566-3000

Transportation and storage of Hazardous and Non-Hazardous Waste.

National Academy Press LDC
2101 Constitution Ave., N.W.
Washington, DC 20418
202/334-3313

The National Academy Press was created by the National Academy of Sciences to publish the reports issued by the Academy and by the National Academy of Engineering, the Institute of Medicine, and the National Research Council, all operating under the charter granted to the National Academy of Sciences by the Congress of the United States.

Nat'l Env'l Tech. Appl. Corp.
(NETAC) 0213
615 William Pitt Way
Pittsburgh, Pa 15238
412/826-5511

The National Environmental Technology Applications Corporation (NETAC) facilitates commercialization of promising environmental technologies. NETAC services include technical and commercial assessments; technology development assistance; testing and demonstration, market analysis and business development; permitting and regulatory assistance; identification of financial sources. NETAC was created in 1988 through cooperative between the U.S. Environmental Protection Agency and the University of Pittsburgh to help move environmental technology to the marketplace.

National Draeger, Inc. 2507
101 Technology Dr.
Pittsburgh, PA 15275
412/787-8383

National Draeger offers a wide range of products within the respiratory, instrumentation, and detector tube lines. The Model 190 Datalogger is the most advanced portable gas monitor available for industrial hygiene and safety professionals. It detects toxic gas and alarms independent of the microprocessor function. National Draeger's air-purifying respirators include cartridges for organic vapors, and gases and ammonia, as well as high efficiency particulate filters for dust, fumes, mists, radionuclides, and asbestos.

National Environmental Products 2521
Greenwood Ave., P.O. Box 38
Newfield, NJ 08344
609/697-1066

"Drum Stix" environmental sampling tools for liquids, solids and sludge. Call out toll-free number for more information: 1-800-542-6816.

National Environmental
Testing, Inc. 1312/1314
220 Lake Drive East
Cherry Hill, NJ 08002
609/779-3373

A growing nationwide network of environmental

testing laboratories, dedicated to providing high quality analytical services backed by a comprehensive field services which include field sampling, stack testing and industrial hygiene services.

National Express
Laboratories, Inc. 1712
6801 Press Dr., East Building
New Orleans, LA 70126
504/283-4223

NatEx is a network of environmental laboratories located in strategic regions of the country serving industry, engineering/consulting firms and governmental agencies. Each network laboratory is a participant in the EPA Contract Laboratory Program and has expertise in analytical methodologies in support of RCRA, CERCLA, SARA and CAA regulations. At NatEx, we emphasize responsive client services and meeting committed turnaround times, in addition to high quality analytical services.

National Library of Medicine 1612
8600 Rockville Pike, Building 38A, 3S308
Bethesda, MD 20894
301/496-6531

The National Library of Medicine plans to exhibit Environmental Protection Agency's (EPA's) Toxic Chemical Release Inventory (TRI87, TRI88) databases on NLM's Toxicology Data Network (TOXNET) System. TRI databases contain information on the annual estimated releases of toxic chemicals to the environment. It is mandated by Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986. The Inventory contains provisions for the reporting, by industry, on the releases of over 300 toxic chemicals into the air, water and land. NLM also will perform on-line demonstrations of searching the other files of TOXNET System such as HSDB, RTECS, CORIS, IRIS, DART, ETICBACK, EMICBACK and DBIR.

National Lime Association 2414
3601 North Fairfax Dr.
Arlington, VA 22201
703/243-5463

Lime - Calcium Magnesium Oxides and Calcium Magnesium Hydroxides - *Man's Oldest and Most Versatile Chemical*. Nature's gift for the stewardship of our planet. It almost does it all: neutralization, chemical fixation, stabilization and solidification of toxic and hazardous materials. Lime may be the natural, cost-effective solution to your hazardous waste problems.

National Seal Company 0318
1245 Corporate Blvd., #300
Aurora, IL 60504
708/898-1161

National Seal Company manufactures and installs flexible membrane liners, drainage netting and geotextiles for landfills, hazardous waste storage, leach pads and reservoirs. Computerized manufacturing system produces competitively priced liners that are twice as good as industry standards. NSC's unique seaming procedure enhances liner strength and leakage resistance.

National Solid Wastes
Management Association 1714
1730 Rhode Island Ave., N.W., Suite 1000
Washington, DC 20036
202/659-4613

CWTI (Chemical Waste Transporters Institute), ICWM (Hazardous Waste Treatment and Disposal Institute) and RCI (Remedial Contractors Institute) are components of National Solid Wastes Management Association to promote safe transport and cleanup of hazardous waste sites. NSWMA is the only association representing these interests for Superfund and other state cleanups.

Normandeau Associates, Inc. 2005
25 Nashua Rd.
Bedford, NH 03102
603/472-5191

Normandeau Associates, Inc., has been providing specialty environmental consulting services since 1970. These specialty services include ecological risk assessment, aquatic toxicology, analytical laboratory services, wetland mitigation, water quality studies, and a full range of environmental specialists at over 12 locations throughout the eastern U.S.

Northeast Research
Institute, Inc. 1121
309 Farmington Ave., Ste. A-100
Farmington, CT 06032
203/677-9666

NERI provides Petrex soil gas surveys, and Industrial Hygiene and Analytical Lab Services. Technical representatives will discuss how the Petrex soil gas method is used for site assessments, LUSTs, property transfers, etc. Custom analyses of Petrex samplers can now be achieved by GC/MS to meet sophisticated survey objectives.

Northeastern Analytical
Corporation 1307/1309
4 East Stow Road
Marlton, NJ 08053
609/985-8000

Environmental Services: Complete Environmental Field Sampling, In-house Gas Chromatography/Mass Spectrometry (GS/MS) Laboratory Analysis, Hazardous Site Training (40 Hours), Asbestos Inspection & Management & Abatement Monitoring Services, Asbestos Analysis by Transmission Electron & Optical Microscopy, Underground Storage Tank Testing, Excavation, Removal and Installation, Stack Emission and Ambient Air Testing.

OHM Corporation 0403/0405
16406 U.S. Route 224 East
Findlay, OH 45840
800/537-9540

OHM's subsidiaries provide the following environmental services: Environmental Testing and Certification Corp. (5 laboratories) - analysis and management; OHM Remediation Services Corp. (21 response centers) - assessment, engineering, design, on-site remediation for soil, groundwater, lagoons, facilities, waste sites; OHM Resource

Recovery Corp. (Part B facility): Waste treatment and disposal.

OLDOVER CORPORATION 1909
P.O. Box 228
Ashland, VA 23005
804/798-7981

Oldover Corporation provides comprehensive waste management services including transportation, fuel blending, thermal destruction, recycling and drum recovery. State-of-the-art equipment and multiple locations assure prompt, dependable service. A 17-year no-lost-time accident record demonstrates Oldover's commitment to the safe handling of hazardous wastes.

**OSCO Environmental
Management** 0308
618 Grassmere Park Dr., #7
Nashville, TN 37211
615/832-0081

The new treatment facility in Nashville, Tennessee, processes all types of liquid and solid wastes including waters, oils, sludges, acids, bases and cyanides. Solids stabilization is offered in bulk. Waste is received in bulk and drums by truck or rail. Transportation is available in 42 states. Remediation and professional consulting services are offered nationwide.

**OCCUPATIONAL HAZARDS
Magazine** 1412
1100 Superior Ave.
Cleveland, OH 44114
216/696-7000

OCCUPATIONAL HAZARDS Magazine is edited for management officials who are responsible for workplace safety, health and environmental compliance. Editorial material includes coverage of major legislative, regulatory, scientific and other developments affecting the field, as well as practical "how-to" articles.

