United States Environmental Protection Agency Robert S. Kerr Environmental Research Laboratory Ada, OK 74820 EPA/600/R-92/002 January 1992

Research and Development

€PA

General Methods for Remedial Operation Performance Evaluations

General Methods for Remedial Operations Performance Evaluations

Project Officer

Randall R. Ross Extramural Activities and Assistance Division

Robert S. Kerr Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820

Notice

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement No. CR-812808 to the National Center for Ground-Water Research. It has been subjected to the Agency's peer review and administrative review, and it has been approved for publication as an EPA document. The material presented in this document was extracted and edited by R.R. Ross and J.W. Keeley from a report entitled "Remedial Operations Performance Evaluation Methodologies," written by Dr. J.F. Keely for EPA.

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve environmentally related measurements and did not involve a Quality Assurance Project Plan. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Foreword

EPA is charged by Congress to protect the nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the oil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to soil and subsurface environment, for the protection of this resource.

The pump-and-treat process, whereby contaminated ground water is pumped to the surface for treatment, is one of the most common ground-water remediation technologies used at hazardous waste sites. In fact, pump and treat is a necessary component of practically all ground water remediation systems, whether for restoration or for plume containment. However, recent research has identified complex chemical and physical interactions between contaminants and the subsurface media which may impose limitations on the extraction part of the process. This has raised questions about the effectiveness of ground water restoration systems and methods for evaluating that effectiveness. This report was developed to summarize the technical considerations involved in evaluating the performance of ground-water remediation activities.

Clinton W. Hall Director Robert S. Kerr Environmental Research Laboratory

Table of Contents

| FIGUI | RES | iv |
|-------|--|----------|
| TABL | ES | iv |
| SUMN | MARY | v |
| I. | INTRODUCTION | 1 |
| | Source Characteristics | |
| | Hydrogeologic Complexities | |
| | Man-made Complexities | |
| | Pump-and-Treat Limitations | |
| | Innovations in Pump-and-Treat | 5 |
| II. | COMPONENTS OF PERFORMANCE EVALUATIONS | |
| | Performance Evaluation Strategies | |
| | 1. Locations for Plume Monitoring | |
| | 2. Monitoring Criteria for Performance Evaluations | |
| | 3. Strategies for Monitoring Locations and Criteria | |
| | 4. Measures of Operational Effectiveness | |
| | 5. Measures of Operational Efficiency | |
| | 6. Strategies for Determination of Success/Closure | |
| | Data Collection Considerations | |
| | 1. Purposes of Data Collection | |
| | 2. Relevant Scale(s) of the Problem | |
| | 3. Actual Scale of the Measurements | |
| | 4. Data Quality vs. Quantity | |
| | Hydrogeologic Data | |
| | 1. Topographic and Geographic Data | |
| | 2. Geomorphologic and Geologic Data | |
| | 3. Flow Rates | |
| | 4. Hydraulic Parameters | |
| | 5. Fluid-Behavior Data | |
| | 6. Fluid Levels and Pressures | |
| | Chemical and Geochemical Data | |
| | 1. Natural Ground-Water Chemistry Data | |
| | Soil Chemistry Data Contaminant Production Data | |
| | 3. Contaminant Reaction Data | |
| | Biological Data Quality Assurance and Quality Control Data | |
| | | 0.1 |
| III. | METHODS AND PROTOCOLS | |
| | Performance Evaluation Methods | |
| | 1. Computational Methods | |
| | Statistical Methods Graphical Mathods | |
| | Graphical Methods Theoretical | |
| | 4. Theorem and the second seco | |
| | 1. General Protocol for Selection of Monitoring Criteria and Reporting Requirements | |
| | General Protocol for Violations Reporting and Responses | |
| | General Protocols for Design and Operation Modifications | 28 29 |
| | | 29 |
| | | |

| REFERENCES | 30 |
|------------|----|
|------------|----|

List of Figures

| Figure 1. | Pump-and-treat limitations may result in the rebound of | |
|------------|--|----|
| C | contaminant concentrations after the termination of pumping | 3 |
| Figure 2. | Flow velocities developed during pumping may limit | |
| - | desorption of contaminants and prevent removal of maximum concentrations | 4 |
| Figure 3. | Site characterization efforts should be conducted throughout | |
| • | the RI/FS process to allow data refinement during assessment and remediation | 6 |
| Figure 4. | Possible monitoring point locations in a ground-water | |
| • | contamination plume undergoing pump-and-treat remediation | 8 |
| Figure 5. | Concentration vs. time data plot and multiple regression line with | |
| - | confidence bounds for judging persistence of the clean-up | 13 |
| Figure 6. | The results of contouring a dataset by various mathematical | |
| - | techniques may be significantly different | 24 |
| Figure 7. | Pattern diagram for selected VOCs | 24 |
| Figure 8. | PERT Chart illustrating interdependency of tasks to produce outputs | 25 |
| Figure 9. | Outline of key efforts needed to select and use monitoring and | |
| • | reporting requirements | 27 |
| Figure 10. | Key efforts needed to identify, verify, and correct inadequate | |
| • | performance of the remediation | 28 |
| Figure 11. | Key efforts needed to prepare for, implement, and | |
| - | verify modifications of the remediation | 29 |

List of Tables

| 1. | Useful Statistical Methods for Performance Evaluations | |
|----|--|----|
| | Analysis of Variance (ANOVA) Techniques | 23 |

Summary

This document was developed by an EPA-funded project to explain technical considerations and principles necessary to evaluate the performance of ground-water contamination remediations at hazardous waste sites. This is neither a "cookbook," nor an encyclopedia of recommended field, laboratory, and data interpretation methods. Rather, this report presents and discusses suggested generic principles for formulating site-specific performance evaluation strategies for ground-water contamination remediations.

It is widely accepted that ground-water contamination problems cannot be adequately defined or addressed until the governing physical, chemical, and biological processes which affect the fate and transport of contaminants are characterized in detail. Recent research has led to a better understanding of these complex processes and how they control the movement of contaminated ground water through the subsurface. This research has demonstrated that pump-and-treat remediations are far more complicated than previously thought . Many of the complications result from the tortuosity of the ground-water flowlines that are generated by the remediation wellfield and the re-distribution of contaminant pathways that occurs. An immediate consequence of this re-distribution is that historical trends of contaminant concentrations at local monitoring wells may no longer be useful for predictions and evaluations regarding the growth or reduction of the contaminant plume. Further, the pattern of flow velocities and directions that resulted from the remediation wellfield may change substantially over time, thus complicating attempts to evaluate the progress of the pump-and-treat remediation.

The increased ground-water flow velocities created by remediation wellfields may also introduce significant hydrodynamic and chemical limitations to contaminant transport and subsequent remediation locally. Such limitations include hydrodynamic isolation of portions of remediation wellfields, diffusively restricted movement of contaminants in lowpermeability subsurface materials, and failure to meet local chemical equilibrium requirements for maximal desorption and liquid-liquid partitioning. For each well that is utilized to remove fluids from the subsurface, there is a stagnation zone downgradient where contaminants do not receive active flushing while the well is pumping. Everywhere that water levels have been lowered by the action of the remediation wellfield, there are sediments that may release additional contaminants upon cessation of pumping and return of the water levels to normal levels. Throughout the sediments that overlie and comprise the contaminanted aquifer there may be inclusions of low-permeability sediments. Such inclusions may act as longterm contaminant reservoirs which release contaminants much more slowly (often, by diffusion only) than the surrounding sediments where the vast majority of the ground water flows. The presence of nonaqueous phase liquids (NAPLs) may represent one of the most significant limitations to pump-and-treat remediations. These immiscible liquids may leave a trail of residual contaminants, trapped by capillary forces, as they move through the unsaturated and saturated zones. This residual contaminant mass may serve as a long term source of ground-water contamination. Proper site-specific characterizations of these limitations are essential in evaluating the performance of pump-and-treat remediation systems.

Emphasis is given to the need to develop a monitoring strategy at each site which ensures that sampling locations and schedules are meaningful, not only as early-warning alarm systems, but in measuring progress toward remediation goals and to make adjustments to improve performance. Emphasis is also given to the use of data reduction, presentation, and interpretation techniques that may be used in evaluating the performance of the remediation. These nominally include ground-water flow and contaminant transport models, statistical analyses, graphical techniques, and theoretical relationships.

The optimal effectiveness (extent and uniformity of cleansing) and efficiency (minimization of costs and duration) of a remediation can often be obtained by managing the pump-and-treat system in terms of flowrates and extraction locations in response to reductions in contaminant mass in portions of the plume. Active management of this kind must be supported by the continuous gathering of key site characterization data.

I. Introduction

Ground-water pump-and-treat systems are the most common remedial technology used to remediate and/or contain ground-water contaminants at hazardous waste sites. Pump-and-treat remedial actions involve the extraction of contaminated ground water and subsequent treatment for contaminant removal. This report presents a review of the factors and subsurface processes which may affect the performance of pump-and-treat remediations. Also discussed are the basic components of performance evaluations, and suggested methods and protocols for evaluating performance. It is assumed that the reader is familiar with the basic concepts of hydrogeology. For additional information refer to U.S. EPA, 1989a, 1989b, and Mercer and others, 1990.

Pump-and-treat remediations are planned or have been initiated at many ground-water contamination sites across the country. Regulatory responsibilities require that adequate oversight of these remediations be made to answer the question: What can be done to demonstrate whether or not a remediation is generating the desired control?

Recently, other questions have evolved with the realization that many pump-and-treat remediations are not functioning as well as had been expected:

- 1. What can be done to determine whether or not the remediation will meet its proposed timelines? and,
- 2. What can be done to determine whether or not the remediation will stay within budget?

It may be possible to better answer these questions with the aid of sophisticated data analysis tools, such as computerized mathematical models of ground-water flow and contaminant transport.

Computer models can be used to make predictions about future performance, but the results are highly dependent on the quantity and quality of field and laboratory data utilized. This is also true of models used for ongoing performance evaluations of pump-and-treat remediations. They must be supported by detailed site information that is continually updated. In most instances, an accurate performance evaluation cannot be made simply by comparing data obtained from monitoring wells during remediation to the water quality data generated prior to the onset of remediation. Historical trends of contaminant levels at local monitoring wells are often not useful for comparisons with data obtained during the operation of pump-and-treat remediations. This is a consequence of the complex ground-water flow patterns produced by extraction and injection wells as compared to the relatively simple natural flowlines.

Detailed field investigations are required during remediation to determine the locations of flowlines generated by a pump-and-treat operation. It is likely that mathematical and statistical models will be required to organize and analyze this data. Ongoing site characterization efforts must include examinations of the contaminant source characteristics, the local and regional hydrogeologic complexities, contaminant-specific behavior and plume dynamics.

Source Characteristics

There are many potential sources of ground-water contamination at hazardous waste sites. These may be categorized as either "point" or "nonpoint" sources, depending on their geometry, and generally are engineered structures with recognizable physical boundaries. Some may release significant volumes of contaminants to the environment during their operating history. Pits, ponds, and lagoons, for example, constructed without lined bottoms or sides are notorious for large fluid losses. Industrial and municipal landfills are point sources that tend to generate leachate by chemical reactions of the waste with infiltrating precipitation. Such leachate very often contains high concentrations of dissolved metals, inorganic salts, and organic chemicals.

Historically, shallow injection wells have been used to dispose of untreated stormwaters from city streets, parking lots, highways, and airports and represent the most direct avenue of contaminant introduction to ground water. Deep injection wells continue to be used for the disposal of liquid industrial waste. Point sources of ground-water contamination also include leaks and spills at manufacturing facilities such as refineries, pharmaceutical plants, fertilizer plants, and other chemical production plants. Leaking underground storage tanks and associated piping at gasoline service stations and fuel depots also pose a serious point source contamination problem. Some point sources, such as abandoned wells, are very small and particularly difficult to locate; whereas other point sources, such as mining operations or municipal and industrial landspreading operations are readily located, but their large size makes identification of specific points of contaminant releases difficult.

The more commonly recognized nonpoint sources of ground-water contamination include agricultural applications of fertilizers, herbicides, and pesticides. Other traditional practices and activities that may result in widespread releases of contaminants to underlying ground water include the application (and storage) of salts to streets and highways for winter de-icing, and the spraying of waste-oils on unpaved roads for dust suppression. Small spills that typically occur during dispensing or refilling operations at transfer points and storage locations often go unnoticed or are ignored because of their minor size. The aggregate effect of many small spills may be equivalent to a non-point source of contaminant releases to the underlying ground water. It is generally easier to identify, control, and eliminate point sources than nonpoint sources. The control of nonpoint sources is often limited to prevention or restriction of the activities which generate the contaminant.

The mechanism by which sources introduce contaminants to ground water has a profound effect on the duration and areal extent of the resulting contamination. The duration of a source release may affect the extent of contamination. For example, a small spill at the surface may be attenuated over a short distance while contaminants introduced below the surface, such as leaking tanks and pipelines, will have much less attenuation. The hydraulic impacts of such sources may impart a three-dimensional character to the local groundwater flow regime. Interactions with streams and other surface water bodies may also impart three-dimensional flow characteristics to contaminated ground water.

In ideal settings, the design of a pump-and-treat system might be limited to the configuration of the extraction/ injection wellfield and the flowrates of the individual wells. Unfortunately, there are few natural settings that appear to be ideal at the scale of interest in pump-and-treat remediations. Karst and fractured rock aquifers frequently exhibit highly complex flow and contaminant transport behaviors, as do many interbedded sand-and-gravel aquifers (e.g., diffusively restricted flow in silt and clay strata) (Barker and others, 1988; Feenstra and others, 1984; Spayed, 1985; White, 1988). The general physiographic setting may also be highly restrictive to pump-and-treat remediation, such as in wetlands and wildlife sanctuaries.

The properties and size of the contaminant source and resulting plume are also key features of the remedial action setting. The amount of contaminant that may be readily removed by pump-and-treat remediation in a reasonable amount of time may be only a small portion of what is in the subsurface (Hossain and Corapcioglu, 1988; Hunt and others, 1988a and 1988b; Keely and others, 1986; Stover, 1989; Testa and Paczkowski, 1989).

Hydrogeologic Complexities

The geologic processes that shape the surface of the earth are so varied it is easy to understand why most aquifers do not exist as a single horizontal stratum of uniform composition and thickness. As a result, the hydraulic impact of extraction wells is often distorted, and if this occurs in the zone of remediation, the system may not be as effective as anticipated and additional pumping might be required. By examining some of the more common hydrogeologic complexities, it may be possible to anticipate these additional requirements and account for them in the system design.

Some of the most complex hydrogeologic settings for pump-and-treat remediations are those that involve the contamination of zones of low-permeability. These formations can be categorized as active aquifers, despite very low yields and high drawdowns. Remediations in these types of settings may be further complicated by the presence of limited occurrences of high permeability sediments, such as sand and gravel, or fractures.

Pump-and-treat remediation in low-permeability formations may be limited because yields are too low to allow continuous pumping. Extraction wells may be designed to operate on demand or, in some cases, it may be possible to maintain continuous pumping by providing recharge over the capture zone of each well.

Minor pump-and-treat problems can also be found in highpermeability formations. Flow net complications can result from the minor occurrence of low-permeability strata. For example, in formations such as alluvial floodplains and glacial outwash deposits, it is common to find thin clay and silt lenses extending tens to hundreds of feet in the direction of flow.

In some geologic settings, most of the ground-water flow occurs through fractures in low-permeability rock formations (Barker and others, 1988; Feenstra and others, 1984; Spayed, 1985). Contaminant movement through fractures may be primarily controlled by advective forces. However, flow through the bulk matrix of many rocks is so slow that contaminant movement may be dominated by molecular diffusion.

Extensively fractured rock may exhibit hydraulic behavior similar to porous media. In fractured rock aquifers characterized by a very high degree of fracturing, many of the equations developed for porous media may be applied with reasonable confidence for the design of remediation wellfields (Bear and Verruijt, 1987; de Marsily, 1986; Mercer and Faust, 1981). When only a few fractures dominate flow, the relationship of flowrate to drawdown may be highly nonlinear and unpredictable. Equations have been developed which allow prediction of drawdowns for situations where a single horizontal fracture or a single vertical fracture passes through a pumping well, but there are no generically useful equations for multi-borehole or multi-fracture situations. The usual design approach for systems dominated by discrete fractures is to try to position each extraction well such that it intersects as many fractures as possible. In such cases it will probably be necessary to conduct several pilot tests of extraction wells to develop site-specific relationships of flowrate to drawdown. Such empirical relationships may be highly nonlinear as a result of changes in the fracture aperture during pumping due to nonuniform drainage along the fracture face and the siphoning effects of irregular fractures. In settings where the flowrate-drawdown relationship at one extraction well differs markedly from that of another, the wellfield design strategy must default to well-by-well installation and testing. Each extraction well should be tested singly, and in concert with existing extraction wells to determine the short-term effectiveness in providing the desired gradient control. Supplementary extraction wells may be necessary where additional control is needed.

Similar considerations and measures may be required for hazardous waste sites located in karst terrains. Two flow regimes, open-channel and pipe flow, occur in karst settings that rarely occur elsewhere in the subsurface (White, 1988). Because of these complexities, advection and dispersion of contaminants through karst aquifers are not adequately describable by Darcy's Law and other porous media concepts.

It has been shown that streams and springs control the flow through karst terrain. Although dye tracers have proven useful in studying fluid movement in karst aquifers, such studies have not yielded relationships that can be transferred from one site to another. While it may seem reasonable to locate extraction wells on the basis of intersecting karst streams, one should not expect a consistent response as the drawdown and flowrate may vary substantially over short periods of time.

Man-made Complexities

It is not uncommon for the construction of extraction wells to be hampered by buried tanks and utility lines, streets, sewers, and water and gas pipes. Railroads, canals, and power transmission lines can present similar location difficulties as well as add safety hazards. This lack of access can create major difficulties for pump-and-treat remediations, not only from the standpoint of well locations, but the required piping network as well.

