United States
Environmental Protection
Agency

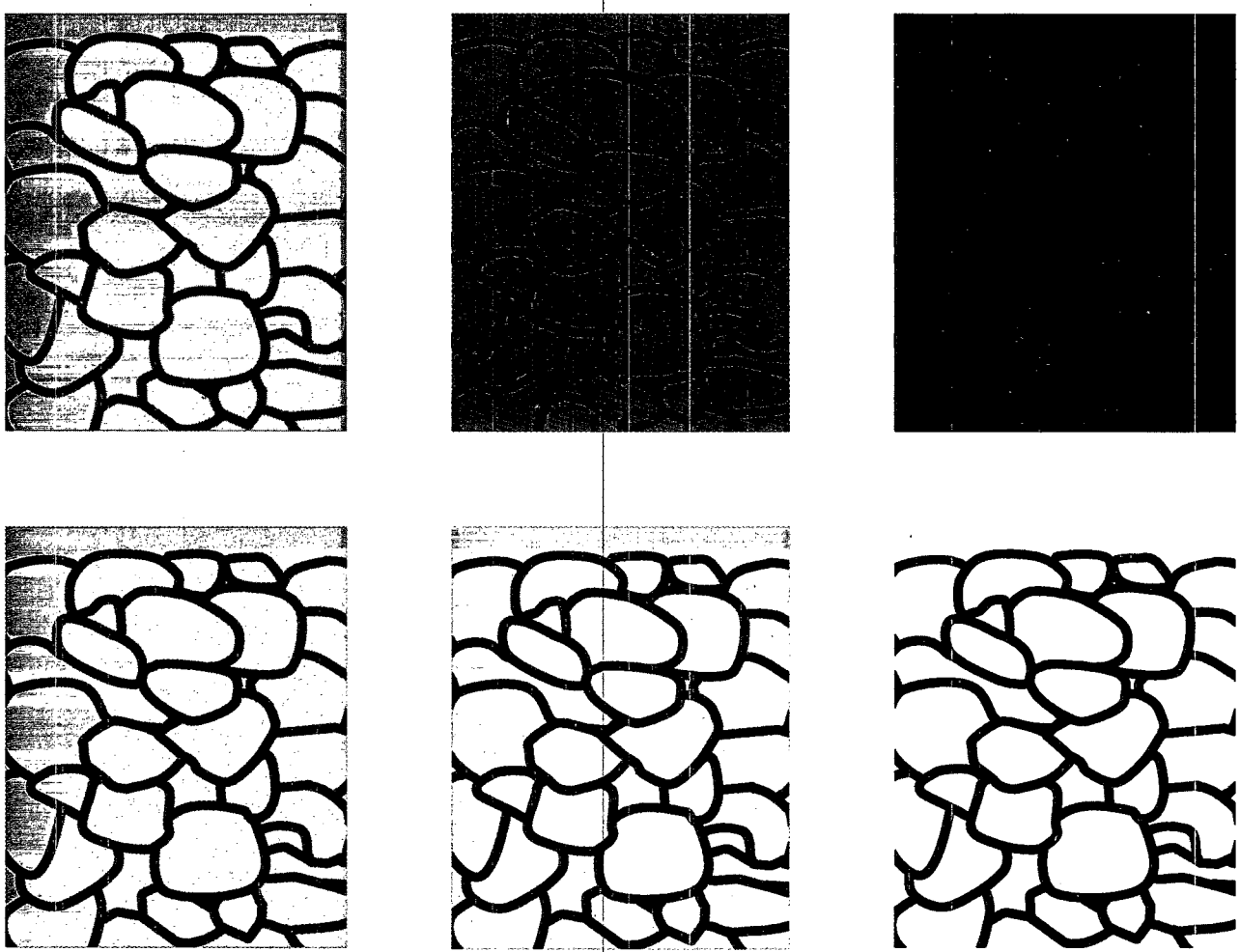
Office of Research and
Development
Washington, DC 20460