**Ogden Environmental
Services, Inc.** 1308/1310
3550 General Atomics Ct.
San Diego, CA 92121-1194
800/876-4336

Turnkey site remediation services and in-plant destruction solutions. Ogden's transportable incinerator provides cost effective, environmentally safe, remediation alternatives.

**On-Site Instruments/
EnviroRENTAL** 0704/0706/0708
689 North James Rd.
Columbus, OH 43219
1/800/766-7483

On-Site Instruments/EnviroRENTAL sells, rents and services a complete line of industrial hygiene, laboratory and environmental monitoring instruments and equipment. Rent-to-own and leasing options are also available. Our service department provides technical and applications assistance, while our distribution center handles all accessory orders. On-Site also offers training classes at our Columbus, Ohio, facility. Call 1-800-7-On-Site for more information.

**P.E. LaMoreaux &
Associates, Inc. (PELA)** LDC
P.O. Box 2310
Tuscaloosa, AL 35403
205/752-5543

P.E. LaMoreaux and Associates, Inc. (PELA), consulting hydrologists, geologists, engineers and environmental scientists, offers hydrological, geological, environmental and hazardous waste consultation services. Other services provided include sampling, laboratory analysis, development of monitoring programs and installation of wells, reclamation, permitting, court testimony, and graphics and communications programs.

PACE Incorporated 0702-0801
1710 Douglas Dr. North
Minneapolis, MN 55422
612/544-5543

PACE is a national environmental laboratory and consulting firm serving all regions of the United States. Services are provided through a national network of 10 facilities. Services offered include: field sampling, organic and inorganic laboratory analyses for water, soil, and air; bioassay toxicity testing; and, asbestos, industrial hygiene, air pollution and risk assessment consulting services.

**POLLUTION EQUIPMENT NEWS/Rimbach
Publishing Inc.** 1023
8650 Babcock Blvd.
Pittsburgh, PA 15237
412/364-5366

POLLUTION EQUIPMENT NEWS, published bi-monthly, provides product information to the person responsible for air, water, wastewater and hazardous waste. An annual CATALOG & BUYER'S GUIDE provides buying source information. INDUSTRIAL HYGIENE NEWS, published bi-monthly, provides information on products and services for measuring and controlling health hazards in the work environment.

**PRC Environmental
Management, Inc.** 1510
303 East Wacker Dr., Suite 500
Chicago, IL 60601
312/856-8700

PRC EMI provides environmental services to both government and industry. Headquartered in Chicago, Illinois, PRC EMI maintains major offices in McLean, Virginia, San Francisco, and Denver as well as 13 other offices throughout the country. Specialties include remedial investigations/feasibility studies, endangerment assessments, remedial design and implementation, compliance audits, permitting support, waste reduction audits, risk management support, environmental and systems engineering, policy and regulatory analysis, economic analysis, and program management support.

PacTec, Inc. 0915
28701 Allen Rd.
Clinton, LA 70722 800/272-2832

PacTec, Inc., offers polyethylene liners utilized in dump trucks, roll-off assemblies and rail gondolas for transporting bulk solids and sludges. These liners reduce the risk of leaking, help eliminate washout costs and increase container longevity.

Pacific Analytical, Inc. 1610
1989-B Palomar Oaks Way
Carlsbad, CA 92009
619/931-1766

Pacific Analytical (PA) is an innovative, high technology environmental analysis laboratory oriented toward work with unusually complex samples. PA specializes in providing high quality analysis results for volatile and semivolatile organics, and pesticides using 500 series, 600 series, 1600 series and SW-846 methods; dioxins by 8280 (LRMS), 8290 and 1613 (HRMS); and metals by 6020 and 200.8.

Pennsylvania Drilling Company 0214
500 Thompson Ave.
McKees Rocks, PA 15136
412/771-2110

Pennsylvania Drilling Company will be demonstrating capabilities for installing monitoring wells on a variety of sites under a variety of conditions. In addition, they will be displaying drilling tools and monitoring well equipment made in their new shop in McKees Rocks near Pittsburgh, Pennsylvania.

Peoria Disposal Company 2515
4700 N. Sterling Ave.
Peoria, IL 61615
309/688-0760

RCRA Treatment, Disposal Facility, Analytical Services, Transportation, Remediation, Consulting and Engineering Services.

PermAlert ESP, Inc. 1912
7720 Lehigh Ave.
Niles, IL 60648
708/966-2190

Manufacturers of the Double-Pipe™ secondary contained piping systems. PAL-AT™ cable type leak detection and location system, and TankWatch™ leak detection system. DOUBLE-PIPE is a preengineered and prefabricated system available in steel, fiberglass and thermoplastics. The PAL-AT leak detection system is microprocessor based, UL listed and intrinsically safe for Class 1, Groups C & D, Div. 1.

Peroxidation Systems 0205/0207
4400 E. Broadway, Suite 602
Tucson, AZ 85711
602/327-0277

Peroxidation Systems supplies services and equipment for UV/hydrogen peroxide chemical oxidation of organic materials in water or wastewater.

**Photovac International
Incorporated** 2410/2412
25-B Jefryn Blvd. West
Deer Park, NY 11729
516/254-4199

Photovac will display portable instruments for environmental toxic monitoring in groundwater, soil, and ambient air: TIP™, a hand held Total Organics analyzer; the 10S Series Portable Gas Chromatographs; and MicroTIP™, a hand held analyzer which incorporates advanced microprocessor technology for real time digital or graphic assessment of toxic gases and vapors.

Poly-John Trailer Division 2514/2516/2518
P.O. Box 1037, Old U.S. 31 South
Rochester, IN 46975
219/223-6566

Poly-John Trailer Division's Decontamination Units are state of the art design and construction. Special attention is given to every detail insuring users of comfort and safety with a functional and practical floorplan. Any industry dealing with contaminated materials must take every precaution possible for the safety of its employees and the environment. Poly-John has created these units to meet these strict requirements and to put your mind at ease.

Polyfelt, Inc. 0109
1000 Abernathy Rd., Suite 1520
Atlanta, GA 30328
404/668-2119

Polyfelt, Inc. is a worldwide manufacturer of spunbonded, continuous filament, needlepunched geotextiles with a major focus in the Waste Containment industry. Our product lines range from 2.7 - 22 oz/sy. We provide technical support, geotechnical design guidelines and data, QC/QA certifications, and a worldwide distributor network.

**Princeton Testing
Laboratory, Inc.** 1116
P.O. Box 3108
Princeton, NJ 08543
609/452-9050

Environmental Analysis; Industrial Hygiene; RCRA/ECRA; industrial wastewater; NPDES; groundwater; OSHA workplace surveys; asbestos monitoring & evaluation; complete NIOSH laboratory methodology; asbestos & HAZ-MAT training courses; Right to Know compliance; Microbiology; Bioassay; Underground Storage Tank testing; AIHA accredited. Certified for:NJ DEP; NYDOH; PA DER; CT; RI; & DE.

Project Time & Cost, Inc. 0810
3390 Peachtree St., NE, 16th Floor
Lenox Tower South
Atlanta, GA 30326-1108
404/239-0220

Skillful management of cost, time and quality is essential to the successful completion of any project plan, especially in today's environmental arena. Project Time & Cost, a full-service cost engineering and project management consulting firm, possesses the experience and resources required to provide these essentials to both governmental and private sector clients.