Seasonally operated pumps and on-demand pumping may produce unanticipated hydraulic impacts locally. If a pumpand-treat remedy is designed without the knowledge of local pumping wells, it may not overcome the hydraulic impact sufficiently to maintain effective containment of contaminants (Keely, 1984; Keely and Tsang, 1983; Ward and others, 1987). Potential failure of the remediation by this avenue is unlikely to be recognized unless hydrodynamic monitoring is instituted for both horizontal and vertical gradient control.

Drilling restrictions may be in effect for other purposes such as water conservation, water rights, or to minimize upconing of saline water. Fortunately, many institutional controls are negotiable, particularly if the potential impacts of operation of a pump-and-treat remediation can be shown to be controllable or of only a temporary nature.

Pump-and-Treat Limitations

Conventional pump-and-treat remediations are based on the operation of extraction and injection wells. The level of contamination measured at monitoring wells may be greatly reduced in a moderate period of time, but low levels of contamination may persist indefinitely. The contaminant mass removed may decline over time and gradually approach a residual level in the latter stages (Figure 1). At that point, large volumes of water are treated to remove small amounts of contaminants. Depending on contaminant residuals within the aquifer, this may cause a remediation to be continued indefinitely. An increase in ground-water contaminant levels may follow if the remediation is discontinued prior to removal of all residual contaminants. Several contaminant transport processes are potentially responsible for the contaminant rebound effects and may include:

- (1) diffusion of contaminants in low-permeability sediments,
- (2) hydrodynamic isolation within wellfields,
- (3) desorption of contaminants from sediments, and
- (4) partitioning of immiscible fluids into ground water.

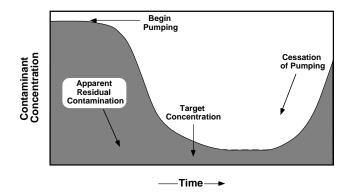


Figure 1. Pump-and-treat limitations may result in the rebound of contaminant concentrations after the termination of pumping (after Keely, 1989).

Local variations in ground-water flow results from the heterogeneous nature of interlayered high-permeability and low-permeability sediments (Anderson, 1979; Guven and Molz, 1986; Keelv, 1984; Keelv and others, 1986; Matheron and de Marsily, 1980; Molz and others, 1986 and 1988; Osiensky and others, 1984; Satlin and Bedient, 1988). When operating a remediation wellfield, these variations in flow may result in relatively rapid cleansing of the higherpermeability sediments, which may conduct most groundwater flow. Contaminants are removed from the lowerpermeability sediments very slowly primarily by diffusion. The specific rate at which this diffusive release occurs is dependent on the concentration gradient within and external to the low-permeability sediments. As the higherpermeability sediments are remediated, the concentration gradient drawing contaminants from the lower-permeability sediments is at its greatest and is exhausted only when the chemical concentrations are at equilibrium.

Fine-grained sediments generally have lower permeabilities and orders-of-magnitude greater surface areas than coarsegrained sediments (Bitton and Gerba, 1984; Corey, 1977; Hillel, 1982; Keely and others, 1986; Mackay and others, 1986; Piwoni and Banerjee, 1989). Much greater amounts of contaminants may accumulate in low-permeability sediments by adsorption, ion-exchange, or other surface chemical processes as compared with contaminant accumulations in a like volume of high-permeability sediments (Bouchard and others, 1989; Enfield and Bengtsson, 1988). The occurrence of low-permeability materials in higher-permeability formations may be a major limitation to pump-and-treat remediations. Diffusive transport of contaminants from the low-permeability stratum to the surrounding high-permeability formation may dictate the time necessary for complete remediation.

If substantial occurrences of low-permeability materials are adequately characterized it may be possible to target these selectively during the pump-and-treat remediation for excavation, in-situ soil washing, hydrofracturing, or other remedial methods. However, if low-permeability materials occur as heterogeneously distributed microstrata that defy physical removal or in-situ treatment, conventional pumpand-treat technologies may be implemented for the containment of ground-water contaminants, rather than remediation.

The operation of any wellfield results in the formation of hydrodynamically isolated stagnation zones downgradient of extraction wells and upgradient of injection wells. Mass transport into or out of the isolated zone occurs mainly by diffusion. Remedial action wells located within the bounds of a contaminant plume may have stagnation zones which are not effectively remediated. Flowline patterns must be altered by changing the locations of pumping wells, or by altering the balance of flowrates among pumping wells to remediate the stagnation zones.

Adsorption and desorption of organic chemicals by sediments are not always instantaneous processes as hundreds of hours may be required for certain compounds to reach chemical equilibrium (Bahr, 1989; Bouchard and others, 1988; Brusseau and others, 1989; Curtis and others, 1986; Goltz and Roberts, 1986 and 1988; Lee and others, 1988; Mackay and others, 1986; Miller and others, 1985; Nkedi-Kizza and others, 1985; Piwoni and Banerjee, 1989; Valocchi, 1988; Woodburn and others, 1986). When a pump-and-treat remediation is implemented, ground-water flow velocities will be significantly increased and it may not be possible for passing ground water to achieve or maintain chemical equilibrium with the contaminants (Figure 2). Consequently, large volumes of mildly contaminated water may be produced over a long period of time.

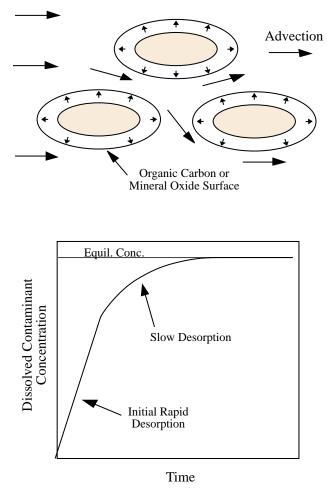


Figure 2. Flow velocities developed during pumping may limit desorption of contaminants and prevent removal of maximum concentrations (after Keely, 1989).

Immiscible, or nonaqueous phase liquids (NAPL), may impose significant limitations on pump-and-treat remediations. NAPLs are characterized as either light (LNAPL) or dense (DNAPL) with respect to their density relative to that of water. LNAPLs, often referred to as "floaters," may accumulate at the top of the saturated zone while DNAPLs, often referred to as "sinkers," are capable of moving vertically through the unsaturated zone and portions of the saturated zone.

Both light and dense immiscible liquids are subject to capillary forces of sediments which may retain or trap portions of the liquid in pore spaces (Huling and Weaver, 1991: Faust, 1985; Hinchee and Reisinger, 1987; Hunt and others, 1988a and 1988b; Stover, 1989; Taylor, 1987). This may be particularly troublesome when an extraction well is utilized when a continuous phase (free product) LNAPL is present as both the water and free product flow into the cone of depression. The cone of depression may contain a significant volume of trapped residual contaminant below the water-table, which will serve as a continuous contaminant source long after the extraction well stops operating. The extent of contamination generated by the residual contaminant source may exceed that generated by the LNAPL pool prior to the onset of pumping.

Contaminant plumes composed of components of an immiscible liquid are generated by the dissolution of the NAPL into adjacent ground water, according to liquid-liquid partitioning principles (Hunt and others, 1988a and 1988b; Stover, 1989; Stumm and Morgan, 1981). Generally, the lower the solubility, the slower the dissolution rate (Stumm and Morgan, 1981; Weast, 1985). In many instances involving pump-and-treat remediations, the contact time between ground water and immiscible fluids may be too short to allow maximum concentrations to develop. Analogous to the limitation posed by slow chemical equilibrium for some adsorptive contaminants, pumpinginduced limitation of liquid partitioning will generate large volumes of mildly contaminated water under continuous operation of the remediation wellfield.

There is evidence that DNAPLs are present at many hazardous waste sites but they may largely go undetected due to the numerous variables influencing their transport and fate. As a result, the presence of DNAPLs may be a limiting factor to ground-water pump-and-treat remediations.

Innovations in Pump-and-Treat

To minimize the potential for poor contaminant removal rates, innovative pumping strategies may be required. These involve reconfiguring the remediation wellfield, adopting unconventional pumping schedules, or integrating pumping with other remediation technologies such as subsurface barrier walls.

One innovation in pump-and-treat remediations is pulsed pumping. Pulsed operation of hydraulic systems is the cycling of extraction or injection wells in active and resting phases. The resting phase of a pulsed-pumping operation may allow sufficient time for contaminants to diffuse out of low-permeability zones into adjacent high-permeability zones and allow sorbed contaminants and NAPL residuals sufficient time to reach equilibrium. Subsequent pumping then removes maximum contaminants in a minimum volume. Pulsed pumping will also bring zones of stagnation into active flowpaths.

Other methods to enhance the efficiency of ground-water remediations currently being pursued include the use of surfactants, biorestoration, fracture enhancement, and physical containment.

II. Components of Performance Evaluations

Performance Evaluation Strategies

Performance evaluations of remedial actions may be conducted at hazardous waste sites for a variety of reasons. One of the most common reasons is to satisfy the monitoring requirements established by negotiated or court settlements, thus ensuring that the desired controls on ground-water flow and contaminant transport are maintained. Another reason may be to determine if the remedial action objectives can be accomplished using the selected remedial action alternative(s). The strategy adopted for conducting a performance evaluation must focus on the kinds of data that will be collected and how those data will be presented for interpretation and decision making purposes. It is best to start building a strategy, therefore, by examining the data collection studies that have been done in the past at a site.

The phases of work conducted in site investigations follow a pattern of increasing detail and focus (Figure 3). This can be viewed as a continuous data collection program that may be extended into the remediation phase to benefit oversight monitoring and operational management purposes alike. In the Superfund site investigation process, the preliminary assessment phase involves collection of readily obtainable information which may include technical data for a screening-level assessment of the potential need for further investigation. Where the preliminary assessment indicates a need for additional characterization, the next phase of work

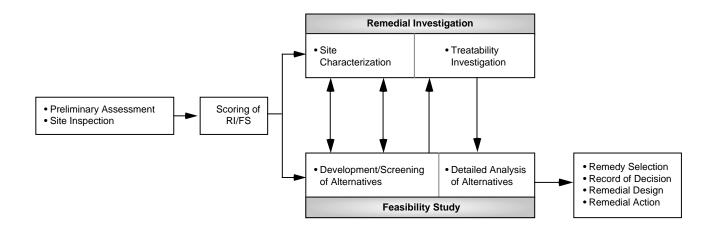


Figure 3. Site characterization efforts should be conducted throughout the RI/FS process to allow data refinement during assessment and remediation.

most often consists of site visits for visual appraisal and limited sampling.

If these additional efforts indicate the need for further characterization, then a preliminary assessment/site investigation (PA/SI) is performed and the data used to score the site using the Hazardous Ranking System. This score determines whether the site will be listed on the NPL and, consequently, whether Superfund resources can be utilized. If so, a remedial investigation and feasibility study (RI/FS) are undertaken. The remedial investigation is a focused field and laboratory study of the distribution of contaminants and potential transport and exposure pathways. The feasibility study is a detailed examination of the remedial action alternatives (U.S. EPA, 1988a).

The data collected during the RI/FS, including treatability studies if warranted, should be such that the remediation selection decision is supported and that pertinent parameters can be determined including pumping rates, the number and location of extraction wells, and other remediation features. In some cases, however, additional information may be required and collected during predesign. Experience has shown that it may also be useful to conduct periodic operational studies to support active management of a remediation system (U.S. EPA, 1989a). Such studies may consider the effects of changing flow rates, adding or deleting wells, altering the treatment train or other changes in the remedial action.

Strategies for performance evaluations should view data gathering activities during the remediation as an extension

of the historical data gathering and characterization of the site. For the sake of continuity and the ability to conduct meaningful comparisons at future dates, the performance evaluation program should (i) expand the collection of key hydrodynamic and chemical data; and (ii) continue and expand the site characterization efforts to refine the databases regarding the hydrogeology and transport processes, to the full extent that this is needed for both oversight monitoring and operational management purposes.

Traditionally, the key controls on the form and quality of the technical data obtained during remediations have been the monitoring criteria that are selected and the monitoring point locations at which those criteria are to be applied. This traditional collection of ground-water samples for chemical analyses and measurements of water level elevations has not been adequate for detailed performance evaluations. There is a need for ongoing improvement of the site characterization database. This database may be updated by periodic or opportunistic testing, which may include analysis of chemical extracts of aquifer sediment samples collected from new boreholes, and aquifer testing, geophysical and geological logging of new wells. Such information would allow refinement of ground-water velocity and flowpath estimates under various pumping conditions.

The collection of aquifer sediment samples for identification and quantification of contaminant mass reserves is an example of a technical activity that should be routine for pre-operational site characterization studies, but which is rarely done during operation of remedial actions. This is unfortunate because it may provide one of the few direct means of evaluating the general effectiveness of the remedial action (e.g., the magnitude of contaminant mass reduction obtained during a given time period). However, due to the inherent heterogeneous nature of the subsurface this may only provide general indication of a remediation's effectiveness. Together with operational data, information from the analyses of aquifer samples can be used to estimate the future rate of contaminant mass reduction under the existing wellfield configuration and pumping schedule.

With the same information, it should also be possible to estimate the best performance of the remediation, which is defined here as the lowest contaminant concentration profile maintainable. However, this assumes that the contaminant sources have been accurately delineated and that no immiscible contaminant sources are present. Continuous characterization of the site during remediation will provide the basis for determining the optimal wellfield configuration and pumping schedule for the next forecast period, and for projecting the best performance during that period. One of the best reasons for active remediation management is based on economics. Pumping the minimum volume at the highest concentrations and in the minimum time frame is the prime avenue to cost minimization.

Note, however, that even if an initially optimized remediation is operated continuously without any changes in wellfield configuration or pumping schedule, occasional reestimation of its best performance may be necessary, due to technological advances and because estimates of the contaminant masses in reserve and their effective rates of depletion may change with time. As a consequence, there is a need for continuous collection of routine monitoring and operational data during remediation. Operational data is critical for system optimization, and must be obtained regularly to achieve and maintain the most efficient and effective remediation. Important data include:

- (i) flow rates of extraction and injection wells;
- (ii) water-level elevations in all wells and piezometers; and
- (iii) the concentrations of contaminants in monitoring wells, extraction and injection wells, and the influent and effluent of each treatment process unit.

1. Locations for Plume Monitoring

It has long been recognized that it is important to provide continuous information on what is happening downgradient of the plume boundary, because this is the means by which potential receptors may be warned of the advance of the plume. It is also important to monitor inside the plume during remediation. Such actions may make it possible to determine which parts of the plume are being remediated effectively and efficiently. This facilitates management of the remediation wellfield for best performance. For example, this may be accomplished by reducing flowrates from extraction wells producing water from relatively clean zones and increasing the flowrates from wells producing water from highly contaminated zones. By contrast, the exclusive use of oversight monitoring points downgradient of the plume boundary does not allow an understanding of plume behavior during remediation, except to indicate when contaminants have migrated beyond the zone of remedial action.

There are many kinds of monitoring points which are useful for performance evaluations. Natural water quality or background sampling locations are the most widely used monitoring points and are positioned outside of the plume boundary (Figure 4). The location is chosen such that:

- (i) it is neither in the plume nor in adjacent areas that may be affected by the remediation;
- (ii) if downgradient, it is in an uncontaminated portion of the aquifer through which the plume would migrate if the remediation failed; and
- (iii) its location minimizes the possibility of detecting other potential sources of contamination (e.g., relevant to the target site only).

Data gathered from background monitoring points located upgradient or cross-gradient of a contaminant plume may also serve to indicate when contaminants have migrated beyond the zone of remedial action. This latter might occur when injection wells are used to return treated water to the aquifer at the upgradient edge of the plume and simultaneously have the unintended effect of forcing a portion of the contaminant plume outward. The upgradient and cross-gradient locations of background monitoring points may also be useful in providing a continuous check on the regional water quality, thus providing early warning of previously undetected contaminants flowing into the area.

Public water supply wells located downgradient of a plume are a second kind of beyond-plume monitoring point. These wells were originally drilled in locations suitable for water supply purposes and were never intended to serve as monitoring wells. However, they may be sampled to assure the quality of ground water that is delivered to consumers using monitoring criteria that are related to specific contaminants associated with a site and maintenance of existing quality, or other health-based standards. Gradient-control is a third type of compliance which is being used with increasing frequency. It is established specifically for determinations of the directions and magnitudes of hydraulic gradients. Such a monitoring "point" is comprised of a cluster of small diameter wells that have very short screened intervals (e.g., piezometers), and is usually located just outside the perimeter of the plume. Water level measurements obtained from wells that are screened over comparable stratigraphic intervals are used to prepare detailed contour maps from which the directions and magnitudes of local hydraulic gradients can be approximated. An evaluation of the vertical gradients can be made in a similar fashion by comparing water level measurements from adjacent wells screened at different depths. It is usually just as important to determine the vertical hydraulic gradients as the horizontal hydraulic gradients, because a remediation wellfield may control only the uppermost portions of a contaminant plume (e.g., when remediation wells are too shallow or have insufficient flow rates).

Less often utilized than any of the foregoing are withinplume monitoring points. Most of these are installed during the site investigation phase, prior to the remediation. These wells are needed to monitor the progress of remediation. These can be subdivided into on-site plume monitoring points, located within the property boundary of the facility that contains the source of the contaminant plume, and offsite plume monitoring points that are located beyond the facility boundary.

2. Monitoring Criteria for Performance Evaluations

It is convenient to identify four categories of monitoring and performance evaluation criteria: chemical, hydrodynamic, treatment efficiency, and administrative control.