EPA/540/R-94/515
August 1994

EPA

Symposium on Intrinsic Bioremediation of Ground Water

Hyatt Regency Denver
Denver, CO
August 30 – September 1, 1994



EPA/540/R-94/515
August 1994

Symposium on Intrinsic Bioremediation of Ground Water

Hyatt Regency Denver
Denver, CO
August 30 to September 1, 1994

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC

Printed on Recycled Paper

Disclaimer

The projects described in this document have been reviewed in accordance with the peer and administrative review policies of the U.S. Environmental Protection Agency and the U.S. Geological Survey, and have been approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Acknowledgments

The papers abstracted in this book were presented at the Symposium on Intrinsic Bioremediation of Ground Water, held August 30 to September 1, 1994, in Denver, Colorado. The Symposium was a joint effort of the U.S. Environmental Protection Agency's (EPA's) Biosystems Technology Development Program and the U.S. Geological Survey (USGS), with additional sponsorship from the U.S. Air Force. Fran V. Kremer (EPA, Cincinnati, Ohio), John T. Wilson (EPA, Ada, Oklahoma), and Gail E. Mallard (USGS, Reston, Virginia) served as co-organizers of the Symposium, along with support from Lt. Col. Ross N. Miller, Headquarters, U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.

Contents

Site Characterization: What Should We Measure, Where (When?), and How?
Michael J. Barcelona 1

Processes Controlling the Distribution of Oil, Air, and Water
John L. Wilson 10

New Tools To Locate and Characterize Oil Spills in Aquifers
Bruce J. Nielsen 25

Microbiological and Geochemical Degradation Processes
E. Michael Godsy 35

Field and Laboratory Results: Getting the Whole Picture
Mary Jo Baedecker 41

In Situ Bioremediation at the Seventh Avenue Site in Denver: Remediation of Soils and Ground Waters
Christopher Nelson 47

The Role of Intrinsic Bioremediation in Closure of Sites After Cleanup Through *In Situ* Bioremediation: The Regulator's Perspective
Mark E. Walker and Lisa C. Weers 49

The Importance of Knowledge About Intrinsic Bioremediation for Cost-Effective Site Closure: The Client's Perspective
Harry E. Moseley 51

The Role of Intrinsic Bioremediation in Closure of Sites After Cleanup Through *In Situ* Bioremediation: The Role of Mathematical Models
Tissa H. Illangasekare, David C. Szlag, and John T. Wilson 53

Intrinsic Bioremediation of JP-4 Jet Fuel
John T. Wilson, Frederick M. Pfeffer, James W. Weaver, Don H. Kampbell, Todd H. Wiedemeier, Jerry E. Hansen, and Ross N. Miller 60

A Natural Gradient Tracer Experiment in a Heterogeneous Aquifer With Measured *In Situ* Biodegradation Rates: A Case for Natural Attenuation
Thomas B. Stauffer, Christopher P. Antworth, J. Mark Boggs, and William G. MacIntyre 73

Traverse City: Distribution of the Avgas Spill
David W. Ostendorf 85

Traverse City: Geochemistry and Intrinsic Bioremediation of BTX Compounds
Barbara H. Wilson, John T. Wilson, Don H. Kampbell, Bert E. Bledsoe, and John M. Armstrong 94

Mathematical Modeling of Intrinsic Bioremediation at Field Sites
Hanadi S. Rifai 103

Biogeochemical Processes in an Aquifer Contaminated by Crude Oil: An Overview of Studies at the Bemidji, Minnesota, Research Site
Robert P. Eganhouse, Mary Jo Baedecker, and Isabelle M. Cozzarelli 111

Simulation of Flow and Transport Processes at the Bemidji, Minnesota, Crude-Oil Spill Site
Hedeff I. Essaid 121

An Overview of Anaerobic Transformation of Chlorinated Solvents
Perry L. McCarty 135

Contamination of Ground Water With Trichloroethylene at the Building 24 Site at Picatinny Arsenal, New Jersey
Mary Martin and Thomas E. Imbrigiotta 143