QED Environmental Systems, Inc. 1025-1027
P.O. Box 3726
Ann Arbor, MI 48106
313/995-2547

Well Wizard® Dedicated Sampling Systems; Sample Pro® Groundwater Sampling Supplies; Pulse Pump® Recovery Pumping Systems; Hydro-Punch® Groundwater Sampling Without Wells.

QUALTEC, Inc. 0803-0805
11300 U.S. Highway One, Suite 600
Palm Beach Gardens, FL 33408
407/775-8395

QUALTEC, Inc., specializes in on-site remedia-

tion utilizing stabilization via fixation/solidification. QUALTEC also provides construction/closure of landfills and RCRA caps; treatability studies; pilot studies; site restoration; groundwater remediation; construction management; and fixation equipment and personnel leasing. QUALTEC's state-of-the-art cementitious fixation process has been utilized at Superfund sites across the nation.

Quantum Analytics, Inc. 0201
363-D Vintage Park Dr.
Foster City, CA 94404
415/570-5656

Quantum Analytics rents state-of-the-art analytical instruments and portable GCs. Products include GC, LC, AA, IR, UV, FL, TOC, and TOX.

R & G Sloane 1907
7660 N. Clybourn Ave.
Sun Valley, CA 91352
818/767-4726

ContainIt - secondary containment piping system fits over virtually any piping system. It is available with either split or solid pipe and split fittings, making it ideal for both retrofit and new system installations. The ContainIt systems injection bonding method allows it to be pressure rated up to 75 psi.

R.E. Wright Associates, Inc. 1305
Environmental Restoration Systems
3240 Schoolhouse Rd.
Middletown, PA 17057

REWAI designs and manufactures groundwater treatment and subsurface towers, pneumatic pumps and the Auto-Skimmer. REWAI provides turnkey systems - pre- and/or post-treatment, off-gas treatment and installation and maintenance contracts.

R.J. Lee Group, Inc. 1003
350 Hochberg Rd.
Monroeville, PA 15146
412/325-1776

RJ Lee Group provides analytical and consulting services in materials characterization. A wide variety of analytical equipment is used with emphasis on optical, scanning and electron microscopy. Materials investigated include metals, ceramics, powders, air particulates, semi-conductors and bio materials. Complete in-house chemical laboratory. Products include Zeppelin microimaging and MICROSURE® OPTICAL FIBER COUNTING COMPUTER systems.

**RMC Environmental
Services, Inc.** 1113
R.D. #1, Fricks Lock Rd.
Pottstown, PA 19464
215/326-9662

Environmental Consulting, Engineering and Analytical Services; including hazardous waste site investigations, hydrogeological investigations, aquatic and terrestrial ecological studies, wetland studies, natural resource damage assessments, regulatory compliance audits, hazardous waste volume and toxicity reduction, permit assistance, underground storage tank systems assis-

tance, waste treatment system engineering, and environmental chemistry laboratory services.

Radian Corporation 2403
8501 MoPac Blvd., P.O. 201088
Austin, TX 78720-1088
512/454-4797

RADIAN CORPORATION PROVIDES A FULL RANGE OF PROCESS, SOLID, AND HAZARDOUS WASTE ENGINEERING SERVICES...including site assessment to remediation design and construction, waste minimization to the design of waste treament or disposal systems, and preparing permit applications to responding to consent orders. In addition, the company has three full-service laboratories providing complete characterization and classification of soils, groundwater, run off, leachates, air emissions, soil vapors, and virtually any other substance or material for which measurements are required. RADIAN also has the unique ability to perform remedial pilot studies on site. This is accomplished through our transportable treatment systems. The unit physical-chemical operations incorporated into these systems can be configured to treat most contaminated waste streams. These systems have sufficient capacity to provide full-scale groundwater remediation.

Recra Environmental, Inc. 1410
10 Hazelwood Dr.
Amherst, NY 14228
716/691-2600

Recra Environmental, Inc. is an independently owned and operated corporation providing a wide range of organic and inorganic analyses on waters, soils and waste matrices. Recra is a U.S. EPA CLP laboratory with laboratories in Amherst, NY, Columbia, MD, Cleveland, OH and Detroit, MI. Data management, electronic transfer, individualized programs are provided with rapid, professional, high quality analytical services.

Remcor, Inc. 1506/1508
701 Alpha Dr.
Pittsburgh, PA 15238
412/963-1106

Remcor, Inc., provides the full spectrum of hazardous waste consulting and remediation services. By uniquely integrating expertise in engineering, construction, and environmental field services, Remcor performs projects ranging from investigations and assessments through actual remediation. As a turnkey contractor, Remcor has completed numerous projects including building decontaminations, surface impoundment and landfill closures, storage tank management, asbestos removals, groundwater remediation and mixed waste cleanups.

**Remediation Technologies,
Inc. (ReTeC)** 0614
22419 - 72nd Avenue South
Kent, Washington, 98032
206/872-0247

Remediation Technologies, Inc. (ReTeC), is a field services and engineering company specializing in on-site remediation of contaminants associated with organic wastes at industrial sites. ReTeC provides turnkey services from investigation

through final remediation/closure. ReTeC has designed and implemented bioremediation programs, groundwater treatment systems and thermal treatment systems for numerous RCRA and CERCLA sites.

Research Alternatives, Inc. 0105
966 Hungerford Dr., Suite #1
Rockville, MD 20850
301/424-2803

Research Alternatives, Inc., will be demonstrating the Emergency Information System (EIS) software used for environmental and emergency planning, response, and recovery for natural and technological disasters. This PC-based software combines 19 emergency and regulatory compliance databases with georelational digitized maps and data communication capabilities to provide immediate access to critical information.

Resource Analysts, Incorporated 0314/0316
P.O. Box 778, One Lafayette Rd.
Hampton, NH 03842
800/992-0724   603/926-7777 in NH

Resource Analysts, Inc., is dedicated to complete customer satisfaction in the area of analytical testing, field sampling, bioassay, bioaccumulation, product registration, FIFRA, TSCA, RCRA, CLP (ino/org) aquatic research organism supplier. Maintains certifications/approval status in numerous states, EPA regions, DOD, ACOE, and regulatory agencies.

Response Rentals 0502
1460 Ridge Rd. East
Rochester, NY 14612
800/242-3910

Response Rentals provides rental instrumentation for remedial investigation studies, compliance surveys and substance emergencies. The instrumentation is easy to operate, reliable and represents the best names in the industry. Broad product line meets virtually every application need and includes, X-Met, OVA's, CGI's, PID's Isothermal GC's, ELF Radiation and more.

Riedel Environmental Services, Inc. 0307
4611 N. Channel Ave.
Portland, OR 97217
503/286-4656

Riedel Environmental Services, Inc., provides to its governmental and private clients turnkey environmental services which include site investigations, real estate audits, environmental engineering and design, groundwater assessment, design and operation of vapor and liquid recovery systems, remedial cleanup utilizing alternative cleanup technologies, underground storage tank management, 24 hour emergency response to hazardous material incidents and operation of treatment, storage and disposal facilities.

Robertson's Barrier Systems Corporation 0901
580 Hornby St., Suite 800
Vancouver, BC Canada V6C3B6

Robertson Barrier Systems - Testable, High Security Geomembrane Liner Systems. The Robertson

Barrier Liner is a unique patented liner geomembrane system specifically designed for the safe containment of hazardous, toxic or valuable materials or wastes. Unique because it allows testing for the presence of potential leaks at any time without letting any of the contained liquid escape. It can be used for ponds and surface impoundments, landfills, underground storage tanks and as secondary spill containment. You can: Test for leaks both during construction and operation; Detect the onset and location of leaks; Control and isolate potential leaks. All this means reduced risk and liability for the owner, operator and the public.