Although several federal statutes impose limitations on chemical concentrations in fresh water, EPA's 1985 National Contingency Plan (NCP) revision and the Superfund Amendments and Reauthorization Act (SARA) of 1986 provide the concept of applicable or relevant and appropriate requirements (ARARs) that derive from any and all federal statutes. ARARs also effectively include regional, state, and local statutes, because EPA is required to consider these (which a state may actively encourage by withholding its concurrence signature in the site settlement). Chemical monitoring criteria may be based on a combination of:

- Maximum Contaminant Levels (MCLs) that have been promulgated for drinking water supplies under the Safe Drinking Water Act of 1974, as amended by the SDWA Amendments of 1986;
- (ii) Alternate Concentration Limits (ACLs) that are health/risk-driven and technology-driven are site-specific to ground-water corrective action plans (CAPs) under the Resource

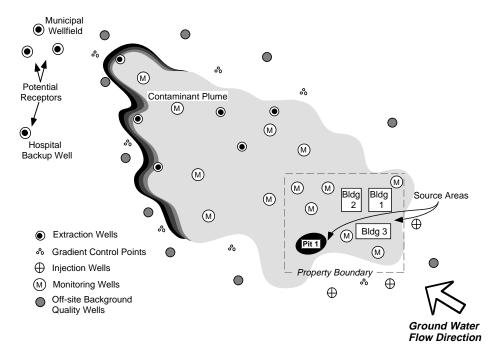


Figure 4. Possible monitoring point locations in a ground-water contamination plume undergoing pump-and-treat remediation.

Conservation and Recovery Act of 1976, as amended by the Hazardous Waste Amendments Act of 1984;

- (iii) State Water Quality Standards that derive from the Clean Water Act of 1972 and other statutes that protect aquatic wildlife and their habitat; and
- (iv) county, municipal, or regional restrictions on the quality of water that may be discharged to local lands, or other requirements for the return of pumped water in water-short areas.

The actual numerical levels of chemical oversight monitoring criteria may be affected by detection limits, and natural water quality. For example, the acceptable concentration level for a given contaminant in health-based terms may actually be much lower than can be physically determined with routine instrumentation, or the natural levels of certain contaminants (e.g., arsenic or selenium) are greater than ARARs.

Hydrodynamic monitoring criteria include:

- (i) prevention of infiltration through the unsaturated zone;
- (ii) maintenance of an inward hydraulic gradient at the boundary of a plume of ground-water contamination; and
- (iii) providing minimum flows in streams or wetlands.

Vertical profiles of moisture content may be used to determine whether there is effective prevention of infiltration through the unsaturated zone (e.g., below a site cap). The requirement that an inward hydraulic gradient be maintained at the periphery of a contaminant plume undergoing pump-and-treat remediation is imposed to ensure that no portion of the plume migrates away from the zone of remedial action.

Evaluations of the hydraulic gradients exerted by remediation wellfields require many measurements. To assess this performance adequately, the hydraulic gradients must be measured accurately in three dimensions between each pair of adjacent pumping or injection wells. Velocity divides may occur in the horizontal plane near active wells and may develop in the vertical dimension if the well hydraulically influences only the upper portion of the aquifer. The ground-water velocity is essentially zero at the stagnation point which forms downgradient of pumping wells.

The performance standards that are applied to the treatment plant portion of a pump-and-treat remediation are most often phrased in terms of treatment efficiency criteria. Although simple comparisons of total organic chemical loading in the influent and the effluent of the treatment train give some idea as to overall treatment efficiency, it is important to make a detailed examination of the influent and effluent to each treatment unit.

In some cases, individual compounds present limitations to the treatment process because of effluent quality standards for discharging to a local stream (e.g., National Pollutant Discharge Elimination System (NPDES) permit requirements). In other cases, after some time of pumping VOC-laden water for treatment solely by air-stripping, nonvolatiles may begin to arrive in the influent and require the addition of carbon filtration to the treatment train. In still other cases, there is a need for examination of key locations within the treatment process to troubleshoot the effects of certain contaminants on treatment units. Iron and calcium, for example, may precipitate in an air stripper and dramatically decrease throughput.

Administrative control monitoring criteria may be codified governmental rules and regulations (e.g., for fire safety and electrical hazards), but they also include:

- effective implementation/enforcement of drilling bans and other access-limiting administrative orders;
- (ii) proof of maintenance of site security; and
- (iii) reporting requirements, such as frequency and character of operational monitoring reports.

Combinations of chemical, hydrodynamic, treatment efficiency and administrative control monitoring criteria are generally stipulated at monitoring points. The exact combination for a specific monitoring point depends on its location relative to the source of contamination and the potential receptors.

3. Strategies for Monitoring Locations and Criteria

Each kind of monitoring point has a specific and distinct role to play in evaluating the progress of a remediation. In choosing chemical monitoring criteria, it is essential to recognize the interdependency of the criteria at different monitoring locations.

The monitoring point locations and criteria should be selected initially on the basis of a detailed site characterization, from which transport pathways prior to remediation are identifiable, and from which the probable transport pathways during remediation may be predicted. It may be useful to complete pre-design studies and pilot studies of remediations prior to selection of certain monitoring point locations and criteria to allow consideration of the effects of system operation on flow and transport pathways.

Specifically, monitoring point locations and criteria should be keyed not only to the no-action transport pathways, but also to the probable transport pathways during routine operation and under partial operational failures. Generally, complete failure may be presumed to be the same as noaction, though this may not be true if the pump-and-treat remediation is augmented by other technology such as subsurface barrier walls. Since the chemical composition and flow pattern of the zone of remedial action may change substantially as the remediation progresses, the monitoring point locations and criteria may also need to change.

Assuming that a remediation wellfield is operated with constant system configuration and pumping schedule, it will still generate flow velocities that are highly variable throughout the zone of remedial action. In part, this is due to the heterogeneous nature of the subsurface sediments (e.g., hydraulic conductivity may vary considerably over short distances). This may also occur because each pumping well causes local velocity variations.

There may be a need to relocate or add extraction or injection wells to better remediate portions of the interior core of the contaminant plume. These kinds of system modifications underscore the need to anticipate changes in chemical patterns at monitoring locations, by taking into account the detailed flowlines generated by the wellfield, and the changes in contaminant concentrations that might result from variations in the influences of transport processes along those flowlines.

One way to organize studies of possible monitoring point locations is by mapping flowlines generated by remediation wellfields in sufficient detail to characterize the capture zones generated by extraction wells and mounding zones produced by injection wells. For each remediation well, the location of a stagnation point and the maximum width of the capture zone should be identified. A different flowline plot may be required for each change in key variables (e.g., well flowrates and locations, natural hydraulic gradient, etc.). Provided that the estimates of key parameters are reasonably accurate, such flowline illustrations should form a sound starting point for selections of monitoring point locations. It is important to ensure that external stresses (e.g., local wells) are accounted for when mapping flowlines.

4. Measures of Operational Effectiveness

At the heart of a remediation performance evaluation is the need to evaluate its operational effectiveness, which may be measured in a number of ways. One may view it as the general degree of hydrodynamic control exerted and/or the general degree of contamination clean-up achieved. To quantify the general degree of hydrodynamic control exerted, one may compute the mathematical average of several estimates of the horizontal and vertical gradients along the outer bounds of the contaminant plume. The average value of the hydraulic gradients should be inward, toward the core of the plume. To quantify the general degree of contamination clean-up achieved, one may compute the average value of the total contaminant loads (e.g., total VOCs) at all monitoring locations and compare this computed average with previous values.

The total contaminant mass present at any monitoring point may be estimated by analyses of chemical extracts of subsurface sediment samples. The physicochemical basis of this estimation procedure is that chemical extraction techniques recover all of the contaminant mass present in the sediment sample, regardless of phase. Obviously, the sampling technique, spatial coverage of sampling efforts, and extraction efficiencies are quality control considerations that must be considered for this technique to generate reliable estimates. Under ideal hydrogeologic conditions (e.g., homogeneous and isotropic sediments) the estimated values should trend downward over time if the remediation progresses satisfactorily.

However, there may be significant limitations to such contaminant mass estimation methods. The degree of heterogeneity of subsurface sediments will strongly influence estimate reliability. Slight variations in vertical and horizontal hydraulic conductivity may significantly affect the migration of both aqueous phase and immiscible phase contaminants. Furthermore, it is generally accepted that the adsorptive capacity of sediments for organic contaminants increases with decreasing grain size. As a result, contaminant mass estimations using sediment extraction techniques may only provide general indications of the effectiveness of a remediation. As the degree of hydrogeologic complexity increases, the likelihood of obtaining replicable sampling and analytical results decreases.

The total contaminant mass present at a monitoring location has often been estimated from contaminant concentrations in ground-water samples. This approach employs adsorption isotherms to infer the concentration of contaminant adsorbed by subsurface sediments from the measured contaminant concentrations in ground-water samples. Unfortunately, this approach may seriously underestimate the mass present, because the assumptions on which the method is based may be easily violated.

The total contaminant mass present at monitoring locations has also been represented by the direct sum of the

concentration values of the contaminants found in groundwater samples. However, this is a near-meaningless approach for many pump-and-treat remediations, primarily because remediation wellfields cause increased flow velocities locally and induce invasion of the plume by uncontaminated water beneath and adjacent to the plume. These and other factors serve to depress contaminant concentrations in the ground-water, at least until pumping ceases and chemical equilibrium can be re-established.

The general degree of hydrodynamic control or clean-up, as represented by averaged values of hydraulic gradients or total contaminant mass, is an informative and useful measure of operational effectiveness, but it does not address the variations in degree of control or clean-up. Therefore, a second way one may view the operational effectiveness of a pump-and-treat remediation is with regard to the spatial uniformity of the control exerted and/or the clean-up level achieved. In this context, hydrodynamic control should be evident along the periphery of the plume at each location where hydraulic gradients are determined from water-level elevation measurements. Likewise, the total contaminant load at each within-plume monitoring point should not vary significantly from the average.

Operational effectiveness may also be viewed in terms of the persistence of the desired effects of the remediation. Is hydrodynamic control of a contaminant plume maintained continuously, regardless of seasonal variations in the recharge and flow rates of the regional system? Do concentration profiles remain stable or are they affected by residual contaminants as the water table rises and falls throughout the year? Are concentration profiles affected by increased infiltration due to aging, settling and slumping of materials beneath an on-site cap? Any of the foregoing may cause the desired effects of a pump-and-treat remediation to be diminished over time. Persistence of desired effects is a very real concern when evaluating operational effectiveness.

5. Measures of Operational Efficiency

While operational effectiveness may be the primary focus of regulatory entities, operational efficiency is more often the focus of those who bear the financial responsibility for the remediation. There are a number of ways to measure operational efficiency, and some are germane to both regulatory and fiscal interests.

The minimization of total costs, while reaching and maintaining the remediation targets, is the most economically-oriented view of operational efficiency. Total costs can be tracked on a quarterly or annual basis to provide a relatively simple picture but, the operation of the system may affect this picture positively or negatively. For example, reduced downtime and stabilized operations usually follow the initial shakedown period of operation; automation of some manual operations may be possible as experience is gained with the system or as technology advances. The total costs per year may decline continuously as the remediation progresses. However, the costs may also be erratic, because of changes in the specific pattern of contaminant removal. For example, portions of the plume may not respond to remedial actions as predicted, particularly if any previously undelineated sources are present (e.g., NAPLs). Such sources may serve as longterm reservoirs and continue to release contaminants for a very long time (U.S. EPA, 1989a, Mercer and others, 1990 and Huling and Weaver, 1991).

Unfortunately, the tracking of total costs also can be a misleading measure of operational efficiency unless costs are normalized for the effects of inflation, interest rates, and depreciation of recoverable assets. Very real trends of improved operational efficiency may be completely hidden until costs are normalized. This can be a confusing task because such factors may vary substantially from region to region, and from small to large organizations.

A less complicated means of evaluating the operational efficiency of a pump-and-treat remediation is to look for maximization of contaminant removal per unit volume of pumped and treated ground water. This approach focuses on the mechanical efficiency, from which bottom-line economics may be inferred without regard to market forces. It is generally acknowledged that costs are inversely proportional to the contaminant levels of the treated water (e.g., it normally costs less on a per pound basis to remove contaminants from a concentrated wastestream than from a dilute wastestream). Hence, to evaluate the operational efficiency by this approach, the concentration levels of the contaminants in the pumped waters must be tracked. Under idealized conditions the management of a remediation system should be such that the most contaminated wastestream is continuously produced. This concentration would gradually decrease as the aqueous phase contaminants are depleted from the subsurface. However, the presence of residual contaminants adsorbed to aquifer materials and/or immiscible contaminants (e.g., NAPLs) may result in elevated contaminant concentrations for very long periods of time.

One consequence of maximizing the wastestream concentrations is that the minimum volume of contaminated water may be produced over the lifetime of the remediation. This is of interest particularly to regulators where ground water is in short supply. The total volume of pumped and treated ground water may therefore be a measure of operational efficiency. Naturally, there are economic attractions to minimizing the total volume of pumped and treated ground water. It is generally accepted that costs are directly proportional to the amount of material handled for a given contaminant concentration level. It is also clear that the electrical and maintenance costs of extraction and injection well pumps depend directly on the volume of ground water handled.

A concurrent benefit of minimizing the total volume of pumped and treated ground water is that the time for completion of the remediation may be minimized. This is of interest to both regulators and the financial backers of remediations, since they share sensitivity to public perceptions of progress at the site. The time for completion of major phases of the remediation may also be considered a measure of operational efficiency. The obvious regulatory benefits of minimization of time for completion of remediation are the abbreviated costs of oversight efforts, and enhanced credibility with the public. The economic benefits to the financial backers of remediations may include reduced labor and operational costs, and increased value of salvageable assets.

6. Strategies for Determination of Success/Closure

Measures of the operational effectiveness and efficiency of a pump-and-treat remediation can be used to monitor the progress of the remediation. Endpoints must be selected to bring the remediation to termination. Such endpoints may involve absolute or relative measures of success and may include statistical considerations.

Absolute measures of the desirability of terminating the operational phase of a pump-and-treat remediation can be as simple as the removal of a specific mass of contaminants, such as recovery of the total estimated volume of free product in gasoline-contaminated sediments. Conversely, absolute measures may be such things as achieving specific contaminant concentration levels (e.g., MCLs). The former is much less likely to be accepted by regulators than the latter, primarily because it is often extremely difficult to accurately estimate the total mass of contaminant present in the subsurface. Consequently, pre-operational decisions to remove only a specific mass or volume run the risk of terminating the remediation without significant reduction of risk to human health and the environment. Absolute measures are more likely to meet opposition by those responsible for the operation of the remediation because of the difficulties associated with ensuring clean-up to specific levels. A similar concern may be expressed by the regulators, since it is difficult to foresee what technological innovations may develop during the years of remedial operations. Fortunately, absolute measures need not be chosen as stand-alone endpoints; contingencies for demonstrated limitations or technological innovations can be integrated into the phrasing of absolute measures.

Relative measures of the success of remedial operations specify that specific percentage reductions of contaminant

concentrations be achieved. These have not been used as stand-alone criteria for termination of remediations, but are often implemented as requirements such that the treatment process operates continuously at a known efficiency of contaminant removal. There is merit to considering relative measures for a contaminant plume, since specific percentage reductions of contaminant concentrations can be translated into risk reductions to human health and the environment.

For all practical purposes, however, percentage reductions that are applied to known pre-operational contaminant concentration levels are equivalent to absolute measures since the resulting concentrations are readily computed. One major incentive for phrasing clean-up targets as specified percentage reductions from pre-operational concentration levels is the public relations benefits. Most individuals can readily grasp the idea that 99.99% of the contaminants were removed, whereas far fewer are schooled in what specific concentration levels may mean.

Regardless of whether absolute or relative measures of the success of a pump-and-treat remediation are employed, it is clear that a single round of water-level measurements or samples will not suffice to justify termination of a pump-and-treat remediation. At a minimum, successive sampling on a monthly or quarterly basis is needed. The results are examined to determine whether or not the remediation has truly reached the specified targets. Such examinations of the datasets inevitably reveal that the data values vary from one sampling/measurement event to the next. While it is possible to view these data value variations rigidly, such that each value from each sampling/measurement event must be at or below the target concentration level, this approach may be unduly restrictive and may not be justified statistically.

The evaluation of pre-termination datasets with statistical measures entails plotting the contaminant concentration values versus time and fitting a multiple/nonlinear regression line to the plotted values (Figure 5). Two kinds of outcomes of the regression line fitting are acceptable initial indications that the remediation may be ready for termination. The first being that the contaminant concentrations have leveled off and the regression line has a slope equal to zero at an average contaminant concentration value that is at or below the target concentration. The second being that the regression line has a negative slope and concentrations are below the target concentration.

The slope of a fitted regression line is an insufficient statistical measure by itself, since data values inevitably vary about this line. A Student's t-test should be performed to ascertain that the slope of the fitted regression line is not greater than zero at a 95% level of confidence. Quality control considerations also indicate that the vast majority of the data values should fall within a 95% confidence interval

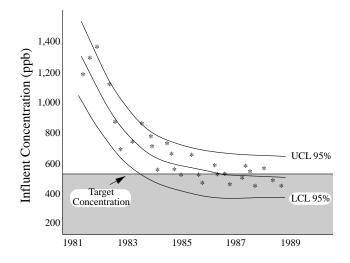


Figure 5. Concentration vs. time data plot and multiple regression line with confidence bounds for judging persistence of the clean-up.

about the regression line. Regulators are concerned only with the upper 95% confidence interval boundary for most parameters.

Following termination of the remediation, the sampling/ measurement events should be continued to assure persistence of the effects of the remediation. A declining frequency of sampling/measurement events is most appropriate for this approach. For example, monthly sampling events for the first three or four months immediately following termination may be adequate. This should be followed by quarterly sampling events until the end of the second post-operational year, and annual sampling events until the end of the post-operational regulatory period. Data obtained during these sampling events should be used to update regression plots. Reactivation of the remedial actions and/or re-evaluation of the appropriateness of the remedy may be indicated when the slope is no longer statistically at or below zero, or when two or more successive data values are above the upper 95% confidence interval bound of the regression line.

It may seem desirable to base the decisions to terminate or re-activate a pump-and-treat remediation on examination of a single regression plot that represents all monitoring point locations. Technically, it may be possible to justify the grouping of results from monitoring point locations of a certain kind. For example, on-site monitoring point locations may fall into this category. At downgradient background monitoring point locations, however, grouping of results may have undesirable sociopolitical consequences. The idea that one potential receptor is better protected than another is generally unacceptable—although it may be acceptable in some cases if the natures of the potential receptors differ substantially (such as a water-supply wellfield versus an ecological habitat).