Intrinsic Bioremediation of TCE in Ground Water at an NPL Site in St. Joseph, Michigan
John T. Wilson, James W. Weaver, and Don H. Kampbell 154

Poster Session

Technical Protocol for Implementing the Intrinsic Remediation With Long-Term Monitoring Option for Natural Attenuation of Fuel-Hydrocarbon Contamination in Ground Water
Todd H. Wiedemeier 163

Wisconsin's Guidance on Naturally Occurring Biodegradation as a Remedial Action Option
Michael J. Barden 170

Assessing the Efficiency of Intrinsic Bioremediation
Francis H. Chapelle 171

A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water
Paul M. McAllister and Chen Y. Chiang 172

The Use of Low Level Activities To Assist Intrinsic Bioremediation
Robert D. Norris, Jeffrey C. Dey, and Daniel P. Shine 173

Natural Attenuation of Jet Fuel in Ground Water
Greg Doyle, Dwayne Graves, and Kandi Brown 175

Evaluation of Intrinsic Bioremediation at an Underground Storage Tank Site in Northern Utah
R. Ryan Dupont, Darwin L. Sorensen, and Marion Kemblowski 176

Case Studies of Field Sites To Demonstrate Natural Attenuation of BTEX Compounds in Ground Water
Chen Y. Chiang and Paul M. McAllister 178

Demonstrating Intrinsic Bioremediation of BTEX at a Natural Gas Plant
Keith Piontek, Tom Sale, Steve de Albuquerque, and John Cruze 179

Demonstrating the Feasibility of Intrinsic Bioremediation at a Former Manufactured Gas Plant
Ian D. MacFarlane, Edward J. Bouwer, and Patricia J.S. Colberg 181

Natural and Enhanced Bioremediation of Aromatic Hydrocarbons at Seal Beach, California: Laboratory and Field Investigations
Harold A. Ball, Gary D. Hopkins, Eva Orwin, and Martin Reinhard 183

The Complete Dechlorination of Trichloroethene to Ethene Under Natural Conditions in a Shallow Bedrock Aquifer in New York State
David Major, Evan Cox, Elizabeth Edwards, and Paul W. Hare 187

Site Characterization: What Should We Measure, Where (When?), and Why?

Michael J. Barcelona
Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI

Abstract

Site characterization represents the initial phase of the active monitoring process that occurs as part of intrinsic organic contaminant bioremediation efforts. Initial characterization work sets the stage for evaluating the progress of the natural transformation of contaminants. The following have frequently been observed: parent compound disappearance, active microbial populations with biotransformation capabilities, and the appearance or disappearance of organic and inorganic constituents that provide evidence of bioremediation at contaminated sites. Quantitative evidence is lacking, however, for net removal of toxic compounds from complex mixtures solely by biological processes. This is due largely to the reliance on monitoring well samples for evidence of biological activity, rather than on identifying the mass of contaminants (and total reactive organic carbon) and estimating the net removal/transformation of reactive compounds over time.

A dynamic approach to quantitative site characterization is needed that recognizes intrinsic bioremediation as an active cleanup approach. Careful attention must be paid to the identification of the three-dimensional distribution of contaminant mass. Then the correspondence between contaminant distribution and favorable physical, geochemical, and microbial conditions in the subsurface over time provides a basis for net contaminant-removal estimates. Mere adaptations of detective ground-water monitoring networks are insufficient for quantitative evaluation of intrinsic bioremediation technologies.

Introduction

The practice of site characterization for remediation of subsurface organic contaminants has evolved slowly in the past decade. Early guidelines (1-3) for minimal ground-water contamination detection monitoring (i.e., monitoring wells upgradient and downgradient) have been applied to many sites of potential concern from detection through remedial action selection phases.

This minimal approach has been applied widely, regardless of the physicochemical characteristics of contaminant mixtures or the complexity of hydrogeologic settings. With soluble inorganic constituents, this approach may be adequate for detection purposes, but assessment efforts require substantially more comprehensive approaches. For organic contaminant assessment efforts (i.e., determinations of the nature and extent of contamination), wells alone have been found to be inadequate monitoring tools. Recognition of the value of subsurface soil vapor surveys for volatile organic components of fuel and solvent mixtures has generated a flurry of modified site characterization approaches based on monitoring wells (4). These approaches to site characterization and monitoring network design suffer also from a failure to identify the total mass of contaminant in the subsurface.