Rocky Mountain Arsenal 0707
Public Affairs Office
Commerce City, CO 80022-2180
303/289-0250

Rocky Mountain Arsenal is an inactive installation conducting environmental cleanup, a result of past production practices. Environmental Remediation costs are expected to meet or exceed $1 billion. Because of its complex hazardous waste streams and contamination, RMA has been on the leading edge of technology with innovative techniques for sampling soil, groundwater and buildings.

Rollins Environmental Services, Inc. 0517-0518
P.O. Box 2349 One Rollins Plaza
Wilmington, DE 19899
302/479-3164

The Rollins Environmental Services family of companies provides unparalleled liability protection in hazardous waste management and disposal services which include multiple incineration facilities, laboratory analyses, small quantity waste and lab pack services, PCB removal, transportation, secure land disposal, encapsulation and deepwell injection. In Delaware, phone 302/479-2968 for more information.

Rose-Tillmann Inc. 1601
One Mark Twain Plaza
Suite 200
Edwardsville, IL 62025
800/228-3328

Rose-Tillmann Incorporated is a bonding and insurance brokerage specializing in providing programs nationwide for all types of environmental and pollution cleanup contractors. Specializes in providing hard-to-place programs for hazardous waste, asbestos abatement, underground storage tank removal and toxic and hazardous material transportation.

Rosemount Analytical/ Dohrmann Div. 0312
3240 Scott Blvd.
Santa Clara, CA 95052
408/727-6000

Dohrmann designs and manufactures trace element analyzers for water chemicals and petroleum products; Total Organic Carbon Analyzers, Total Organics Halide Analyzers, and Organic Halide Analyzers, plus analyzers for sulfur, chlorine and nitrogen in oil. Primarily used in product quality control and in pollution prevention and monitoring.

Roy F. Weston, Inc. 1102/1104
Weston Way
West Chester, PA 19380
215/430-3025

WESTON is a full-service environmental engineering firm specializing in analytical laboratory services, consulting and engineering, remediation, facility construction and operations, technical information management and the management of major programs. WESTON employs more than 2,500 people from various disciplines, wholly owns 8 subsidiaries and now has 42 offices nationwide.

S.S. Papadopulos & Associates, Inc. LDC
12250 Rockville Pike, Suite 290
Rockville, MD 20852
301/468-5760

S.S. Papadopulos & Associates, Inc. (SSP&A), is an internationally recognized firm providing specialized services in groundwater. SSP&A offers expert technical assistance in all areas involving water and contamination in the subsurface environment - including groundwater and soil contamination investigations and remediation, computer modeling of hydrogeologic systems and hydrochemical investigations.

SCS Engineers 0611
11260 Roger Bacon Dr.
Reston, VA 22090
703/471-6150

SCS, founded in 1970, provides hazardous and solid waste engineering to state and local governments, the federal government, industries, corporations and developers. Hazardous waste services include: Remedial Investigations, feasibility studies, and remedial designs for CERCLA and RCRA facilities; hazardous waste storage facility design; real estate contamination assessments; underground storage tanks; and wetland studies.

SENTEX SENSING TECHNOLOGY, INC. 1509
553 Broad Ave.
Ridgefield, NJ 07657
201/945-3694

Computerized, self-contained gas chromatographs to provide laboratory analysis, on-site, for emergency response, site evaluation, soil gas analysis and other applications. NEW ITEMS INCLUDE: A portable hand-held Flame Ionization Detector featuring "Point and Shoot" operation for total hydrocarbon detection; a portable Gas Chromatograph/Total Hydrocarbon Analyzer; and a portable Purge and Trap Gas Chromatograph System designed for on-site analysis of drinking, ground and wastewater.

SERROT CORPORATION 1012
5401 Argosy
Huntington Beach, CA 92648
714/895-3010

Specializing in the fabrication and installation of geomembrane liners and floating covers. We can provide backup engineering experience and support to ensure successful installations in a broad span of applications from hazardous waste liners, sewer treatment plants, chemical cell liners and

landfills. In addition we have a large prefabrication facility that makes liners for specialty applications.

SLT North America, Inc.   2506
16945 Northchase
Houston, TX 77060
713/874-2150

SLT the world's originator of High Density Poly-ethylene Lining Systems; manufactures & installs its own patented lining innovation FrictionFlex, from 60-240 mils. SLT also manufactures & installs HyperFlex, UltraFlex & PolyLock for landfills, tunnels, floating covers, primary & secondary containments, leach pads & potable water containments.

**SMC Environmental
Services Group**   2113-2115
Box 859
Valley Forge, PA 19482
215/265-2700

For more than 35 years, SMC Environmental Services Group's Scientists and Engineers have been providing environmental, engineering and consulting support to industry, bankers, lawyers, developers, and government agencies. Areas of expertise include: solid and hazardous waste, industrial hygiene and occupational safety and health, water and wastewater treatment systems, land planning, environmental property and facility audits, wetlands assessments/delineations, and a range of engineering specialties.

SSI Shredding Systems   1019
28655 S.W. Boones Ferry Rd., P.O. 707
Wilsonville, OR 97070
503/682-3633

SSI Shredding Systems provides on-site volume reduction and material processing of solid hazardous waste prior to material treatment. Specific services include pre-processing, feedstock preparation and volume reduction of solid hazardous waste utilizing mobile, low-speed rotary shear shredders. This low RPM equipment is easy to trailer mount and once on-site, is operational within hours. OSHA certified operators are provided. Other services include solvent recovery and volume reduction/blending for stabilization.

**SURETEK: Surety
Teknicians, Inc.**   2512
4830 W. Kennedy Blvd., Suite 600
Tampa, FL 33609
813/281-2550

SURETEK is a National Bond-only agency specializing in all types of Environmental Bonds, including: Remedial Action; Superfund; Lining Systems; Landfill Closure; Contractors; Underground Storage Tanks; Analytical/Laboratory; Monitoring & Detection; Transport; and Consultants/Engineers. We handle Contractors of all sizes, from those needing Small Bonds to Multi-National Public Companies.

Safety Storage, Inc.   LDC
2380 South Bascom Ave.
Campbell, CA 95008
408/559-3901

Sanderson Equipment Inc.   1603
P.O. Box 1066
Princeton, NC 27569
919/936-2042

Sanderson Equipment, Inc., is the USA distributor for the R-B VC Series of Long Reach Excavators. Utilizing a moving counterweight, the VC reaches up to 65' with a one cubic yard bucket which can be placed precisely where needed for a high degree of productivity and safety.

**Science Applications
Internat'l Corp.**   0811
1710 Goodridge Dr.
McLean, VA 22102
703/734-4302

**Scientific Specialties
Service, Inc.**   1107
4030 Benson Ave.
Baltimore, MD 21227
301/644-6200

Scientific Specialties Service, Inc., is showing its line of environmental sampling supplies. Including precleaned and regular vials, bottles, and jars in both glass (which is also available Safety-Coated, if desired) and plastic. They are also showing their Teflon® Capliners and Teflon®/Silicone septa and their line of Teflon® Sealing tapes and Teflon® tubing in an extensive range of sizes.