In those cases where grouping of like locations is determined to be acceptable, there arises the question of how to do the grouping: should individual regression plots be made and their slopes averaged, or should a single regression line be fitted to a dataset containing the values from all of the monitoring point locations belonging to the group? The former option is equivalent to the latter option only when the population distribution forms of the datasets from the individual wells have comparable statistical behavior (e.g., variance and skewness) and are wholly independent of each other.

If the slopes of individual regression plots are averaged from datasets of different monitoring points, the computed 95% confidence interval will be largely independent and insensitive to actual variations of the data in each of the datasets. If a regression line is fitted to a super-dataset that contains data from all monitoring locations, the computed 95% confidence interval will be dependent on the actual variations of the data in all contributing datasets. The confidence interval computed from the super-dataset may be larger than the confidence interval computed by averaging the slopes of individual regression plots. As a result, regulators may prefer the former option (smaller 95% confidence interval), and responsible parties may prefer the latter option (larger 95% confidence interval). Neither is more or less correct statistically.

The foregoing discussion presumes that a decision has been made at each monitoring point regarding whether or not to prepare regression plots of contaminant concentration levels versus time for each contaminant, for groups of contaminants, or for the total contaminant load. In addressing this point, the methods for computing values of 95% confidence intervals may be considered in a manner that is parallel to the foregoing discussion. One may either compute the 95% confidence interval of measurements of each contaminant at a given monitoring point location and then average these results or, combine several (perhaps all) data values into a single dataset and then compute its 95% confidence interval. These computations must be based on normalized data values (e.g., the results of dividing the raw data values of each contaminant by its average value) or the results will be biased toward the contaminant datasets with the highest concentration levels. Again, regulators may prefer the former option (a smaller 95% confidence interval results), and responsible parties may prefer the latter option (a larger 95% confidence interval results). The grouping of the datasets from several contaminants at a given monitoring point location may be desirable only if justified

by similarities in contaminant transport behaviors and the health risks posed by the contaminants to be grouped.

Data Collection Considerations

Efforts made to characterize ground-water contamination problems for remediation have traditionally focussed on the quantification of contaminant levels rather than the potential pathways and mechanisms that affect transport (Bear and Verruijt, 1987; Boutwell and others, 1985; Faust and others, 1981; Keely and others, 1986; Konikow, 1986; Osiensky and others, 1984), however, this bias is diminishing because of a growing recognition of the limited usefulness of chemical samplings of monitoring wells. It is clear that periodic sampling can produce successive snapshots of the distribution of contaminants at a site, but it is equally clear that one can rarely expect to infer key contaminant transport features and parameters from such snapshots. An approach to site characterization is emerging wherein greater emphasis is given to detailed characterization of transport pathways and mechanisms, while retaining a commitment to definition of the full extents and compositions of contaminant plumes (Bouchard and others, 1989 and 1988; Curtis and others, 1986; de Marsily, 1986; Goltz and Roberts, 1986; Jorgensen and others, 1982; Mackay and others, 1986; Major and others, 1988; Matheron and de Marsily, 1980; Molz and others, 1986 and 1988; Scanlon, 1989; Usonoff and Guzman-Guzman, 1989).

1. Purposes of Data Collection

The objectives of collecting data are determined in large part by the intended use (Boutwell and others, 1985; Davis, 1986; Huyakorn, 1984; Krabbenhoft and Anderson, 1986; Loftis and others, 1987; Mercer and others, 1983; Ophori and Toth, 1989). If data are to be used to assess the general potential for contaminant releases and transport at a newly discovered site, the objectives will be limited to problem screening efforts for the time being. Based on the outcome of the screening process, further data collection events may be planned. This is an iterative process, which usually calls for increasingly more detailed data collection which culminates in a comprehensive characterization of the physical extent and chemical makeup of the contamination problem. Traditionally, the identification of transport pathways has been limited to an understanding of the natural flow system in such studies.

An understanding of contaminant migration pathways is essential to the selection and design of an appropriate remedy. Unfortunately, the objectives of past site characterization studies have rarely included sufficiently detailed testing for hydraulic parameters and have often failed to identify key/limiting hydrogeologic processes or features. As a result, the remedy selection process has often proceeded without the benefit of information vital to the proper evaluation of the success of various remedial actions. Instead, such details were often addressed during the design phase following the remedy selection, if at all.

With the benefit of hindsight and an acknowledgement of the growing number of reported ineffective remediations, it is clear that the site screening and site characterization studies that precede remedy selection must include remedial design parameters as primary data collection objectives. This means that detailed hydraulic testing, bench treatability studies, and pilot operations of individual extraction wells must begin during the site characterization studies. Fortunately, this has been recently acknowledged and since 1989 the EPA Regional Offices have supported this approach (Cannon, 1989).

During the process of remedial design, it is essential to formulate data objectives for the operational, closure, and post-closure phases of the site work. While nominally needed for regulatory compliance, data should also be tailored to provide key information for active management of the remediation (e.g., individual flows and chemical loads of all extraction and injection wells, detailed water-level measurements, treatment unit efficiencies). Data collections for regulatory compliance purposes may include samplings from upgradient and downgradient public supply wells, private wells, and industrial supply wells, and from monitoring wells placed close to particularly sensitive ecological habitats.

The objectives of data collections for regulatory compliance purposes extend beyond system effectiveness and efficiency as operational considerations, to the driving force behind all of the site efforts—protection of human health and the environment. In regulatory terms, the effectiveness of the remediation matters because of the potential that each exposure to contaminants poses added, cumulative risk to society. Likewise, the efficiency of the remediation matters because the potential duration of exposure is limited ultimately by the duration of the remediation. Efficiency also matters because of the limited funds and human resources that are available to conduct such work.

2. Relevant Scale(s) of the Problem

Perhaps the most subjective influence on data collection strategies relates to the size of the problem. History suggests that the larger the size of a contamination problem, the more likely the problem will be addressed at a minimal level in screening and site characterization efforts.

From a statistical viewpoint, the scale of the problem can be addressed by breaking it down into definable regions (Davis, 1986; Huntsberger and Billingsley, 1977; Mendenhall, 1968; Steinhorst and Williams, 1985; Taylor, 1987; Ward and others, 1987). For example, the nominal plume may encompass an area of a few hundred acres and an average depth of a few tens of feet. A relatively dense monitoring network is most appropriate within the plume with each monitoring location consisting of a single well or a cluster of monitoring wells. Each monitoring well is thus constructed to sample a different specific zone and allow vertical and horizontal delineation of the contaminant plume.

By contrast, the areas that may be impacted if remedial actions are not implemented may be many hundreds or thousands of feet downgradient from the contaminant source, and may encompass hundreds or thousands of acres. The major data collection objective within the zone between the contaminant plume and potential receptors is to provide an early warning of failure of the remediation to contain the plume. Consequently, it is important to have an understanding of where the plume may migrate if it escapes the remedial action zone. These data needs may decrease with increasing distances down-gradient from the plume. The monitoring well and hydrogeologic testing locations should be skewed toward a dense pattern immediately downgradient of the plume and a sparse pattern farther downgradient.

It is important to understand the connection between the local hydrogeologic setting and the regional flow system in studies of subsurface contaminant transport (Mackay and others, 1986; Osiensky and others, 1984; Scanlon, 1989; Ward and others, 1987). It is often necessary to thoroughly investigate the regional trends in water levels to formulate appropriate boundary conditions and water balances for a model of the local flow system.

3. Actual Scale of the Measurements

There are many ways to estimate the hydraulic conductivity of subsurface materials (Cedergren, 1989; Corey, 1977; Davis and DeWeist, 1966; Freeze and Cherry, 1979; Mercer and others, 1982) and it is not uncommon for the various methods to yield differing results when performed at the same location. There are numerous reasons for this, but one of the major factors relates to the scale of the measurements (Anderson, 1979; Mercer and others, 1982). For example, it has been shown that laboratory measurements of the hydraulic conductivities of clay and silt samples may be as much as two to four orders of magnitude lower than the values determined by field tests and that such determinations tend to have a much greater variability (Anderson, 1979; Klotz and others, 1980; Mercer and others, 1982; Molz and others, 1986a and 1988). Clay and silt samples are often compacted during sampling operations and laboratory analysis. Additionally, the sample volume

may be too small to intercept the macropores and other preferential flow paths that conduct most of the flow through the stratum.

Depending on the magnitude of hydraulic stress created, the hydraulic conductivity values obtained from field tests may vary considerably at the same location. Small-volume tests, such as slug tests, affect only a few cubic feet of formation materials surrounding the well screen. As a result, it is not unusual for the hydraulic conductivity values obtained from slug tests of closely spaced wells to differ by several orders of magnitude. The results are highly sensitive to minor variations in well construction details, especially filter pack, screen position and grouting. The testing locations are effectively isolated despite their proximity to one another. This is underscored by the stochastic character of such measurements. They often appear to be random and fully independent in settings where trends in physiographic features are clearly evident (Dagan, 1982a; de Marsily, 1986; Gelhar, 1986; Vomvoris and Gelhar, 1986).

Conversely, the hydraulic conductivity values obtained from large-volume field methods, such as aquifer pumping tests and two-well tracer tests, may affect thousands to millions of cubic feet of subsurface materials. These field methods often demonstrate considerable dependency and autocorrelation. This is understandable given the potential for physical overlap of the effective areas of testing with large volume tests, but such character is observed even when it is clear that overlaps do not occur. One reason is that autocorrelation is endemic to the occurrence of physiographic trends and the hydraulic forces that help to shape strata. Dipping strata impose directional control on natural flows, as do streambed sediments that are laid and reworked into lenses parallel to the course of a river (Blatt and others, 1980; Compton, 1962; Davis and DeWeist, 1966; Fetter, 1988; Freeze and Cherry, 1979; Heath, 1983; Osiensky and others, 1984; Todd, 1980). These act as intrinsic biases to flow direction, something that can be quantified in terms of anisotropy. The large-scale continuity of physiographic trends makes it highly probable that hydraulic conductivity values determined by large-volume field methods will autocorrelate.

While large-scale continuity is a hallmark of physiographic features, it is by no means a hallmark of contaminant distributions. Consequently, the questions of how to interpolate between measured locations and how to extrapolate contaminant trends in time emerge as a major issue. All too often, these questions have been misinterpreted to mean that sampling locations and frequencies are the only concerns that merit attention. In point of fact, however, the representativeness of each sample is of equal or greater concern. An examination of possible strategies for characterizing the reliability of chemical measurements is warranted, and begins with an examination of sampling techniques.

Bailers or other low-volume sampling devices are commonly used to obtain samples from monitoring wells for organic chemical analyses. Discharging wells such as the extraction wells in a remediation wellfield may also be sampled, but for such wells the contaminant concentration levels are often a function of the duration of pumping. This fact may be exploited by the collection of successive samples as pumping begins and continues (e.g., chemical time-series sampling) with each successive sample representing ground water from a part of the aquifer farther from the extraction well. (Keely, 1982). The overall effect is similar to increasing the number of point-sampled monitoring wells. The volume of the sample is important. because point samples are tacitly presumed to represent the average chemical quality of fairly large volumes of the aquifer from which they were withdrawn; such as occurs in numerical modeling efforts, where grid blocks of several thousand cubic feet are assigned average concentration values.

The use of chemical time-series sampling is quite similar to the use of tracer tests to gain insights into preferential paths of contaminant movement (Keely, 1982). Ground-water tracers are defined as matter or energy transported by water which will give information concerning the direction and velocity of ground water and potential contaminants. Since the time of release and the input concentration of intentional tracers are known but the inputs are unknown for contaminant studies, the interpretation of data from chemical time-series sampling might initially seem to be severely hampered. However, it is the pattern of relative concentrations over time which is actually examined in either case. The absolute values are neither required nor are they readily obtainable under all but the very best controlled field tests in relatively homogenous settings. There are often too many avenues for tracer losses (sorption, ionexchange, biodegradation, etc.) to allow for rigorous mass balances over reasonable distances.

Regardless of whether chemical time-series sampling results in a pattern of chemical arrival that show definite trends or are completely random, the data collected are useful to the investigator in terms of the statistical uncertainties of contaminant concentrations in the plume being defined. Such data can be helpful in deciding when a model has been adequately calibrated and when it is predicting ground-water flow or contaminant transport with reasonable accuracy. They can minimize the amount of adjusting of key hydrogeologic parameters that often accompanies efforts to calibrate a model to field data. Chemical time-series sampling results may be used directly in modeling efforts to generate estimates of uncertainties in the model results. However, care must be taken to understand the autocorrelation of such data, because successive samples are not completely independent since they represent waters that have passed through the zones occupied by previous samples. The ground-water contaminant concentrations will be affected by interactions with sediments and residual contaminants present in those zones.

The simplest approach to predicting the arrival of contaminants at a pumping well from a selected distance involves the relationship of the total volume of water pumped to the distance traveled. Assuming radial flow to a well, the distance waters travel during specific times are indicated by concentric circles. Obviously, samples collected after several hours of pumping represent an average water quality of a larger volume of the aquifer than samples collected only a few minutes after the onset of pumping.

4. Data Quality vs. Quantity

Regardless of the data objectives, there eventually comes a point in planning where one faces a trade-off between quality and quantity. In ground-water investigations, the descent from high to poor quality data is easily made. It is extremely difficult to plan for data of moderate quality sophisticated field methods are either performed properly or they are not. The economics of bad data collections are painfully obvious. Not only can the magnitude and extent of the contamination problem be wholly misunderstood, but the selected remedy can be so off target as to actually worsen the problem. However, there are many field methods which produce good relative information that may prove valuable to site characterization. The usefulness of such methods and their results should not be underestimated.

Hydrogeologic Data

1. Topographic and Geographic Data

Topographic and geographic data are most commonly available as elevation contour maps. These are available from the U.S. Geological Survey (USGS), the U.S. Forest Service, the U.S. Army Corps of Engineers, and various State agencies. At the local/site scale, subdivision plats and city planning maps provide contour spacings as small as 0.25 feet. Aerial photographs of many cities are available from several government agencies at five to ten year intervals starting in the late 1940's. Remote sensing images are also available from various government agencies. Such maps and photos are useful for gaining an understanding of the physiographical trends and structural controls on ground-water movement. It is essential to measure all depths to water against a common datum and most topographic maps are not accurate enough for this purpose. Differences of only a few feet may be comparable to the seasonal changes in water levels at many sites. The elevations of the tops of the monitoring wells must be surveyed to an accuracy of better than 0.1 feet. Otherwise, the potential for misinterpretation of the hydraulic gradient and direction of ground-water flow may be significant. Surveyed elevations should be checked periodically because of the potential for slumping and settlement of capped waste and compaction of pumped strata.

2. Geomorphologic and Geologic Data

Maps which describe the geomorphologic character of large tracts of land are available from the USGS and State geologic agencies. Specifically, it is common for basin boundaries and structural features to be illustrated on maps that cover an entire state or physiographic province. Fault lines and fracture trace orientations are often detailed on such maps, but these may have little direct applicability at the local or site scale. Although geologic maps which describe regional stratigraphic and lithologic features are available, it is essential to have an experienced geologist detail the local setting. Principally, the geologist will rely on inspection of local exposures, drill cores, and excavations. Geophysical techniques, particularly the borehole methods, can be of great assistance to the geologist in evaluating the nature and extent of specific strata, as well as the general water quality.

3. Flow Rates

Rainfall events, streambed losses, and snowmelt provide the majority of natural recharge to the subsurface. Precipitation records are kept by the National Oceanic and Atmospheric Administration. Estimates of effective recharge are made by the U.S. Department of Agriculture for crop purposes, and by the USGS and State geological agencies for water supply purposes. However, these estimates are generally based on basinwide studies and do not provide much detail at the site level. Aquifers also may be recharged purposely by infiltration basins and injection wells. These artificial recharge mechanisms are manmade and directly measurable.

Soil scientists have devised a number of methods for measuring the movement of water through the unsaturated zone. However, most of these methods are intended primarily for use in relatively shallow surface soils. The most traditional methods include tensiometers, gypsum blocks and collection pans. State-of-the-art methods for determining soil moisture content include the use of neutron probes, pressure transducers, and time-domainreflectometry (TDR). These sophisticated methods are subject to interference and produce data which must be properly interpreted to quantify fluid movement.

The flow rates of springs can be measured with ordinary surface-water weirs or flumes. Likewise, baseflow recession curves can be used to estimate the discharge from an aquifer to streams. Aquifer discharges can also be approximated by using estimates of the hydraulic conductivity and hydraulic gradient in Darcy's Law. The cross-sectional area through which the aquifer is discharging is also needed for this analysis. Errors in the cross-sectional area are unlikely to be more than two- or three-fold. This is negligible given the possible order(s)-of-magnitude uncertainty that may be associated with hydraulic conductivity estimates. Ground-water flownets have been used traditionally to estimate aquifer flows, with reasonable success at the basin level, but not necessarily at the local/site level. However, flow nets can be useful for determining ground-water flow direction, making time of travel estimates and assessing ground-water vulnerability (U.S. EPA, 1989b).

4. Hydraulic Parameters

There are several methods of estimating the hydraulic conductivity of an aquifer. Hydraulic conductivity values obtained from laboratory permeameter methods represent point estimates only. Unconsolidated sands and gravels may become disordered and compressed during extraction from the field and emplacement in the permeameter columns, which may significantly alter their hydraulic properties. Clays may be extracted from the field with less disturbance, but they often undergo compression during emplacement into permeameter columns. Additionally, high hydraulic gradients are required to induce flow through clay samples in laboratory permeameter studies. From practical experience, it is easy to see that laboratory estimates of the hydraulic conductivities of aquifer materials may be variable.

It may be difficult to take a sample that accurately represents the amount of secondary permeability present in the clay resulting from macropores or other preferential flow paths. This lack of representativeness usually accounts for the common observation that many clay units determined to be impermeable from laboratory tests are often characterized as relatively permeable units by field tests. This takes on great importance in many settings because estimates of the potential effectiveness of a remediation often depend heavily on the properties of low permeability strata.