**Sevenson Environmental
Services, Inc.**   1406/1408
2749 Lockport Rd.
Niagara Falls, NY 14302
716/284-0431

Sevenson Environmental Services, Inc., provides remedial construction services to government and industry in site restoration; excavation, characterization, transportation, and disposal of bulk and drummed wastes; secure landfill and lagoon construction/closure; slurry wall construction; sludge solidification; recovery and treatment systems installations for groundwater, soils and air; leachate collection and treatment systems construction; on-site incineration; biological remediation; facilities decontamination and demolition; dewatering; and storage tank removal/remediation.

**Shields Manufacturing/
Unified Safety Corp.**   0604-0606
624 Maulhardt Ave.
Oxnard, CA 93030
805/988-1055

Environmental Compliance Products, HazMat Storage Facilities, Secondary Containment Systems, Fire Rated and Non-Fire Rated, **First** and **Only** Non-combustible Fire Rated, Factory Mutual Approved Units in the U.S.A.

**Shimadzu Scientific
Instruments, Inc.**   1707
7102 Riverwood Dr.
Columbia, MD 21046
301/381-1227

Shimadzu is among the three largest scientific instrument companies in the world. The broad product line includes gas & liquid chromatographs, spectrophotometers, TOC and thermal analyzers, oil content meters, and balances, turn key

and/or special application instruments such as Environmental GC, TOGAS, and Carbamate analyzers are also available.

Site Reclamation Systems, Inc.   0516
P.O. Box 11
Howey-in-the-Hills, FL 34737
904/324-3651

Manufacturing, Remediation: Mobile Rotary Kiln/Afterburner System designed to treat soils contaminated by light petroleum products such as gasoline, aviation gas and diesel fuel.

Skolnik Industries, Inc.   2510
4900 South Kilbourn Ave.
Chicago, IL 60632
312/735-0700

New steel containers (carbon, composite and stainless), SALVAGE DRUMS and OVERPACKS, drum tools and accessories, heavy-duty dolly, utility carts, components and drum replacement parts, drum liners and hoist paks.

**Solarchem Environmental
Systems**   1814
40 West Wilmot St., Unit #5
Richmond Hill, Ontario L4B 1H8
416/764-9666

SOLARCHEM ENVIRONMENTAL SYSTEMS is the manufacturer of RAYOX®, a second generation enhanced oxidation process for the destruction of toxic and hazardous organic contaminants in industrial process wastewater and contaminated groundwater. RAYOX® has also been applied to contaminated water from Superfund sites.

Soils Magazine   LDC
10229 E. Independence Ave.
Independence, MO 64053
816/254-8735

Solinst Canada Ltd.   2400
The Williams Mill, 515 Main St.
Glen Williams, Ontario, Canada L7G 3S9
416/873-2255

Manufacturers of high quality groundwater monitoring instrumentation, known for the Waterloo Multilevel System and reliable water level indicators. New this year are: a Water Level Meter tape marked each 1/50 ft. and improved environmental probe. Also an Interface Meter which measures the level and thickness of both floating and sinking hydrocarbons.

Solmar Corporation   0813
625 West Katella Ave. Suite 5
Orange, CA 92667
714/538-0881

Advanced Bio Cultures - Formulated bacterial products for the remediation of hazardous waste, containment soils and groundwater, and industrial and municipal wastewater. Solmar is a customer-oriented service company providing excellent support for our products, with years of experience in bioremediation.

Southdown Environmental   1206
Systems, Inc.   1208/1210
1200 Smith St., Suite 2400
Houston, TX 77002
713/653-8043

Advanced Organics-Processing Technologies.

997

**Southern Bonding and
Insurance Brokers, Inc.** 2321
2540 Professional Rd., Suite 8
Richmond, VA 23235
804/320-8390

Southern Bonding and Insurance Brokers is an
agency established to service the needs of contractors and consultants working in the environmental
field. Unique experience and knowledge of the
specialized area of environmental liability and
risk management, provide our clients the opportunity to choose the product best suited to their
needs. Call (703) 525-8060 for more information.

**Southwest Laboratory
of Oklahoma** 0417
1700 West Albany - Ste. C
Broken Arrow, OK 74012
918/251-2858

Quality and service oriented laboratory offering:
CERCLA, SARA, RCRA, Priority Pollutants,
Dioxins/Furnas, Appendix IX, Explosives and
TCLP. SWLO is a full participant, in good standing, in the CLP program with contracts for organics, inorganics, and high concentration organics.
Also, certified by Corps of Engineers for explosives and DERA PROJECTS.

Southwest Research Institute 1615
6220 Culebra Rd.
San Antonio, TX 78228-0510
512/522-2687

Southwest Research Institute provides commercial leak location surveys of geomembrane liners
for landfills, impoundments, and lined tanks to
accurately locate leaks in the material and seams.
Analytical laboratory systems and techniques will
be presented for both the sampling and analysis of
environmental pollutants. Bio-degradation techniques will also be discussed.

**Specialized Environmental
Equipment, Inc.** 0809
311 Three & Twenty School Rd.
Easley, SC 29642
803/859-8277

Mobile Laboratories: Chemical Analysis Units,
Water Pollution Analysis Units, Decontamination
Units. Special Service Units: Emergency Preparedness Trailers. Flow-Thru Proportional Bioassay
Dilutor Systems; Dual Purpose Pumps; Water
Baths; Reactors; and Oxygen Demand Apparatus.

Staff Liners Industries 1417
240 Chene St.
Detroit, MI 48207
313/259-1818

Liners and Caps fabricated and installed worldwide for hazardous and non-hazardous sites.
RCRA and all Agency compliance. Forty (40)
hour OSHA trained and medical'd crews with
immediate response capability. 1910.120,134 All
materials - PVC, CPE, CSPE (Hypalon®, EIA (XR-5®), LDPE and HDPE. References. Call (800) 526-1368 or (303) 259-1820 for more information.
Our FAX number is (313) 259-0631.

Stearns and Wheler 1407
1 Remington Park Dr.
Cazenovia, NY 13035
315/655-8161

Stearns & Wheler is an environmental engineering and scientific consulting firm. With nearly 200
professionals and support personnel, the firm
offers services in property audits, petroleum engineering, hydrogeologic investigations, remedial
investigation/feasibility studies, remedial designs, industrial hygiene, and risk assessments.
Headquartered in Cazenovia, New York, the
branches are in Tampa, Florida, Darien, Connecticut, and Bedford, New Hampshire.

Stout Environmental, Inc. 1120/1122
101 Jessup Rd.
Thorofare, NJ 08086
609/384-8000

Stout Environmental, Inc., is a full service environmental management company providing treatment and disposal of hazardous, industrial, and
municipal wastes, along with a broad range of
specialized support services. Our 15 service divisions enable us to offer a turnkey approach to
environmental problems providing timely and
cost-effective solutions.

Sverdrup Corporation LDC
801 North Eleventh
St. Louis, MO 63101
314/436-7600

With over 60 years of providing total project management, Sverdrup Corporation continues to
maintain its status as one of the most diversified
companies in the industry. Our Environmental
Divisions continue to provide a growing list of
clientele with engineering services in the areas of
hazardous waste, wastewater treatment, ultrapure
water, and air quality control.

**Sybron Chemicals, Inc./
Biochemical Div.** 2007
P.O. Box 66
Birmingham Rd.
Birmingham, NJ 08011
609/893-1100

Leaders in the application of Augmented Bioreclamation (ABR) for the treatment of contaminated soil and groundwater. Capabilities include
biosystems engineering services and supply of
selectively adapted organisms for specific containments. Technology useful for cleanup of
chemicals from leaking storage tanks, pipeline
spills, train derailments, etc. Advantages are ultimate disposal technology and low cost.