Numerous small-volume field tests for determining hydraulic conductivity have been described in the literature (Bouwer and Rice, 1976; Papadopulos and others, 1973). Most methods involve displacement of a fixed volume (slug) of water in a piezometer and relating the observed hydraulic response to the properties of the aquifer in the immediate vicinity of the piezometer. Storage coefficients obtained from slug tests may not be representative of the aquifer due to the small volume of aquifer being tested. This is important because both the transmissivity and the storage coefficient are needed for the well hydraulics computations used to size and position wells for remedial actions.

Recent developments in electromagnetic and thermal borehole flowmeter technology allow the determination of horizontal hydraulic conductivity values as a function of vertical position within an aquifer (Young and Waldrop, 1989; Hess and Paillet, 1989). However, the hydraulic conductivity, transmissivity and storage coefficient values obtained at most hazardous waste sites are estimated using various mathematical analyses of aquifer pumping test data. The average saturated thickness of that portion of the aquifer affected by the pump test must be determined from drilling records or estimated by geophysical methods. If the formation is very fine-grained, the capillary fringe above the water table may be large enough to comprise a non-negligible portion of the effective saturated thickness. In such cases, continuous coring may be extremely valuable in defining the magnitude of the capillary rise locally. If the formation is coarse-grained, the capillary fringe will comprise a negligible portion of the effective saturated thickness.

In addition to the hydraulic conductivity, the porosity and hydraulic gradient must be estimated in order to compute the average rate of movement of the ground water. Tracer tests may be used in the field to estimate the effective porosity, but this is possible only if the hydraulic conductivity has been defined with very high accuracy. In practical terms, it may not be possible to achieve such accuracy because the variations in hydraulic conductivity about the mean value at a given site may have a range of two or more orders of magnitude. By contrast, effective porosity values for most aquifers lie between ten and forty percent and may be estimated within a factor of two.

Tracer tests can be conducted by injection and subsequent withdrawal of a tracer solution in a single well through an isolated injection zone. The extreme sensitivity of single-well tracer tests to well construction details and the small volume of aquifer affected limits the applicability of this method for site characterization studies. However, two- well tracer tests have been devised to avoid most of these problems. Two basic kinds of two-well tests include natural gradient and forced gradient tracer tests. Natural gradient tracer tests are conducted releasing a small volume of concentrated tracer solution in an upgradient well and monitoring the concentration of the tracer over time in the downgradient well. Forced gradient tracer tests involve injecting a dilute tracer solution in one well, while the other well withdraws ground water at an identical rate. While both natural gradient and forced gradient tracer tests can ostensibly yield the same information, they differ in their sensitivity to dispersive forces, due to the radically different velocities that are involved. Natural gradient tracer tests tend to be biased toward large dispersion coefficients and forced gradient tracer tests tend to be biased toward smaller dispersion coefficients. The distinction is irrelevant for most pump-and-treat remediations, however, because they generate such strongly advective flows that dispersive forces are usually negligible by comparison. Forced gradient tracer tests are intrinsically suited to provide appropriate estimates of hydraulic parameters for pump-andtreat remediations, because of the obvious similarities in hydraulic and hydrodynamic behavior.

5. Fluid-Behavior Data

Several important fluid-behavioral properties include miscibility, density, solubility, and viscosity. Miscibility is the property that describes the ability of one fluid to dissolve into or completely commingle with another fluid. Miscible fluids do not exhibit stratification or separation of distinct phases. Familiar examples of organic solvents that are miscible in water include ethanol, ethylene glycol, and acetone. Immiscible fluids, or NAPLs, exhibit separation of fluids at a distinct interface. Familiar examples of immiscible fluids are gasoline, creosote, trichloroethylene (TCE) and ether.

Dense immiscible fluids (DNAPLs) exhibit fingering during advancement, as well as loss of residuals by snap-off in small pore-throats and trapping in dead-end pores. Because of the existence of a wetting phase (water) on subsurface grain surfaces prior to percolation of spills or subsurface releases from pipelines and tanks, the penetration of TCE and other DNAPLs into intergranular pores is highly sensitive to a critical effective pore size and the acceptable surface tension that results at the interface between the two fluids for that pore size. This description presumes that the water film on the grains is at residual levels after complete gravity drainage; if water is present beyond that needed to satisfy the hygroscopic force of the wetting tension, it will be present as a pendular ring at the bottom face of the grain, and may coalesce with heavy films from other grains and thereby gain sufficient mass so that the acceleration of gravity overcomes the total wetting tension and downward flow occurs. Because of the orders-ofmagnitude range of variability of effective pore sizes in most settings, dense immiscible fluids such as TCE penetrate nonuniformly.

6. Fluid Levels and Pressures

Some of the most important measurements taken at groundwater contamination sites are water level elevations as hydrogeologic features and hydraulic parameters can often be estimated with such data. Many sites are located in highly active hydrologic and hydraulic settings where large daily water level fluctuations are possible, due to the influence of local streams and industrial and municipal wells, but hourly variations may occur also. Such variations are not uniform regionally or locally, and tend to die out logarithmically away from the source of the disturbance. It is essential to collect consistent data, so that differences in water level elevations recorded at various wells represent the spatial distribution of water levels and not temporal variations.

Wells of comparable construction (e.g., screen length) must be used. Small diameter wells with short screens are the most suitable for providing detailed information on horizontal and vertical gradients. Clusters of such wells are effective and efficient for delineating horizontal and vertical gradients.

In terms of hydrostatic position, it is incorrect to group water level measurements from wells whose screened intervals occur at greatly differing elevations. This is especially important at sites with significant vertical hydraulic gradients. Otherwise, contour maps drawn from the resulting data will present a picture that is an indefinable mixture of the horizontal and vertical components of hydraulic gradient. It may be important to measure water pressure rather than water level elevations, especially where there is the possibility of the contaminant plume being more dense than the native formation water (e.g., plumes with total dissolved solids in excess of 1,000 parts per million).

Water supply wells, irrigation wells, and industrial supply wells are usually constructed with lengthy screens and often without annular seals above the filter pack. Consequently, measurements of their static water level elevations are integrated averages of vertical head differences over a large section of the aquifer. Such measurements should not be combined with measurements from observation wells or monitoring wells to produce contour maps.

Water level measurements obtained from water supply wells or other production wells during operation are greatly affected by the pressure drop that occurs as ground water passes through the entrance openings of the wellscreen. The magnitude of the effect varies from well to well, over time, and as a function of the flow rate. It is very difficult to accurately estimate water level elevations immediately outside wellscreens.

There are numerous methods for measuring water-level elevations. The most common are chalked steel measuring tapes, electrical probes and pressure transducers. Chalked tapes have been used for decades because of their simplicity, reliability, and accuracy (about 0.01 ft). The method is

extremely slow and most suitable for static measurements. Electric water level probes usually come with crimped foot or meter markers, but may become unreliable due to the tendency of the wire to stretch over time. A steel measuring tape should be used to measure the length of electrical wire lowered into the well when practical.

Pressure transducers utilize very sensitive strain gauges and amplification circuitry to measure changes in hydrostatic pressure, which may be converted to water level elevations. Most pressure transducers incorporate an internal atmospheric venting tube that prevents pressure measurements from being affected by barometric fluctuations. Pressure transducer measurements are easily automated, so that no re-positioning need be done to acquire successive measurements, and extremely rapid measurements (greater than one per second) are possible. The acquired measurements are stored in data loggers that often allow real-time analyses of the data.

Chemical and Geochemical Data

1. Natural Ground-Water Chemistry Data

The goal of most aquifer remediations is to return ground water to its beneficial uses where practicable; therefore, it is necessary to characterize the chemical and biological composition of nearby uncontaminated wells to determine natural ground-water quality. Samples from uncontaminated wells should be obtained with the same rigor and care given to samples collected from suspected zones of contamination. At a minimum, samples should be analyzed for major cations and anions to allow the computation of cation/anion balances. Descriptive graphical analyses methods utilize such data, and are time-proven methods of characterizing natural water quality (Cheng, 1988; Freeze and Cherry, 1979; Loftis and others, 1987; Novak and Eckstein, 1988; Ophori and Toth, 1989; Rogers, 1989; Scanlon, 1989).

2. Soil Chemistry Data

For complete characterization and transport evaluation, native soils must be collected and analyzed for major ion chemistry (Corey, 1977; Hillel, 1982; Mercado, 1985; Mercer and others, 1983; Osiensky and others, 1988; Rogers, 1989). In addition, the organic carbon content of the soil should be determined because of the significant role it plays in the retardation of organic contaminants (Bouchard and others, 1989; Lee and others, 1988; Mackay and others, 1986; Nkedi-Kizza and others, 1985, 1987 and 1989; Piwoni and Banerjee, 1989).

Soils and subsoils can be easily sampled from the sidewalls of excavated pits, but deeper sediments must be obtained from cores obtained during drilling operations. Traditional split-spoon and Shelby tube samplers may be used to obtain core materials for use in chemical analyses, lithologic and stratigraphic mapping, and laboratory batch studies. However, special coring devices and modified laboratory glove boxes purged with an inert gas may be used to retrieve cores used in fate and transport evaluations, and microbiological studies (Nkedi-Kizza and others, 1989; Scalf and others, 1981; Siegrist and McCarty, 1987).

3. Contaminant Reaction Data

Contaminated soils are generally sampled similarly to uncontaminated soils. However, air-tight sample containers are necessary when sampling volatile organic contaminants. Laboratory studies of contaminant transport behavior often utilize soil columns packed with subsurface sediments (Bitton and Gerba, 1984; Siegrist and McCarty, 1987). Columns packed with uncontaminated soil samples are used to determine retardation coefficients for specific contaminants. Column studies may also be used to obtain estimates of the number of pore volumes of water that must be flushed through the material to reduce contaminant concentrations to specific levels.

Batch, or flask studies may be utilized to determine site specific distribution coefficients for contaminants and sediments. These data may be used to predict the effects of retardation on the transport of contaminants through the subsurface. The fraction of organic carbon (foc) present in subsurface materials will strongly influence the mobility of many contaminants.

Biological Data

Until recently, it was presumed that the subsurface was largely devoid of bacteria. This was shown to be untrue in the early 1980's, when various microbial populations were found in subsurface sediment samples (Scalf and others, 1981; Bitton and Gerba, 1984). Since then, researchers have attempted to identify which organisms might be responsible for the degradation of specific organic chemical contaminants. Presently, it is generally accepted that no single strain of microbe is responsible; rather, consortiums of bacteria engage in degradation activities concomitantly.

The population dynamics of subsurface biota depend heavily on limiting nutrients (Bitton and Gerba, 1984; Bouwer and Wright, 1988; Major and others, 1988; Molz and others, 1986; Tinsley, 1979). The carbon atom skeleton of an organic chemical contaminant represents a fuel source to biota, but they cannot utilize it unless they are able to acquire sufficient supporting nutrients, such as nitrogen and phosphate (Molz and others, 1986; Roberts and others, 1989; Tinsley, 1979). Threshold concentration effects have also been observed, so that it is possible to have an adequate supply of nutrients but still generate little degradation because of the low concentration level of the fuel source, the contaminant (Borden and others, 1989; Flathman and others, 1989; Jensen and others, 1988; Roberts and others, 1989; Spain and others, 1989; Srinivasan and Mercer, 1988). Typically, total dissolved carbon loads of less than 100 parts per billion represent an inadequate source of energy to stimulate bioactivity.

Contaminants may be present in certain portions of a plume at concentration levels that are toxic to the indigenous biota. However, if the biota are able to survive and function minimally, they may adapt to the contaminant and begin degradation. Hence, the rate of transformation of specific contaminants may change over time. Great interest has been taken in the possibility of stimulating bio-activity by the addition of nutrients and/or fuel sources (e.g., methanol or ethanol) to subsurface sediments. Both laboratory and field experiments are under way at a number of locations across the nation to investigate this possibility (Bouwer and Wright, 1988; Major and others, 1988; Roberts and others, 1989; Spain and others, 1989; Thomas and Ward, 1989). The laboratory experiments are often conducted in flow columns.

Quality Assurance and Quality Control Data

There are a great number of texts available that describe quality assurance and quality control methods (e.g., Davis, 1986; Huntsberger and Billingsley, 1977; Mendenhall, 1968; SAS Institute, 1988c and 1989b). Quality control methods presume that the data possess specific statistical properties and yield results that must be narrowly interpreted. The repeatability of a result from a measurement of any parameter is termed the precision of the method of measurement. The accuracy of a measurement of any parameter is the degree of closeness of its value to the actual/real value. Accuracy and precision do not adequately describe the appropriateness of a measurement for its intended use. The degree of representativeness is by far an overriding consideration. For example, measurements of the concentration of a contaminant in ground water removed from a monitoring well may be obtained with extreme care, such that one concludes that they are probably highly accurate, but there is no guarantee that such measured values represent the contaminant levels 10 feet, 100 feet, or more away.

III. Methods and Protocols

Performance Evaluation Methods

The proper selection and use of computational, statistical, graphical and other methods for performance evaluations of pump-and-treat remediations are as important as the strategies being pursued. This is because the inferences that are drawn and the perceptions that are generated depend to a great extent on the manner in which the data are processed and presented. For detailed discussions of the methods applicable to ground-water contamination data the reader is referred to publications on methods of numerical analyses (Bear and Verruijt, 1987; Burden and others, 1981; Chau, 1988; de Marsily, 1986; Faust and others, 1981; Gerald and Wheatley, 1984; Javendel and others, 1984; Mercer and Faust. 1981: Press and others. 1986: Remson and others. 1971; van der Heidje and others, 1985; Walton, 1985 and 1987; Wang and Anderson, 1982; Yeh and Han, 1989), statistical analyses (Asbeck and Haimes, 1984; Davis, 1986; Hallenbeck and Cunningham, 1986; Huntsberger and Billingsley, 1977; Mendenhall, 1968; SAS Institute, 1988a, 1988c, 1988d, and 1989b; Taylor, 1987; Keely, 1989; Vomvoris and Gelhar, 1986; Vouk and others, 1985), graphical construction techniques and analyses (Cedergren, 1989; Cheng, 1988; GIS World, 1989; SAS Institute, 1989a and 1989b; Tufte, 1983; van der Heijde and Srinivasan, 1983; Watson, 1984), and theoretical relationships (Bitton and Gerba, 1984; Corey, 1977; Hillel, 1982; Krabbenhoft and Anderson, 1986; Kueper and Frind, 1988; Stumm and Morgan, 1981; White, 1988). Although space limitations prohibit detailed discussions of the foregoing methods, some general precautions are cited which may be valuable to the reader in selecting and applying methods of data presentation and analysis.

1. <u>Computational Methods</u>

Methods for the computation of key indicators of performance range from simple arithmetic to highly sophisticated transport models incorporating chemical, physicochemical, and biological reaction rates. The use of a particular method should be justified by the conditions to which it is being applied. Such justifications should be supported by the appropriate quantity and quality of requisite data.

Subsurface contaminant transport models incorporate a number of theoretical assumptions about certain natural processes governing the transport and fate of contaminants. However, these assumptions may be violated at many sites. In order to make solutions tractable, simplifications are made in applications of theory to practical problems. A common simplification is the assumption that flow towards a well is horizontal. This may then allow the application of a two-dimensional model, rather than a more data intensive three-dimensional model, to many sites. Two-dimensional models typically do not represent complexities of threedimensional flow regimes. Most pump-and-treat remediations use partially penetrating wells, which induce significant vertical flow, whereas the two-dimensional models implicitly assume that the remediation wells are screened throughout the saturated thickness of the aquifer.

The majority of these models assume that the density and viscosity of the fluid(s) are equal to that of pure water. It is known that fluid density differences may cause threedimensional flow (e.g., high TDS leachate from landfills). However, if the limitations of the models are realized and accounted for, they may serve as useful tools to predict ground-water flow and contaminant transport relatively accurately at many sites.

It is essential to have appropriate field and laboratory determinations of natural process parameters and variables. These may be used to determine the validity and usefulness of each modeling attempt. Errors arising from inadequate data are not addressed properly by mathematical tests such as sensitivity analyses, or by the application of stochastic techniques for estimating uncertainty. Such tests and stochastic simulations assume that the underlying conceptual basis of the model is correct (Andersen and others, 1984; Bear and Verruijt, 1987; Dagan, 1982b; El-Kadi, 1988; Konikow, 1986; Krabbenhoft and Anderson, 1986; Smith and Freeze, 1979a and 1979b). A conceptual model should be modified only if the data justify the change. The high degree of hydrogeological, chemical, and microbiological complexity typically present in field situations requires site-specific characterization of various natural processes by detailed field and laboratory investigations.

It is also important that both the mathematics that describe the models and the input parameters used by the models be subjected to rigorous quality control measures. Otherwise, results from field applications of models may be qualitatively and quantitatively incorrect. If done properly, mathematical modeling may be used to organize vast amounts of disparate data into a sensible framework that may provide realistic appraisals of the performance of ground-water remediations.

Some of the more traditional appraisals conducted with mathematical models include:

- evaluation of changes in size and relative concentrations of conservative solute plumes, using flow models;
- (ii) evaluation of changes in size and relative concentration of reactive solute plumes, using flow models;
- (iii) evaluation of changes in size and average concentration of conservative plumes, using contaminant transport models; and
- (iv) evaluation of changes in size and average concentration of reactive plumes, using contaminant transport models.

Models may also be used to evaluate the effects of changes in basic design and operating parameters, so that the most effective and efficient remediation can be attained.

Geochemical speciation models and reaction rate models can likewise be employed to improve the interpretation of data that might otherwise be appraised by simple cation/ anion balances. The outputs of speciation and reaction rate models may yield useful information concerning the release rates of contaminants, treatment needs, and disposal options.

Quality control procedures have been developed for the creation, documentation, and intercomparison of models (Huyakorn, 1984; Mercer and Faust, 1981; Mercer and others, 1982; Remson and others, 1971; van der Heijde and others, 1985). These include:

- (i) functionality testing of subroutines and linkages between subroutines and the main driver of a program;
- (ii) double key entry of all test data, spell-checking, automatic syntax checking, and debugging;
- (iii) rate-of-convergence and other stability checks; comparison of model outputs with known solutions to analytical equations; and
- (iv) partial validation by blind prediction of controlled experiments.

The development of quality control procedures for applications of models to field problems has not progressed beyond the bounds of individual professional judgment.

2. Statistical Methods

The potential power of statistical methods has been tapped infrequently in ground-water contamination investigations, aside from their use in quality assurance protocols. There are other important uses of statistical methods, however, as shown in Table 1. While data interpretation and presentation methods vary widely, most site documents lack statistical evaluations. Many site reports present inappropriate simplifications of datasets, such as grouping or averaging broad categories of data, without regard to the statistical validity of those simplifications.

Laboratory scientists use analysis of variance (ANOVA) and covariance (ANCOVA) to analyze the sources of error in sample analyses. Certain errors, such as those associated with operator error, may be identified and segregated from the irreducible errors associated with instrumental limitations. It may then be possible to institute changes that minimize and control such errors within specific confidence

Table I. Useful Statistical Methods for Performance Evaluations Analysis of Variance (ANOVA) Techniques

ANOVA techniques may be used to segregate errors due to chemical analyses from those errors that are due to sampling procedures and from the intrinsic variability of the contaminant concentrations at each sampling point.

Correlation Coefficients

Correlation coefficients can be used to provide justification for lumping various chemicals together (e.g., total VOCs), or for using a single chemical as a class representative, or to link sources by similar chemical behavior.

Regression Equations

Regression equations may be used to predict contaminant loads based on historical records and supplemental data, and may be used to test causeand-effect hypothesis about sources and contaminant release rates.

Surface Trend Analysis Techniques

Surface trend analysis techniques may be used to identify recurring and intermittent (e.g., seasonal) trends in contour maps or ground-water elevations and contaminant distributions, which may be extrapolated to source locations or future plume trajectories.

bounds (Davis, 1986; Huntsberger and Billingsley, 1977; SAS Institute, 1988c and 1989b; Taylor, 1987)

Multiple or linear regression plots may be used to examine time-wise or space-wise trends in contaminant concentrations and water-level elevations. When used in conjunction with Student's t-test and Fischer's F-test, regression equations can test hypotheses about cause-andeffect relationships (Huntsberger and Billingsley, 1977; SAS Institute, 1988c, 1988d and 1989b). Correlation coefficients may be computed for one variable versus another to study the association between them, and to justify grouping, averaging, or selection of class/category representatives. Datasets that contain too few observations or wildly fluctuating values may be analyzed with non-parametric methods to gain some sense of average or expected value and associated uncertainty.

The general linear model (GLM), auto-regressive moving average (ARMA), and auto-regressive integrated moving average (ARIMA) techniques may provide some additional information about the direction in which the mean is trending and its stability (SAS Institute, 1988c and 1988d). Geostatistical methods, such as kriging, cokriging, and conditional simulations, offer similar capabilities for twoand three-dimensional evaluations. The expected values at key locations and the uncertainties associated with them may be estimated at specified confidence levels (Steinhorst and Williams, 1985; Usunoff and Guzman-Guzman, 1989). Cluster analyses and principal component analyses may also be used to examine two- and three-dimensional datasets to identify dominant or recurring patterns.

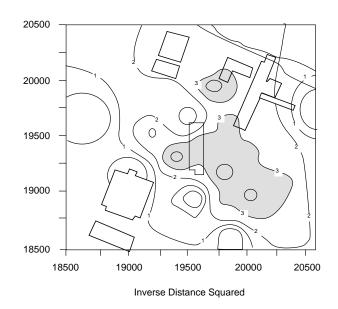
3. Graphical Methods

Graphical methods of data presentation and analysis have been used heavily in ground-water flow and geochemical evaluations (Cedergren, 1989; Freeze and Cherry, 1979; Javendel and others, 1984; Keely, 1984; Keely and Tsang, 1983; Watson, 1984; Cheng, 1988; Rogers, 1989; Stumm and Morgan, 1981; Tinsley, 1979).

Flowline plots offer much information because velocity computations are typically provided as a vehicle for obtaining the flowlines. Most flowline plotting software allows the user to create a flowline plot on which are superimposed plots of injection fronts or arrival fronts for specific durations of pumping. From analysis of such plots, it is possible to estimate the number of pore volumes of ground water that will be removed over a set period of time of constant pumping, at different locations in the contaminant plume.

Contour maps of contaminant concentrations or water-level elevations are probably the most common graphics prepared in site studies. When contour maps are prepared by hand, the practitioner's judgment is automatically applied to shaping and smoothing contours. Beyond purely mathematical decisions regarding the interpolation (e.g., linear, geometric, lognormal) of values at locations that lie between measured points, there is the need to account for the behavior of real physical boundaries (e.g., streams, valley walls and bedrock).

When contour maps are prepared for identical data sets by different automated mathematical routines dissimilar outcomes are possible (Figure 6). The perceptions that may be generated by examination of contour maps that have been prepared by different automated mathematical interpolation schemes can vary substantially because both the shapes of the contours and the areas contained by specific contours may vary considerably. It is clear that there are contouring techniques, such as kriging, that allow measured data points to be predicted precisely. However, even these are subject to map-edge effects and often have difficulty with boundaries. The shapes of the contours that are generated by kriging depend on the kind of model that the data are postulated to follow (e.g., spherical, parabolic). Moreover, by varying the density of the grid of data or the number of contours used to produce a contour map, major differences in the locations and bounded areas of the contours may occur.



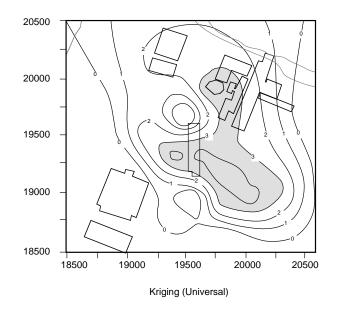


Figure 6. The results of contouring a dataset by various mathematical techniques may be significantly different.

Uni-directional plots, such as contaminant concentration levels versus distance between source areas and potential receptors, may also be used in performance evaluations. These are constructed by plotting contaminant concentration as a function of distance along a specific flowline. If the flowline patterns shift due to the influence of pumping wells, transport extrapolations will no longer be valid. Extrapolations must be validated by proof of duration of transport to allow sufficient time for contaminants to traverse the length of the flowline in a single orientation. Time plots of contaminant concentration levels on a monthly or quarterly basis may be prepared for specific monitoring locations, but caution must be used to validate decreasing or increasing trends of concentration levels. Changes in contaminant concentration levels may occur as a result of any combination of (i) source release characteristics, (ii) depletion of the contaminants, and (iii) flowline pattern shifts.

Stiff diagrams are multivariate plots of the milli-equivalence values of the major cations and anions of water samples that produce readily recognizable patterns of the chemical composition of ground-water. The major ionic composition of contaminated ground water may differ significantly from the natural ground-water quality in adjacent areas, often resulting in different Stiff diagram patterns. Water quality specialists use the diagrams to differentiate zones of varying water quality, such as leachate plumes emanating from landfills and the upconing of saline water due to pumping. Geochemical prospectors also use this and similar graphical techniques to identify waters associated with mineral deposits.

Recently, multivariate plots similar to Stiff diagrams have been adapted to display organic chemical contaminants (Lesage and Lapcevic, 1990). For example, a compound of interest such as trichloroethene may be evaluated in terms of its contribution to the total organic contaminant load, or against other specific contaminants, so that some differentiation of source contributions to the overall plume can be obtained (Figure 7).

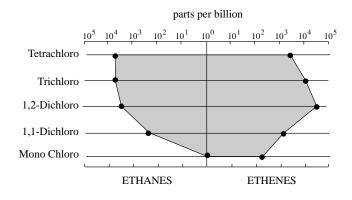


Figure 7. Pattern diagram for selected VOCs.

Aside from the plotting of discrete quantitative values of chemical concentrations or water-level elevations, plots of qualitative information are useful. Soil survey maps, drillers' logs, geologic cross-sections, and fence diagrams of sediment sequences are common qualitative methods of presenting data. All are subject to major errors when data points are sparse or inappropriately sampled; most tend to be used in a manner that understates the true uncertainties involved. For example, it may not be appropriate to detail the possible linkages of strata denoted on the geologic log of one location with that of another when the strata are known to occur as remnants of stream channels and reworked floodplain deposits. Inspection of raw datasets by those whose judgment has been shaped by many hours at local sites can provide valuable input for decisions on how strongly to associate occurrences of similar sediments.

In addition to quantitative and qualitative plots and maps, certain charts and illustrations can be prepared for use in management of the remedial activities. Program evaluation and review technique (PERT) charts may be used to map the dependencies of each task on those that precede it, and can be configured to facilitate analysis of the operations by the critical pathway method (CPM), in which the chain of core tasks that must be completed to lead to a specific output can be identified and protected during modifications to the list of tasks (Figure 8). Although this may seem trivial when a single individual is charting tasks for a single project, it is clearly more complex when coordinating the tasks of many individuals or projects.

Other hierarchal action diagrams, such as sample selection and routing protocols, are useful tools for improvement of the efficiency and effectiveness of pump-and-treat remediations. Database management systems, particularly those that operate under a geographical information system (GIS) are also extremely valuable for analysis and presentation of hydrogeologic and ground-water contamination data.

4. Theoretical

General indicators of physicochemical reaction potential include the cation-exchange-capacity (CEC), alkalinity, and acidity of subsurface samples. Theoretical relationships link CEC, alkalinity, and acidity to the reserve of reactants, and consequently to the potential products. Theoretical equations have also been developed and tested for various wastewater treatment unit designs.

Batch sorption isotherms and static microcosms can be used to generate estimates of limiting reaction rates of specific contaminants. Information on the dynamics of such reactions is obtained from flow-through column studies utilizing labelled tracers. It is most common to evaluate

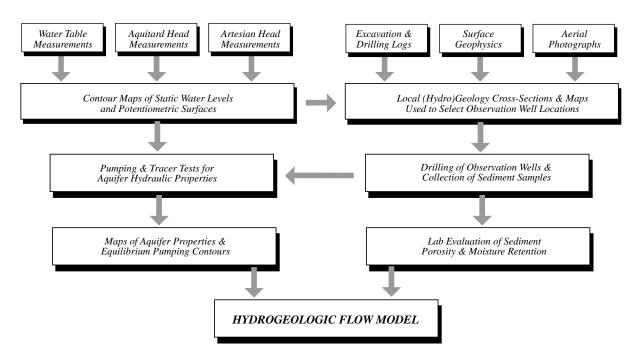


Figure 8. PERT Chart illustrating interdependency of tasks to produce outputs.

data from such experiments by comparison to an equation that has been derived from theory, as opposed to the use of empirical relationships.

The probable reaction rates and products of some compounds may be predicted by quantitative structureactivity relationships (QSAR). These relationships typically utilize information such as the physical and symmetry properties of the molecule to draw analogies to the behavior of other molecules.

General Protocols for Performance Evaluations

The protocols presented here are generalized and should be refined on a site-specific basis. The flowcharts that are provided are neither exhaustive nor exclusive, but should serve as reasonable skeletons on which to build site-specific charts of key activities. The latter can be accomplished most fruitfully by utilization of software that create and allow interactive modification and automated updating of PERT charts.

1. <u>General Protocol for Selection of Monitoring</u> <u>Criteria and Reporting Requirements</u>

(1) Begin the selection of performance evaluation and monitoring criteria by reviewing the data

collection history at the site to determine the potential need for adoption of specific spatial or temporal patterns of sampling to ensure continuity with previous efforts.

- (2) Pre-operational programs for sample collection and analyses, quality control, and data interpretation will be required between the completion of the RI/FS and effective start-up of the remediation. These will be needed to provide current information regarding the threat to human health and the environment, and the size and orientation of the zone of remedial action that should be established to prevent loss of portions of the contaminant plume to downgradient areas. Select monitoring criteria appropriate to these data needs.
- (3) Bench treatability studies and pilot plant demonstrations may be called for by design engineers prior to commencement of construction of the final remedy.
- (4) Consider conducting studies at flow rates equivalent to those expected for different locations within the proposed remediation wellfield.
- (5) Obtain samples of subsurface sediments for chemical extraction analyses of contaminant

residuals and for key transport properties such as total organic carbon during opportunities presented by pre-construction activities (e.g., excavations, trenching, drilling). Evaluate the potential for NAPLs at the site.

- (6) Overlay plots of all sampling events and sample types to identify locations of inadequate sampling and to set a schedule to fill such vacancies. Select performance evaluation criteria appropriate to these activities.
- (7) Prepare brief reports of sample collection and analyses as data becomes available, rather than wait for all items to be synthesized into a major report. This information can affect ongoing preparations for commencement of operation.
- (8) Modify the frequency and locations for sampling during operation, as necessary. Specifically focus on characterization of the flowlines that will result from operation of the remediation wellfield, and on tracking the transport of contaminants along the flowlines. Anticipate flowline shifts due to partial shutdowns or operational failures.
- (9) Provide adequate coverage of monitoring wells and piezometers beyond the horizontal and vertical bounds of the plume, such that transgressions of flowlines originating in the plume can be tracked to ensure eventual capture by an extraction well, and such that the contribution of uncontaminated ground water to the total volume pumped can be examined.
- (10) Make provisions for measurements germane to active management of the operation, such as flow rates and contaminant concentration levels for (i) individual extraction wells, (ii) treatment plant influent, (iii) key treatment units, and (iv) the plant effluent.
- (11) Reduce the frequency of chemical sampling (but not water-level elevation measurements) if stable trends of contaminant concentration levels are apparent, and provide contingencies for increased sampling in response to those periods when the data are highly erratic.
- (12) Continue filling gaps in the site characterization database with opportunistic and periodic testing.
- (13) Evaluate the rate of depletion of the residual contamination by collection of sediment samples for chemical extraction and analysis. This

operation should be accompanied by a statistical evaluation of contaminant distribution at each sampling point. Chart the estimated mass of contaminants removed, both total and per location; compare these estimates with the mass of contaminants removed by the treatment system.

- (14) Plot and examine water-level elevation contours to determine the adequacy of hydrodynamic control and to identify stagnation zones for subsequent action.
- (15) As the concentration-time plots begin to flatten out, try varying the flowrates of a few extraction wells at a time to determine the potential for improvement with wellfield scheduling or configuration changes.
- (16) When all potential improvements have been attempted and exhausted, prepare for termination of the remediation by increasing the sampling frequency to build a statistically significant database for plotting regressions with 95% confidence bounds so that success can be judged.
- (17) Throughout the operational phase of the remediation, utilize monitoring data as soon as they become available, for active management purposes; prepare comprehensive annual reports for regulatory oversight purposes.
- (18) If the regression plots indicate that the target contaminant concentration levels have been reached, propose termination of the remediation.
- (19) If permission to begin termination is granted by the regulators, continue the sampling program at the same (high) frequency for up to two years to test the need to re-activate and/or re-evaluate the remediation. Prepare brief reports quarterly for management and regulatory purposes during this period.
- (20) Subsequently reduce the frequencies of collecting and reporting on samples and measurements to an annual basis to monitor the persistence of the effects of the remediation; continue at that level until the end of the regulatory period.

2. <u>General Protocol for Violations Reporting and</u> <u>Responses</u>

(1) Examine the data collected during each sampling event for internal consistency prior to accepting the accuracy or relevancy of anomalous values. If a

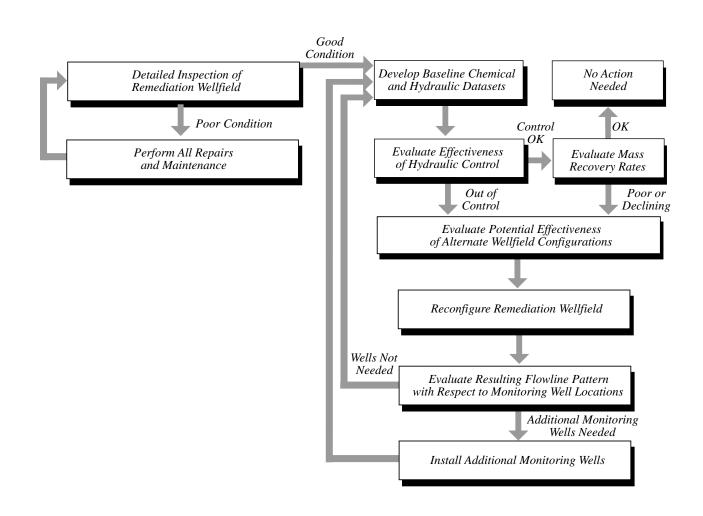


Figure 9. Outline of key efforts needed to select and use monitoring and reporting requirements.

single monitoring point indicates an unacceptable level of a particular contaminant, check the concentration levels of other contaminants at the same location to see if they have approximately the same relationship (ratio) to the suspect contaminant as has been shown to occur generally for the plume; if not, reject the suspect value as internally inconsistent.

- (2) If general agreement seems to be indicated, or cannot be judged due to the small number of contaminants associated with a particular plume (e.g., predominantly TCE and nothing else), then compare the suspect value with the concentration levels found in nearby wells; if poor agreement is indicated, reject considering the suspect value as locally inconsistent.
- (3) If the suspect value is not rejected due to internal inconsistency or due to local inconsistency, retain the value in the dataset as valid and immediately resample or remeasure at that location and at two or more adjacent locations (for control). Evaluate the resulting data in the same fashion as the initial data.
- (4) Regardless of the status (rejected or retained) of the first such indication at a specific location, consider successive indications to confirm the loss of adequate control of the zone of remedial action.
- (5) Study the wellfield scheduling to determine at which wells the flowrates may be increased to provide the degree of control needed.