TCT-St.Louis 2408
1908 Innerbelt Business Center Dr.
St. Louis, MO 63114
314/426-0880

TCT-St. Louis (formerly Envirodyne Engineers,
Inc.) is a consulting engineering firm and an analytical laboratory. Our certified laboratory offers
full service capabilities including: radioactive
waste analyses, dioxins/furans, explosives, Appendix VIII/IX, EP Toxicity, TCLP, Priority Pollutants, herbicides, and all conventional inorganic
parameters in wastewater, potable water, soil, air,
and biological matrices. Our engineering services
include site assessments, UST, treatability studies,

groundwater monitoring, RI/FS, design and construction oversight.

TERRA VAC LDC
P.O. Box 2199
Princeton, NJ 08543-2199
609/530-0003

Terra Vac is a subsurface remediation company
providing the full range of technologies, technical
expertise and construction services required for
the resolution of soil and groundwater contamination problems. Terra Vac's services are focused
on the definition and implementation of remedial
programs which utilize on-site technologies to
address subsurface contamination in situ.

TETRA TECH, INC. 1409
630 N. Rosemead Blvd.
Pasadena, CA 91107
818/449-6400

Tetra Tech is a consulting engineering firm with
expertise in designing and implementing environmental engineering projects for private industry
and government. Lines of business include environmental contamination assessment and
cleanup, and innovative engineering solutions for
facilities design, process automation, and waste
management. Current clients represent all sectors
of business and industry as well as federal, state,
and municipal government agencies.

TMS Analytical Services, Inc. 0104
7726 Moller Rd.
Indianapolis, IN 46268
317/875-5894

While specializing in Dioxin/Furan analysis, TMS
offers a full complement of environmental testing,
including those specified by EPA for drinking and
waste waters, air, and solid waste. State of the art
instrumentation includes GC, GC/MS, GC/MS/
MS, GC/HRMS, HPLC, AA, ICP, and IR with
computer interfaces.

**TMS, Inc.
c/o U.S. Department of Energy** LDC
20201 Century Blvd.
Germantown, MD 20874
301/353-0102

TechLaw, Inc. 1201
14500 Avion Parkway, Suite 300
Chantilly, VA 22021-1101
703/818-1000

TechLaw, an environmental consulting firm experienced in the application of legal and technical
principles to tasks in support of RCRA and CERCLA enforcement activities, provides services including: PRP searches, image based case management, computer tracking systems, evidence
audits, documentary inventory systems, legal research, full text databases, transactional data validation, environmental site assessments and compliance audits.

Technical Minerals, Inc. 1910
P.O. Drawer 23028
Jackson, MS 39225-3028
601/944-4758

Technical Minerals, Inc. (TMI) products are the
culmination of a technical approach to problem

solving which involves a unique mixture of proprietary processes and materials. Surface modified minerals from TMI have been specially designed for a broad line of environmental and industrial application.

Tekmar Company 1614
P.O. Box 371856
Cincinnati, OH 45222-1856
513/761-0633

(1) LSC 2000 Series of Purge and Trap/Dynamic Headspace Concentrator; (2) the Automatic Process Sampler samples up to six aqueous streams which may be monitored either sequentially or on a timed basis using an internal real time clock; and (3) Static Headspace System: the SHS 7000 offers an unprecedented approach to static headspace analysis that significantly increases throughput and reproducibility; whether using static headspace for screening or direct analysis, sample integrity is assured by Tekmar's superior product performance.

Thermo Analytical, Inc. 2003
5635 Jefferson Blvd., N.E.
Albuquerque, NM 87109
505/345-9931

Thermo Analytical Inc.'s (TMA's) network of laboratories provides a full range of analyses of environmental contaminants and radioactive materials in soil, water, air, industrial waste and other matrices. TMA laboratories have analytical capabilities for the detection of pesticides, herbicides, industrial solvents, PCBs, dioxins, asbestos, trace metals, and over 200 radionuclides.

**Thermo Environmental
Instruments, Inc.** 0609
8 West Forge Parkway
Franklin, MA 02038
508/520-0430

Thermo Environmental Instruments will display a complete line of portable instruments for the field measurement of toxic vapors and liquids, including the new Model 580B Portable Organic Vapor Meter (OVM).

Tigg Corporation 1205-1207
P.O. Box 11661
Pittsburgh, PA 15228
412/563-4300

Manufacturers of modular adsorbers designed for the remediation of vapor and water pollution. The combination of over 30 years of experience with adsorbents and systems provides unique capabilities of technical expertise and product availability to address specific remedial problems with the most appropriate technology.

Toney Drilling Supplies, Inc. 1301
14060 NW 19 Ave.
Miami, FL 33054
305/685-2453

Complete line of drilling equipment: New/used drill rigs, drill rods, subs and bits. Diamond bits, core barrels, mud and additives; augers, casing and plugs; stainless steel screens, PVC screens, points and pcaps; monitoring and sampling devices; safety clothing, masks, gloves and boots. Consultation and instruction are also available.

Tracer Research Corporation 1602
3855 North Business Center Dr.
Tucson, AZ 85705
602/888-9400

Tracer Research Corporation specializes in leak detection for underground storage tanks, bulk storage, above ground tanks and pipelines; Tracer technology for groundwater monitoring and landfill liner tightness testing; on-site detection of subsurface volatile organic contaminants (Soil Gas Analysis); full-service organic analysis laboratory services.

TreaTek, Inc. 1316
2801 Long Rd.
Grand Island, NY 14072
716/773-8661 or 800/833-3335

TreaTek is an environmental service subsidiary of Occidental Chemical Corporation, and has as its commercial objective the application of advanced microbial and chemical treatment technologies to the remediation of waste streams and containment soil. TreaTek can provide remedial consultation, laboratory treatability studies (biological, chemical & physical), analytical support, system design & specifications and turnkey project management.

Triangle Laboratories, Inc. 0212
801-10 Capitola Dr.
Research Triangle Park, NC 27713
919/544-5729

Triangle Laboratories, Inc. includes two employee-owned contract laboratories specializing in the analysis of organic compounds. Both laboratories offer high quality environmental analysis using EPA approved methods guaranteed by experienced scientists. The Research Triangle Park (NC) facility is nationally recognized for low detection analysis for polychlorinated dibenzo-p-dioxins and dibenzofurans.

**Trinity Environmental
Technologies, Inc.** 0103
6405 Metcalf, Suite 313
Overland Park, KS 66202
913/831-2290

EPA-approved destruction of PCBs in mineral oil dielectric fluid less than 18,000 ppm; EPA-approved destruction of PCBs in other oils less than 500 ppm (fuel, #2, and hydraulic oils); Disposal of PCB-contaminated water; Laboratory analysis for PCBs in oil, water, solids, surface wipes and air monitoring cartridges with fax reporting from our laboratory within 48-hours at no extra charge; PCB sampler/mailer kits for oil, water, solids and surface wipes.

**Troxler Electronic
Laboratories, Inc.** 0709
P.O. Box 12057
Research Triangle Park, NC 27709
919/549-8661

Troxler, the World's leader in depth moisture, surface moisture/density and sediment density technology, has developed a full line of gauges for the hazardous materials industry. Introducing this year, the Sentry 200. A permanently installed,

non-nuclear moisture gauge with the accuracy of our State-of-the-Art Neutron Probe.