- (6) Expect that flowline patterns will shift with the implementation of new pumping schedules, and plan to evaluate the significance of the shift in terms of the need to reposition sampling/ measurement points.
- (7) Verify the operational viability (e.g., minimum hydrodynamic control) of the modified wellfield by increasing the frequency of sampling/measurement for a period of three to six months.
- (8) Utilize information obtained during the increased sampling/measurement period to assess the impacts of the correctional action in terms of changes in the rate of depletion of the contaminant residuals.

3. <u>General Protocols for Design and Operation</u> <u>Modifications</u>

(1) Modifications of system design or operation may be called for either as a result of checking the remediation for readiness for termination or as a result of violations. In either case, if a major modification is anticipated, it is prudent to perform a detailed inspection and analysis of the system first. All piping, valves, and protective shielding should be in good condition; leaks, indications of corrosion or excessive wear, and poor electrical grounds should be repaired. All gauges and electronic monitors should be in calibration and should provide appropriate responses to tests; if not, the deficiencies should be remedied.

- (2) A few sampling/measurement events should then be undertaken to provide a baseline for comparison to data to be collected after the modification, and to provide immediate data for development of the modification.
- (3) Development of the modification should proceed with the targeted hydraulic control and clean-up levels still firmly in mind. If the remediation has

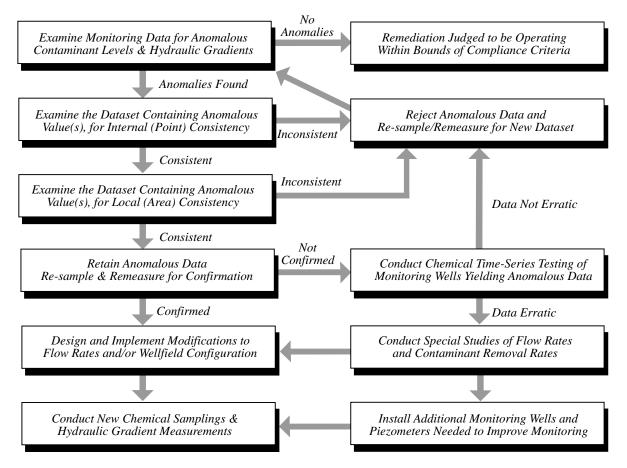


Figure 10. Key efforts needed to identify, verify, and correct inadequate performance of the remediation.

been successful in depleting contaminants from the outermost portions of the plume, it may be sensible to shrink the remediation wellfield inward. If additional control is needed, it may need to be expanded outward.

- (4) In these cases particularly, but also in the case where the overall size remains unaffected and wells are simply relocated within the existing wellfield, it is essential to begin to anticipate the new orientation of the flowline pattern.
- (5) Monitoring point locations may need to be changed, and new trends of contaminant transport and recovery will have to be identified. Hence, an increased frequency of sampling/measurement events will be needed for three to six months following establishment of routine operation of the modified system.

(6) Verification of operational viability and assessment of the impacts of the modification on depletion rates of contaminant residuals then follow.

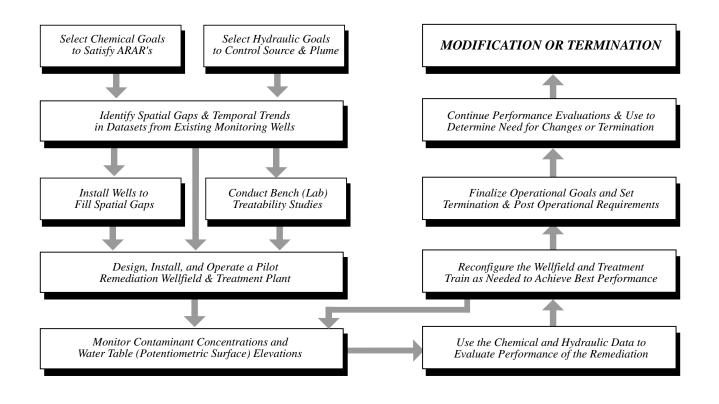


Figure 12. Key efforts needed to prepare for, implement, and verify modifications of the remediation.

References

Abriola, L.M. and G.F. Pinder. 1985. A Multiphase Approach to the Modeling of Porous Media Contamination by Organic Compounds. Water Resources Research 21(1):11-18.

Andersen, P.F., C.R. Faust, and J.W. Mercer. 1984. Analysis of Conceptual Designs for Remedial Measures at Lipari Landfill. Groundwater, 22(2).

Anderson, M.P. 1979. Using Models to Simulate the Movement of Contaminants Through Groundwater Flow Systems. Critical Reviews in Environmental Controls, 9(2):97-156.

Asbeck, E. and Y.Y. Haimes. 1984. The Multiobjective Risk Method. Large Scale Systems, 13(38).

Bahr, J. 1989. Analysis of Nonequilibrium Desorption of Volatile Organics during Field Test of Aquifer Decontamination. Journal of Contaminant Hydrology 4(3):205-222.

Baehr, A.L., G.E. Hoag, and M.C. Marley. 1989. Removing Volatile Contaminants from the Unsaturated Zone by Inducing Advective Air-Phase Transport. Journal of Contaminant Hydrology 4(1):1-26.

Barker, J.F., J.E. Barbash, and M. LaBonte. 1988. Groundwater Contamination at a Landfill Sited on Fractured Carbonate and Shale. Journal of Contaminant Hydrology 3(1):1-25.

Barker, J.F., G.C. Patrick, and D. Major. 1987. Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer. Ground Water Monitoring Review 7(1):64-71.

Bear, J. and A. Verruijt. 1987. Modeling Groundwater Flow and Pollution. D. Reidel Publishing Company; Boston, Massachusetts.

Bengtsson, G., C.G. Enfield, and R. Lindquist. 1988. Macromolecules Facilitate Transport of Trace Organics. Science of the Total Environment 67:159-169.

Bitton, G. and C.P. Gerba (editors). 1984. Groundwater Pollution Microbiology. Wiley Interscience/John Wiley & Sons Inc.; New York.

Blatt, H., G.V. Middleton, and R.C. Murray. 1980. Origin of Sedimentary Rocks (2nd Ed.). Prentice-Hall Inc.; Englewood Cliffs, New Jersey.

Borden, R., M. Lee, J.M. Thomas, P. Bedient, and C.H. Ward. 1989. In Situ Measurement and Numerical Simulation of Oxygen Limited Biotransformation. Ground Water Monitoring Review 9(1):83-91.

Bouchard, D.C., C.G. Enfield, and M.D. Piwoni. 1989. Transport Processes Involving Organic Chemicals, in Reactions and Movement of Organics Chemicals in Soils. Soil Science Society of America, Special Publications Press.

Bouchard, D.C., A.L. Wood, M.L. Campbell, P. Nkedi-Kizza, and P.S.C. Rao. 1988. Sorption Nonequilibrium during Solute Transport. Journal of Contaminant Hydrology 2(3):209-223.

Boutwell, S.H., S.M. Brown, B.R. Roberts, and D.F. Atwood. 1985. Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites. U.S. Environmental Protection Agency publication EPA/540/2-85/001.

Bouwer, E.J. and J.P. Wright. 1988. Transformations of Trace Halogenated Aliphatics in Anoxic Biofilm Columns. Journal of Contaminant Hydrology 2(2):155-169.

Bouwer, H. and R.C. Rice. 1976. A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells. Water Resources Research, v. 12, pp. 423-428.

Brown, J. 1986. Environmental Software Review. Pollution Engineering, 18(1).

Brusseau, M.L., P.S.C. Rao, R.E. Jessup, and J.M. Davidson. 1989. Flow Interruption: A Method for Investigating Sorption Nonequilibrium. Journal of Contaminant Hydrology 4(3):223-240.

Burden, R.L., J.D. Faires, and A.C. Reynolds. 1981. Numerical Analysis (2nd Ed.). Prindle, Weber, and Schmidt; Boston, Massachusetts.

Cannon, J.Z. 1989. Considerations in Ground Water Remediation at Superfund Sites. Directive No. 9355.4-03. Office of SolidWaste and Emergency Response, U.S. EPA, Washington, D.C.

Cedergren, H.R. 1989. Seepage, Drainage, and Flow Nets (3rd Ed.). John Wiley & Sons Inc.; New York, pp.125-147.

Chapuis, R.P. 1989. Shape Factors for Permeability Tests in Boreholes and Piezometers. Ground Water 27(5):647-654.

Chau, T.S. 1988. Analysis of Sustained Ground-Water Withdrawals by the Combined Simulation-Optimization Approach. Ground Water 26(4):454-463.

Cheng, S. 1988. Computer Notes - Trilinear Diagram Revisited: Application, Limitation, and an Electronic Spreadsheet Program. Ground Water 26(4):505-510.

Compton, R.R. 1962. Manual of Field Geology. John Wiley & Sons Inc.; New York.

Corey, A.T. 1977. Mechanics of Heterogeneous Fluids in Porous Media. Water Resources Publications; Fort Collins, Colorado.

Council on Economic Priorities. 1986. Hazardous Waste Management: Reducing the Risk. Island Press; Washington, D.C.

Crow, W.L., E.P. Anderson, and E.M. Minugh. 1987. Subsurface Venting of Vapors Emanating from Hydrocarbon Product on Ground Water. Ground Water Monitoring Review 7(1):51-57.

Curtis, G.P., P.V. Roberts, and Martin Reinhard. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 4. Sorption of Organic Solutes and Its Influence on Mobility. Water Resources Research 22(13):2059-2067.

Dagan, G. 1982a. Stochastic Modeling of Groundwater Flow by Unconditional and Conditional Probabilities: Part 1. Conditional Simulation and the Direct Problem. Water Resources Research 18(4):813-833.

Dagan, G. 1982b. Stochastic Modeling of Groundwater Flow by Unconditional and Conditional Probabilities: Part 2. The Solute Transport Problem. Water Resources Research 18(4):835-848.

Daley, P.S. 1989. Cleaning Up Sites with On-site Process Plants. Environmental Science and Technology 23(8):912-916.

Davis, J.C. 1986. Statistics and Data Analysis in Geology (2nd Ed.). John Wiley & Sons Inc.; New York, pp.227-250.

Davis, S.N. and R.J.M. DeWeist. 1966. Hydrogeology. John Wiley & Sons Inc.; New York.

de Marsily, G. 1986. Quantitative Hydrogeology: Groundwater Hydrology for Engineers. Academic Press Inc.; Orlando, Florida.

Eaton, J.D. 1982. Real Estate Valuation in Litigation. American Institute of Real Estate Appraisers; Chicago, Illinois. El-Kadi, A. 1988. Applying the USGS Mass Transport Model (MOC) to Remedial Actions by Recovery Wells. Groundwater, 26 (3).

Enfield, C.G. 1985. Chemical Transport Facilitated by Multiphase Transport Flow Systems. Water Science and Technology, 17(9):1-12.

Enfield, C.G. and G. Bengtsson. 1988. Macromolecular Transport of Hydrophobic Contaminants in Aqueous Environments. Ground Water 26(1):64-70.

Faust, C.R. 1985. Transport of Immiscible Fluids Within and Below the Unsaturated Zone: A Numerical Model. Water Resources Research 21(4):587-596.

Faust, C.R., L.R. Silka, and J.W. Mercer. 1981. Computer Modeling and Ground-Water Protection. Groundwater, 19 (4).

Feenstra, S., J.A. Cherry, E.A. Sudicky, and Z. Haq. 1984. Matrix Diffusion Effects on Contaminant Migration from an Injection Well in Fractured Sandstone. Ground Water 22(3):307-316.

Fetter, C.W. 1988. Applied Hydrogeology (2nd Ed.). Merrill Publishing Company; Columbus, Ohio.

Flathman, P., D. Jerger, and L. Bottomley. 1989. Remediation of Contaminated Ground Water Using Biological Techniques. Ground Water Monitoring Review 9(1):105-119.

Freeze, R.A. and J.A. Cherry. 1979. Groundwater. Prentice Hall, Inc.; Edgewood Cliffs, New Jersey.

Gerald, C.F. and P.O. Wheatley. 1984. Applied Numerical Analysis (3rd Ed.). Addison-Wesley Publishing Company; Reading, Massachusetts.

Gelhar, L.W. 1986. Stochastic Subsurface Hydrology from Theory to Applications. Water Resources Research 22(9):135S-145S.

Gelhar, L.W. and C.L. Axness. 1983. Three-Dimensional Stochastic Analysis of Macrodispersion in Aquifers. Water Resources Research 19(1):161-180.

Gelhar, L.W., A.L. Gutjahr, and R.L. Naff. 1979. Stochastic Analysis of Macrodispersion in a Stratified Aquifer. Water Resources Research 15(6):1387-1397.

GIS World. 1989. GIS Technology '89: Results of the 1989 GIS World Geographical Information Systems Survey. GIS World, Inc.; Fort Collins, Colorado. Goltz, M.N. and P.V. Roberts. 1986. Interpreting Organic Solute Transport Data from a Field Experiment using Physical Nonequilibrium Models. Journal of Contaminant Hydrology 1(1/2):77-94.

Goltz, M.N. and P.V. Roberts. 1988. Simulations of Physical Nonequilibrium Solute Transport Models: Application to a Large-Scale Field Experiment. J. Contaminant Hydrology 3(1):37-64.

Gschwend, P.W. and M.D. Reynolds. 1987. Monodisperse Ferrous Colloids in an Anoxic Groundwater Plume. Journal of Contaminant Hydrology, 2(4):309-327.

Gschwend, P.W. and S.C. Wu. 1985. On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants. Environmental Science and Technology, 19(1).

Guven, O. and F.J. Molz. 1986. Deterministic and Stochastic Analyses of Dispersion in an Unbounded Stratified Porous Medium. Water Resources Research 22(11):1565-1574.

Hallenbeck, W.H., and K.M. Cunningham. 1986. Quantitative Risk Assessment for Environmental and Occupational Health. Lewis Publishers Inc.; Chelsea, Michigan.

Heath, R.C. 1983. Basic Ground-Water Hydrology. U.S. Geological Survey Water-Supply Paper 2220.

Hess, A.E. and F.L. Paillet. 1989. Characterizing Flow Paths and Permeability Distribution in Fractured-Rock Aquifers Using a Sensitive, Thermal Borehole Flowmeter. Proceedings of New Field Techniques for Quantifying the Physical and Chemical Properties of Heterogeneous Aquifers. National Water Well Association, Dublin, Ohio.

Hillel, D. 1982. Fundamentals of Soil Physics. Academic Press; New York, 2nd edition.

Hinchee, R. and H.J. Reisinger. 1987. A Practical Application of Multiphase Transport Theory to Ground Water Contamination Problems. Ground Water Monitoring Review 7(1):84-92.

Hossain, M.A. and M.Y. Corapcioglu. 1988. Modifying the USGS Solute Transport Computer Model to Predict High-Density Hydrocarbon Migration. Ground Water 26(6):717-723.

Huling, S.G. and J.W. Weaver. 1991. Ground Water Issue: Dense Nonaqueous Phase Liquids. EPA/540/4-91/002. Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, U.S. EPA; Ada, Oklahoma. Hunt, J.R., N. Sitar, and K.S. Udell. 1988a. Nonaqueous Phase Liquid Transport and Cleanup: 1. Analysis of Mechanisms. Water Resources Research 24(8):1247-1258.

Hunt, J.R., N. Sitar, and K.S. Udell. 1988b. Nonaqueous Phase Liquid Transport and Cleanup: 2. Experimental Studies. Water Resources Research 24(8):1259-1269.

Huntsberger, D.V. and P. Billingsley. 1977. Elements of Statistical Inference (4th Ed.). Allyn and Bacon, Inc.; Boston, Massachusetts.

Huyakorn, P.S. 1984. "Testing and Validation of Models for Simulating Solute Transport in Ground Water: Development and Testing of Benchmark Techniques." IGWMC Report No. GWMI 84-13, International Ground Water Modeling Center, Holcolm Research Institute; Indianapolis, Indiana.

James, M.L., G.M. Smith, and J.C. Wolford. 1977. Applied Numerical Methods for Digital Computation with FORTRAN and CSMP (2nd Ed.). Harper & Row, Publishers; New York.

Javendel, I., C. Doughty, and C.F. Tsang, 1984. Groundwater Transport: Handbook of Mathematical Models, AGU Water Resources Monograph No. 10. American Geophysical Union; Washington, D.C.

Jensen, B.K., E. Arvin, and A.T. Gundersen. 1988. Biodegradation of Nitrogen- and Oxygen-Containing Aromatic Compounds in Groundwater from an Oil-Contaminated Aquifer. Journal of Contaminant Hydro. 3(1):65-76.

Jorgensen, D.G., T. Gogel, and D.C. Signor. 1982. Determination of Flow in Aquifers Containing Variable-Density Water. Ground Water Monitoring Review 2(2):40-45.

Keely, J.F. 1982. Chemical Time-Series Sampling. Ground Water Monitoring Review 2(3):29-38.

Keely, J.F. 1984. Optimizing Pumping Strategies for Contaminant Studies and Remedial Actions. Ground Water Monitoring Review 4(3):63-74.

Keely, J.F. 1989. Ground Water Issue: Performance Evaluations of Pump-and-Treat Remediations. EPA/540/4-89/005, Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, U.S. EPA; Ada, Oklahoma.

Keely, J.F., M.D. Piwoni, and J.T. Wilson. 1986. Evolving Concepts of Subsurface Contaminant Transport. Journal Water Pollution Control Federation. 58(5):349-357. Keely, J.F. and C.F. Tsang. 1983. Velocity Plots and Capture Zones of Pumping Centers for Ground Water Investigations. Ground Water 22(6):701-714.

Kipp, K.L., K.G. Stollenwerk, and D.B. Grove. 1986. Groundwater Transport of Strontium 90 in a Glacial Outwash Environment. Water Resources Research 22(4):519-530.

Klotz, D., K.P. Seiler, H. Moser, and F. Neumaier. 1980. Dispersivity and Velocity Relationship from Laboratory and Field Experiments. Journal of Hydrology; 45(1);169-184.

Konikow, L.F. 1986. Predictive Accuracy of a Ground-Water Model - Lessons from a Postaudit. Ground Water 24(2):173-184.

Krabbenhoft, D.P. and M.P. Anderson. 1986. Use of a Numerical Ground-Water Flow Model for Hypothesis Testing. Groundwater, 24(1).

Kueper, B.H. and E.O. Frind. 1988. An Overview of Immiscible Fingering in Porous Media. Journal of Contaminant Hydrology 2(2):95-110.

Lee, L.S., P.S.C. Rao, M.L. Brusseau, and R.A. Ogwada. 1988. Nonequilibrium sorption of Organic Contaminants during Flow through Columns of Aquifer Materials. Environmental Toxicology and Chemistry 7(10):779-793.

Lesage, S., and P.A. Lapcevic. 1990. Differentiation of the Origins of BTX in Ground Water Using Multivariate Plots. Ground Water Monitoring Review, 10(2):102-105.

Loftis, J.C., J. Harris, and R.H. Montgomery. 1987. Detecting Changes in Ground Water Quality at Regulated Facilities. Ground Water Monitoring Review 7(1):72-76.

Macalady, D.L., P.G. Tratnyek, and T.J. Grundl. 1986. Abiotic Reduction Reactions of Anthropogenic Organic Chemicals in Anaerobic Systems: A Critical Review. Journal of Contaminant Hydrology 1(1/2):1-28.

Mackay, D.M., W.P. Ball, and M.G. Durant. 1986. Variability of Aquifer Sorption Properties in a Field Experiment on Groundwater Transport of Organic Solutes: Methods and Preliminary Results. Journal of Contaminant Hydrology 1(1/2):119-132.

Mackay, D.M., D.L. Freyberg, P.V. Roberts, and J.A. Cherry. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 1. Approach and Overview of Plume Movement. Water Resources Research 22(13):2017-2029. Major, D.W., C.I. Mayfield, and J.F. Barker. 1988. Biotransformation of Benzene by Denitrification in Aquifer Sand. Ground Water 26(1):8-14.

Matheron, G. and G. de Marsily. 1980. Is Transport in Porous Media always Diffusive? A Counterexample. Water Resources Research, 16(5):901-917.

McCarthy, J.F. and J.M. Zachara. 1989. Subsurface Transport of Contaminants. Environmental Science and Technology, 23(5):496-502.

Mendenhall, W. 1968. Introduction to Linear Models and The Design and Analysis of Experiments. Duxbury Press; Belmont, California.

Mercado, Abraham. 1985. The Use of Hydrogeochemical Patterns in Carbonate Sand and Sandstone Aquifers to Identify Intrusion and Flushing of Saline Water. Ground Water 23(5):635-645.

Mercer, J.W. and C.R. Faust. 1981. Ground-Water Modeling. National Water Well Association; Dublin, Ohio.

Mercer, J.W., D.C. Skipp, and D. Giffin. 1990. Basics of Pump-and-Treat Ground-Water Remediation Technology. EPA/600/8-90/003, Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, U.S. EPA; Ada, Oklahoma.

Mercer, J.W., P.S.C. Rao, and I.W. Marine. 1983. Role of the Unsaturated Zone in Radioactive and Hazardous Waste Disposal. Ann Arbor Science Publishers; Ann Arbor, Michigan.

Mercer, J.W., S.D. Thomas, B. Ross. 1982. Parameters and Variables Appearing in Repository Siting Models. U.S. Nuclear Regulatory Commission NUREG/CR-3066.

Miller, M.M., S.P. Wasik, G. Huang, W. Shiu and D. Mackay. 1985. Relationships between Octanol-Water Partition Coefficients and Aqueous Solubility. Environmental Science and Technology 19(7):522-529. Miller, S. 1980. Cost-Benefit Analyses. Environmental Science and Technology, 14(12).

Moltyaner, G.L. 1989. Hydrodynamic Dispersion at the Local Scale of Continuum Representation. Water Resources Research 25(5):1041-1048.

Molz, F.J., O. Guven, J.G. Melville, and J.F. Keely. 1986a. Performance and Analysis of Aquifer Tracer Tests with Implications for Contaminant Transport Modeling. U.S. EPA Office of Research and Development: EPA/600/2-86-062. Molz, F.J., M.A. Widdowson, and L.D. Benefield. 1986b. Simulation of Microbial Growth Dynamics Coupled to Nutrient and Oxygen Transport in Porous Media. Water Resources Research 22(8):1207-1216.

Molz, F.J., O. Guven, J.G. Melville, J.S. Nohrstedt, and J.K. Overholtzer. 1988. Forced-Gradient Tracer Tests and Inferred Hydraulic Conductivity Distributions at the Mobile Field Site. Ground Water 26(5):570-579.

Nkedi-Kizza, P., M.L. Brusseau, P.S.C. Rao, and A.G. Hornsby. 1989. Nonequilibrium Sorption during Displacement of Hydrophobic Organic Chemicals and 45Ca through Soil Columns with Aqueous and Mixed Solvents. Environmental Science and Technology 23(7):814-820.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1985. Influence of Organic Cosolvents on Sorption of Hydrophobic Organic Chemicals by Soils. Environmental Science and Technology, 19(10):975-979.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1987. Influence of Organic Cosolvents on Leaching of Hydrophobic Organic Chemicals through Soils. Environmental Science and Technology, 21(11):1107-1111.

Novak, S.A. and Y. Eckstein. 1988. Hydrogeochemical Characterization of Brines and Identification of Brine Contamination in Aquifers. Ground Water 26(3):317-324.

Osiensky, J.L., K.A. Peterson, and R.E. Williams. 1988. Solute Transport Simulation of Aquifer Restoration after In Situ Uranium Mining. Ground Water Monitoring Review 8(2):137-144.

Osiensky, J.L., G.V. Winter, and R.E. Williams. 1984. Monitoring and Mathematical Modeling of Contaminated Ground-Water Plumes in Fluvial Environments. Ground Water 22(3):298-306.

Ophori, D.U., and J. Toth. 1989. Patterns of Ground-Water Chemistry, Ross Creek Basin, Alberta, Canada. Ground Water 27(1):20-26.

Papadopulos, S.S., J.D. Bredehoeft, and H.H. Cooper, Jr. 1973. On the analysis of "slug test" data. Water Resources Research, 9:1087-1089.

Pinder, G.F. and L.M. Abriola. 1986. On the Simulation of Nonaqueous Phase Organic Compounds in the Subsurface. Water Resources Research 22(9):109S-119S.

Piwoni, M.D. and P. Banerjee. 1989. Sorption of Volatile Organic Solvents from Aqueous Solution onto Subsurface Solids. Journal of Contaminant Hydrology 4(2):163-179. Pollock, D.W. 1988. Semianalytical Computation of Path Lines for Finite Difference Models. Ground Water 26(6):743-750.

Poole, V.L., K. Cartwright, and D. Leap. 1989. Use of Geophysical Logs to Estimate Water Quality of Basal Pennsylvanian Sandstones, Southwestern Illinois. Ground Water 27(5):682-688.

Press, W.H., B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling. 1986. Numerical Recipes: The Art of Scientific Computing. Cambridge University Press; New York.

Remson, I., G.M. Hornberger, and F.J. Molz. 1971. Numerical Methods in Subsurface Hydrology with an Introduction to the Finite Element Method. Wiley-Interscience/John Wiley & Sons Inc.; New York.

Roberts, P.V., M.N. Goltz, and D.M. Mackay. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 3. Retardation Estimates and Mass Balances for Organic Solutes. Water Resources Research 22(13):2047-2058.

Roberts, P.V., L. Semprini, G.D. Hopkins, D. Grbic-Galic, P.L. McCarty, and M. Reinhard. 1989. In-Situ Aquifer Restoration of Chlorinated Aliphatics by Methanotropic Bacteria. U.S. Environmental Protection Agency Project Summary EPA/600/S2-89/033.

Rogers, R.J. 1989. Geochemical Comparison of Ground Water in Areas of New England, New York, and Pennsylvania. Ground Water 27(5):690-712.

SAS Institute Inc. 1988a. SAS Introductory Guide for Small Computers, Release 6.03 Edition. SAS Institute Inc.; Cary, North Carolina.

SAS Institute Inc. 1988b. SAS/GRAPHR User's Guide, Release 6.03 Edition. SAS Institute Inc.; Cary, North Carolina.

SAS Institute Inc. 1988c. SAS/STATR User's Guide, Release 6.03 Edition. SAS Institute Inc.; Cary, North Carolina.

SAS Institute Inc. 1988d. SAS/ETSR User's Guide, Version 6, First Edition. SAS Institute Inc.; Cary, North Carolina.

SAS Institute Inc. 1989a. SAS/ORR User's Guide, Version 6, First Edition. SAS Institute Inc.; Cary, North Carolina.

SAS Institute Inc. 1989b. SAS/QCR User's Guide, Version 6, First Edition. SAS Institute Inc.; Cary, North Carolina.

Satlin, R.L. and P.B. Bedient. 1988. Effectiveness of Various Aquifer Restoration Schemes Under Variable Hydrogeologic Conditions. Ground Water 26(4):488-499.

Scalf, M.R., J.F. McNabb, W.D. Dunlap, R.L. Cosby, and J. Fryberger. 1981. Manual of GroundWater Quality Sampling Procedures, Robert S. Kerr Environmental Research Laboratory, U.S. EPA; Ada, Oklahoma.

Scanlon, B.R. 1989. Physical Controls on Hydrochemical Variability in the Inner Bluegrass Karst Region of Central Kentucky. Ground Water 27(5):639-646.

Siegrist, H. and P.L. McCarty. 1987. Column Methodologies for Determining Sorption and Biotransformation Potential for Chlorinated Aliphatic Compounds in Aquifers. Journal of Contaminant Hydrology 2(1):31-50.

Smith, L. and R.A. Freeze. 1979a. Stochastic Analysis of Steady State Groundwater Flow in a Bounded Domain: 1. One-Dimensional Simulations. Water Resources Research 15(3):521-528.

Smith, L. and R.A. Freeze. 1979b. Stochastic Analysis of Steady State Groundwater Flow in a Bounded Domain: 2. Two-Dimensional Simulations. Water Resources Research 15(6):1543-1559.

Spain, J.C., J.D. Milligan, D.C. Downey, and J.K. Slaughter. 1989. Excessive Bacterial Decomposition of H2O2 During Enhanced Biodegradation. Ground Water 27(2):163-167.

Spayed, S.E. 1985. Movement of Volatile Organics Through a Fractured Rock Aquifer. Ground Water 23(4):496-502.

Srinivasan, P. and J.W. Mercer. 1988. Simulation of Biodegradation and Sorption Processes in Ground Water. Ground Water 26(4):475-487.

Staples, C.A. and S.J. Geiselmann. 1988. Cosolvent Influences on Organic Solute Retardation Factors. Ground Water 26(2):192-198.

Starr, R.C., R.W. Gillham, and E.A. Sudicky. 1985. Experimental Investigation of Solute Transport in Stratified Porous Media: 2. The Reactive Case. Water Resources Research 21(7):1043-1050.

Steinhorst, R.K. and R.E. Williams. 1985. Discrimination of Groundwater Sources Using Cluster Analysis, MANOVA, Canonical Analysis, and Discriminant Analysis. Water Resources Research 21(8):1149-1156. Stover, E. 1989. Co-produced Ground Water Treatment and Disposal Options During Hydrocarbon Recovery Operations. Ground Water Monitoring Review 9(1):75-82.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters (2nd Ed.). Wiley Interscience/John Wiley & Sons, Inc.; New York.

Sudicky, E.A., R.W. Gillham, and E.O. Frind. 1985. Experimental Investigation of Solute Transport in Stratified Porous Media: 1. The Nonreactive Case. Water Resources Research 21(7):1035-1041.

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers Inc.; Chelsea, Michigan.

Testa, S. and M. Paczkowski. 1989. Volume Determination and Recoverability of Free Hydrocarbon. Ground Water Monitoring Review 9(1):120-128.

Thomas, J.M. and C.H. Ward. 1989. In-situ Biorestoration of Organic Contaminants in the Subsurface. Environmental Science and Technology 23(7):760-766.

Thomsen, K., M. Chaudhry, K. Dovantzis, and R. Riesing. 1989. Ground Water Remediation Using an Extraction, Treatment, and Recharge System. Ground Water Monitoring Review, 9(1):92-99.

Thorstenson, D.C. and D.W. Pollock. 1989. Gas Transport in Unsaturated Porous Media: The Adequacy of Fick's Law. Reviews of Geophysics 27(1):61-78.

Tinsley, I.J. 1979. Chemical Concepts in Pollutant Behavior. John Wiley & Sons Inc.; New York.

Todd, D.K. 1980. Groundwater Hydrology (2nd Ed.). John Wiley & Sons Inc.; New York.

Tufte, E.R. 1983. The Visual Display of Quantitative Information. Graphics Press; Cheshire, Connecticut.

U.S. Environmental Protection Agency. 1988a. Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA (Interim Final). EPA/540/G-89/ 004, Office of Emergency and Remedial Response, U.S. EPA; Washington, D.C.

U.S. Environmental Protection Agency. 1988b. Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites. EPA/540/G-88/003, Office of Emergency and Remedial Response, U.S. EPA; Washington, D.C. U.S. Environmental Protection Agency. 1989a. Evaluation of Ground-Water Extraction Remedies, Volume 1, Summary Report. EPA/540/2-89/054, Office of Emergency and Remedial Response, U.S. EPA; Washington, D.C.

U.S. Environmental Protection Agency. 1989b. Criteria for Identifying Areas of Vulnerable Hydrogeology Under the Resource Conservation and Recovery Act, Appendix B, Ground-Water FlowNet/Flow Line Construction and Analysis (Interim Final). Office of Solid Waste and Emergency Response, U.S. EPA; Washington, D.C.

U.S. Environmental Protection Agency. 1989d. Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities (Interim Final Guidance). Office of Solid Waste, Waste Management Division, U.S. EPA; Washington, D.C.

Usunoff, E.J., and A. Guzman-Guzman. 1989. Multivariate Analysis in Hydrochemistry: An Example of the Use of Factor and Correspondence Analyses. Ground Water 27(1):27-34.

Valocchi, A.J. 1988. Theoretical Analysis of Deviations from Local Equilibrium during Sorbing Solute Transport through Idealized Stratified Aquifers. Journal of Contamination Hydrology 2(3):191-208.

van der Heijde, P.K.M., Y. Bachmat, J.D. Bredehoeft, B. Andrews, D. Holtz, S. Sebastian. 1985. Groundwater Management: The Use of Numerical Models, 2nd Edition. AGU Water Resources Monograph No. 5, American Geophysical Union; Washington, D.C.

van der Heijde, P.K.M. and P. Srinivasan. 1983. Aspects of the Use of Graphic Techniques in Ground-Water Modeling. IGWMC Report No. GWMI 83-11. International Ground Water Modeling Center, Holcolm Research Institute; Indianapolis, Indiana.

van Zyl, D.J.A., S.R. Abt, J.D. Nelson, and T.A. Shepherd (editors). 1987. Geotechnical & Geohydrological Aspects of Waste Management. Lewis Publishers, Inc.; Chelsea, Michigan.

Villeneuve, J.P., P. Lafrance, O. Banton, P. Frechette, and C. Robert. 1988. A Sensitivity Analysis of Adsorption and Degradation Parameters in the Modeling of Pesticide Transport in Soils. Journal of Contaminant Hydrology 3(1):77-96.

Vomvoris, E.G. and L.W. Gelhar. 1986. Stochastic Prediction of Dispersive Contaminant Transport. U.S. Environmental Protection Agency publication EPA/600/2-86/114. Vouk, V.B., G.C. Butler, D.G. Hoel, and D.B. Peakall. 1985. Methods for Estimating Risk of Chemical Injury: Human and Non-Human Biota and Ecosystems. John Wiley & Sons, Inc.; New York.

Walton, W.C. 1985. Practical Aspects of Ground Water Modeling (2nd Ed.). National Water Well Association; Dublin, Ohio.

Walton, W.C. 1987. Groundwater Pumping Tests: Design & Analysis. Lewis Publishers, Inc.; Chelsea, Michigan.

Wang, H. and M.P. Anderson. 1982. Introduction to Groundwater Modeling: Finite Difference and Finite Element Methods. W.H. Freeman and Company; San Francisco.

Ward, D.S., D.R. Buss, J.W. Mercer, and S.S. Hughes. 1987. Evaluation of a Groundwater Corrective Action at the Chem-Dyne Hazardous Waste Site using a Telescopic Mesh Refinement Modeling Approach. Water Resources Research 23(4):603-617.

Watson, Ian. 1984. Contamination Analysis - Flow Nets and the Mass Transport Equation. Ground Water 22(1):31-37.

Weast, R.C. (editor). 1985. Handbook of Chemistry and Physics (66th Ed.). CRC Press Inc.; Boca Raton, Florida.

White, J.A., M.H. Agee, and K.E. Case. 1984. Principles of Engineering Economic Analysis, 2nd Edition. John Wiley and Sons Inc.; New York.

White, W.B. 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press; New York.

Woodburn, K.B., P.S.C. Rao, M. Fukui, and P. Nkedi-Kizza. 1986. Solvophobic Approach for Predicting Sorption of Hydrophobic Organic Chemicals on Synthetic Sorbents and Soils. Journal of Contaminant Hydrology, 1(1/2):227-241.

Yeh, H.D., and H.Y. Han. 1989. Numerical Identification of Parameters in Leaky Aquifers. Ground Water 27(5):655-663.

Young, S.C. and W.R. Waldrop. 1989. An Electromagnetic Borehole Flowmeater for Measuring Hydraulic Conductivity Variability. Proceedings of New Field Techniques for Quantifying the Physical and Chemical Properties of Heterogeneous Aquifers. National Water Well Association, Dublin, Ohio. Zheng, C., K.R. Bradbury, and M.P. Anderson. 1988. Role of Interceptor Ditches in Limiting the Spread of Contaminants in Ground Water. Ground Water 26(6):734-742.