U.S. Analytical Instruments 1416
1511 Industrial Rd.
San Carlos, CA 94070
415/595-8200

Available for rent and immediate delivery - HNU model 101s, Foxboro OVA 128GCs, and Photovac MicroTips from U.S. Analytical Instruments. In addition, USAI offers for rent or lease GC, HPLC, Fluorescence, UV/VIS, AA and ICP, IR and FTIR instrumentation from major manufacturers such as Hewlett-Packard, Perkin Elmer, Varian, Foxboro, and Waters. We offer flexible rental and purchase option plans designed to meet your financial and instrumentation needs.

U.S. Army Corps of Engineers 0407
P.O. Box 103, Downtown Station
Omaha, NE 68101
402/691-4532

The U.S. Army Corps of Engineers and the U.S. EPA have joined forces to clean up Federal lead hazardous waste sites under the Superfund program. The booth will be manned by Corps personnel to assist architect-engineer firms and construction contractors take advantage of work available to them through the Corps of Engineers.

**U.S. Army Toxic & Haz.
Mat. Agency** 2202
Bldg. E4460, Attn: CETHA-PA
Aberdeen Proving Ground, MD 21010-5401
301/671-2556

U.S. Bureau of Mines 1026/1028
2401 E Street NW, MS 6201
Washington, DC 6201
202/634-1224

The U.S. Bureau of Mines conducts research to help managers, consultants, and engineers better handle mining and minerals processing wastes. In addition, experts at the Bureau analyze the impact of existing and proposed regulations on sectors of the industry. Results of these efforts will be available through free technical publications and the Bureau's exhibit at Superfund '90.

U.S. Bureau of Reclamation 1018
Mail Code D-3800
P.O. Box 25007
Denver, CO 80225
303/236-8646

The U.S. Bureau of Reclamation provides Total Project Management in hazardous waste site cleanup-PA/SI, RI/FS, RD, RA, and O&M. Work may be completed for other government agencies in planning, designs, construction, construction oversight, reviews or research. Work has been completed under RCRA, Superfund, and Federal Facilities section of CERCLA.

U.S. DOE Five-Year Plan 2405
EM-2
1000 Independence Ave., S.W.
Washington, DC 20024
202/586-4373

This five-panel exhibit described the U.S. Department of Energy's Office of Environmental Resto-

ration and Waste Management's Five Year Plan. This plan was developed to set DOE's strategy and activities for cleaning up and restoring its nuclear research and production sites.

U.S. Environmental 2311-2320
Protection Agency 2311-2319
26 W. M.L. King Dr. & 2312-2320
Cincinnati, OH 45268
513/569-7522

The U.S. Environmental Protection Agency is responsible for developing regulations, implementing programs, and conducting research to carry out its mandate established in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA/Superfund) and other Hazardous Waste Management statutes.

U.S. Envirosearch, Inc. LDC
445 Union Blvd., Suite 225
Lakewood, CO 80228
303/980-6600

A nationwide recruiting firm based in Denver, Colorado, specializing in the recruitment of hazardous waste, environmental and incineration personnel. U.S. Envirosearch represents client companies in the areas of: hazardous waste disposal, site remediation, environmental engineering, analytical laboratories, environmental law, air quality, solvent recycling, PCB disposal, industrial cleaning and generators.

U.S. Geological Survey 1020-1024
12201 Sunrise Valley Dr. MS 790
Reston, VA 22092
703/648-4377

Panels depicting research and products of the U.S. Geological Survey dealing with earth sciences.

ULTROX INTERNATIONAL 2200
2435 S. Anne St.
Santa Ana, CA 92704
714/545-5557

The innovative ULTROX® process utilizes ultraviolet light with ozone and/or hydrogen peroxide to destroy toxic organic contaminants in groundwater, surface waters, wastewaters and leachate, on site. No sludges or wastes are generated requiring regeneration, disposal or incineration. UNTROX® is used as a stand alone treatment system and with other technologies.

URS Consultants, Inc. 1511
One Penn Plaza, Ste. 600
New York, NY 10119
212/736-4444

URS' multidisciplinary staff of engineers and scientists provides a full range of hazardous waste management services to governmental and private entities through its 25 offices nationally. Services include remedial investigations, feasibility studies, design of remedial actions, treatment system design, implementation of remedial actions, RCRA services, regulatory and permit support and litigation assistance.

USPCI, Inc. 0703/0705
515 West Greens Rd., Suite 500
Houston, TX 77067
713/775-7800

A full-service hazardous waste management

company. Services include laboratory analysis, transportation, treatment, remediation and disposal.

Union Carbide Industrial
Gases, Inc. 2216
39 Old Ridgebury Rd.
Danbury, CT 06817
203/794-5601

America's leading producer of industrial gases, including oxygen and nitrogen. The LINDE Oxygen Combustion System can safely double the capacity of your incinerator reducing CO excursions and auxiliary fuel consumption. See us to learn about recent Superfund installations.

University of Findlay LDC
1000 N. Main
Findlay, OH 45840
419/424-4540

Training and education provided in the areas of hazardous materials/waste, emergency response, spill response, confined space entry, asbestos removal, 40 hour OSHA, 8 hour OSHA and OSHA site supervisor training. Hands-on training facility. On-site training available upon arrangement.

VFL Technology Corporation 1007
42 Lloyd Ave.
Malvern, PA 19355
215/296-2233

VFL Technology Corporation is a civil/geotechnical construction firm specializing in the design and implementation of solutions to a variety of waste management problems. Services include soil/sludge solidification and stabilization, lagoon/landfill closures, hazardous site remediation, groundwater recovery and treatment, on-site treatment systems, excavation, treatment and disposal of contaminated materials on-site or off-site.

Vapex Environmental
Technologies, Inc. 1716
480 Neponset St.
Canton, MA 02021
617/821-5560

Vapex designs, installs, and operates high technology remediation systems for the cleanup of soil and groundwater. SOIL VAPOR EXTRACTION SYSTEMS FOR VOC SOIL TREATMENT: bench scale and field treatability testing; proprietary 3-D air flow modeling; chemical transport modeling; AIR SPARGING: for groundwater treatment; BIOVENTING: for treatment of semi-volatiles.

Versar Laboratories, Inc. 1213
6850 Versar Center, P.O. Box 1549
Springfield, VA 22151
703/750-3000

Versar Laboratories, Inc. provides comprehensive environmental analytical chemistry services. Capabilities include GC/MS, GC, AA, ICP, HPLC, Bioassay and various general chemistry techniques. Certified by USCOE-MRD, MMES and seven states.

Vesta Technology, Ltd. 0112
1670 West McNab Rd.
Fort Lauderdale, FL 33309
305/978-1300

Mobile On-Site Incineration Service.

Viar and Company, Inc. 1715
300 N. Lee St.
Alexandria, VA 22314
703/684-5678

Viar is an environmental sciences and systems development consulting firm of 250 providing program management and technical support to federal clients. Our services include: QA design/monitoring, data interpretation/validation; program budget, administrative and technical analyses; and all aspects of scientific, financial, and management information systems technology evaluations, design and development, and operational support services.

Vortec Corporation 1807
3770 Ridge Pike
Collegeville, PA 19426
215/489-2255

Vortec brings to the market a revolutionary new approach to solving hazardous waste disposal problems with its Advanced Vitrification/Incineration Process (AVIP). This system offers a new, modern alternative to standard and costly landfilling (in hazardous landfills) which is the current solution for disposal of most solid hazardous wastes.

WATERSAVER
COMPANY, INC. 1211
P.O. Box 16465
Denver, CO 80216
303/289-1818

Watersaver provides the world's most reliable membrane lining systems. Meet all state and federal regulations with Watersaver. Liners and closure caps for a wide variety of applications. Custom fabrication and installation of CSPE, CPER, PVC, XR-5, and others. Continuous service for over 30 years.

WSOS Community Action
Commission, Inc. LDC
P.O. Box 590, 109 South Front St.
Fremont, OH 43420
419/334-8911

WSOS provides head start programs, services for senior citizens, housing and energy programs, food services, outreach services, economic and community development, employment and training programs and environmental programs.

Wadsworth/ALERT
Laboratories, Inc. 1111
4101 Shuffel Dr. N.W.
North Canton, OH 44720
216/497-9396

Laboratory services for environmental and industrial hygiene markets. Analysis of soil/sediment, sludge/waste, and water and air, using state of the

art equipment, including GC/MS, GC, HPLC, AA, ICP, TOX, TOC and IR. Facilities include fixed location and mobile laboratories.

**Waste Abatement
Technology, Inc. (WATEC)**   0513
1300 Williams Dr.
Marietta, GA 30066
404/427-1947

Waste Abatement Technology, Inc. (WATEC), provides a full range of remediation services including: excavation of contaminated soils, waste deposits and drums; drum handling, characterization and removal; industrial UST remediation; surface impoundment closure-in-place stabilization, sludge removal and dewatering; water treatment (process, surface and groundwater); building decontamination; on-site treatment - physical, chemical, biological; transportation and disposal. WATEC, in both the public and private sector, has consistently demonstrated its ability to compete for and then carry projects to successful completion. This success is attributed to our staff of professionals and technicians who are well respected in the hazardous waste cleanup industry and our corporate commitment of placing senior level professionals in charge of site operations. These individuals, combined with our desire to excel in project execution, form the foundation for our record of innovative and successful project completion. WATEC's Marietta, Georgia, location can service sites nationwide. Additionally, we augment our capabilities through staff and services provided to us by our sister company, ATEC Associates, Inc., and its 45 offices.

Waste-Tech Services, Inc.   2409
800 Jefferson County Pkwy.
Golden, CO 80401
303/279-9712

Waste-Tech Services, Inc. (WTS), an affiliate of Amoco Oil Company, is "Making a Difference" in hazardous waste management through the application of proven and innovative technologies in the areas of thermal destruction and waste minimization. WTS offers services from design through operations. Let WTS make your difference!

Water Pollution Control Federation   LDC
601 Wythe St.
Alexandria, VA 22314-1994
703/684-2400

The Water Pollution Control Federation is a technical, professional organization of 36,000 members from Member Associations and affiliated associations throughout the world. Dedicated to "preserving and enhancing water quality worldwide," the WPCF offers more than 80 publications, 8 periodicals, educational training materials, a water curriculum program for schoolchildren, public education materials, career information, safety & health videos, and technical services.

Wayne Associates, Inc.   2001
2628 Barrett St.
Virginia Beach, VA 23452
804/340-0555

We are one of the oldest and largest specialized

recruiting firms serving the hazardous waste industry (since 1978). Our services include both retained contract and contingency search and our expertise covers all areas of the Hazwaste & Environmental market. We effectively service a nationwide client base. Stop by booth 2001 to discuss to discuss your company's needs or to investigate career alternatives.

Well Safe, Inc.   0913-0914
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Richmond, TX 77469
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Hazardous Waste, Petro-Chemical Industry and Oil & Gas Drilling and Production Safety Services. Specializing in on-site breathing air, breathing apparatus, instrumentation, on-site safety supervisors and decontamination services.

Westates Carbon, Inc.   0108
2130 Leo Ave.
Los Angeles, CA 90040
213/722-7500

Westates specializes in activated carbons, water and air pollution control equipment, solvent recovery, odor and corrosion control, precious metal recovery and custom engineered systems. Westates maintains a complete in-house laboratory for quality assurance, carbon testing and evaluation. Sales and service offices in Los Angeles, Oakland, Cincinnati, Houston and New York.

Westbay Instruments Inc.   0305
507 E. Third St.
North Vancouver, BC V7L 1G4
604/984-4215

Westbay manufactures and markets the MP System which allows multi-level groundwater monitoring in a single drillhole. This system reduces project costs and time related to drilling while improving filed quality control. In addition, water sampling with the MP System is achieved without repeated purging, thereby reducing operating costs. For more information, dial (800) 663-8770 (in U.S.).

**Westinghouse Environmental
Systems and Services**   1411/1413
875 Greentree Rd., Bldg. 5, 1st Floor
Pittsburgh, PA 15220
412/937-4061

Westinghouse offers a full range of environmental assessment and engineering approaches, environmental remediation, and hazardous waste treatment, storage and disposal services. Employing the best available technologies at TSD facilities in Minnesota, Kansas and Utah, Westinghouse helps clients deal effectively with stringent environmental requirements for disposing of wastes regulated under TSCA, RCRA and CERCLA.

**Williams Environmental
Services, Inc.**   LDC
1530 Alabama St.
Auburn, AL 36830
205/821-9250

Williams Environmental Services, Inc., does on-

site remediation using mobile equipment, primarily thermal processing, volume reduction and stabilization of hazardous waste.

Wilson Laboratories   0208
525 N. 8th St.
Salina, KS 67401
913/825-7186

Wilson Laboratories provides accurate and timely analytical services to industry, governmental agencies, municipalities and private consultants. Our services include: groundwater, waste water, and drinking water analysis; toxic and hazardous waste analysis for inorganics, organics and PCBs in various matrices.

Woodward-Clyde Consultants   1911
4582 S. Ulster St., Ste. 600
Denver, CO 80237
303/740-2600

Woodward-Clyde Consultants is a professional services firm with over 30 years of experience in geotechnical engineering, environmental, and social sciences. In hazardous waste, we offer total management solutions, from evaluation, permitting and initial investigation through design, construction, and remedial action. Our scientists and engineers represent all disciplines necessary to provide complete services - the earth, physical, and natural sciences as well as environmental, chemical and geotechnical engineering. With offices in 45 cities, we are staffed and positioned to offer nationwide management programs that are both comprehensive and responsive.

Worne Biotechnology, Inc.   0107
1507 U.S. Route 206
Mt. Holly, NJ 08060
609/261-5550

Worne Biotechnology, Inc., is a biotechnology company providing professional environmental and biological consulting services to both government and industry for the biological detoxification of hazardous and toxic organic wastes throughout North America, South America and Asia. WBI uses laboratory remediation studies coupled with environmental analysis, hydrology and feasibility evaluation to define environmental projects and integrates biotechnology with regulatory requirements to solve enviromental problems. WBI high rate biological reactors for industrial wastewater treatment and develops highly effective microbial ecosystems for these reactors to remove recalcitrant halogenated and non-halogenated organic wastes from municipal, agricultural and industrial waste streams.

**Youngstown Barrel &
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Zimpro/Passavant is the developer of the PACT® wastewater treatment system, and wet air oxidation. Used in tandem, or singly, they are effective technologies for treating hazardous wastewaters and sludges, including process discharges, contaminated groundwater of surface runoff, landfill leachates. Portable units, factory-built skid-mounted plants, field-erected systems. Treatability studies and complete analytical laboratory capabilities.

Author Index
1980-1990

Subject Index
1980-1990