This failure occurs for three main reasons. First, although volatile organic compounds (VOCs) are mobile in ground water and are frequently early indicators of plume movement (5), their detection in vapor or well samples and their apparent aqueous concentration distribution do not identify the total mass distribution of organic contaminant (6). Second, efforts to correlate observed soil vapor or ground-water VOC concentrations with those in subsurface solid cores have often been unsuccessful, because current bulk jar collection/refrigeration at 4°C guidelines for solid core samples for VOC analyses lead to gross negative errors (7). Third, "snapshots" (i.e., one-time surveys) of background and disturbed ground-water chemistry conditions have been interpreted as "constant," ignoring temporal variability in subsurface geochemistry.

The unhappy result of the slow improvement in site characterization and monitoring practices has often been the very low probability of detecting the source of mobile organic contaminants. This outcome may be followed by the misapplication of risk assessment or remediation models and fiscal resources. Nonetheless, good reasons exist for a more optimistic view of the future reliability of site-characterization and monitoring efforts.

The shortcomings of previous contaminant detection and assessment efforts have been recognized. New guidelines and recommendations for network design and operations will lead to more comprehensive, cost-effective site characterization (7, 8) in general. Also, excellent reviews of characterization and long-term monitoring needs and approaches in support of *in situ* remediation efforts should guide us in this regard (9, 10). Site characterization efforts provide a basis for long-term monitoring design and actually continue throughout the life of a remediation project.

Advanced Site Characterization and Monitoring

How do we estimate the potential for subsurface intrinsic bioremediation success and track its performance into the future? Clearly, we should seek to design technically defensible characterization and monitoring networks that will provide reasonable estimates of in-place contaminant distributions over time. Therefore, a dynamic, ongoing site-characterization effort includes the following objectives:

- Identify the spatial distribution of contaminants, particularly their relative fractionation in subsurface solids, water, and vapor, along potential exposure pathways, recognizing that the mass of contaminants frequently resides in the solids.

- Determine the corresponding spatial distribution of total reactive organic matter (e.g., degradable normal, aliphatic, and aromatic hydrocarbon compounds), because overall microbial activity and disruptions in subsurface geochemical conditions (and bioremediation indicators) are due to the total mass of reactive organic carbon.

- Estimate the temporal stability of hydrogeologic and geochemical conditions that may favor microbial transformations in background, source, and downgradient zones during the first year of characterization and monitoring.

- Derive initial estimates of net microbial transformations of contaminant-related organic matter over time that may be built into an efficient long-term monitoring network design.

The first three objectives establish the environment of major contamination and the conditions under which bioremediation may occur. The latter two objectives are vitally important, because evaluating the progress of intrinsic bioremediation processes depends on distinguishing compound "losses" due to dilution, sorption, and chemical reactions from microbial transformations. This approach has been suggested emphatically by Wilson (9) and was recently developed into a draft technical U.S. Air Force (USAF) protocol by Wiedemeier et al. (10).

The latter reference focuses directly on the implementation of intrinsic remediation for dissolved fuel contamination in ground water. The general approach is shown in Figure 1, which has been modified from the original work. The draft USAF protocol (10) has as its goals the collection of data necessary to support:

- Documented loss of contaminants at the field scale
- The use of chemical analytical data in mass balance calculations
- Laboratory microcosm studies using aquifer samples collected from the site

These data, if collected in three dimensions for an extended period, should be sufficient to implement intrinsic remediation successfully (11). The data collected in the initial site characterization effort (Figure 1) support the development of a site-specific conceptual model. This model is a three-dimensional representation of the ground-water flow and transport fields based on geologic, hydrologic, climatologic, and geochemical data for a site. The conceptual model, in turn, can be tested, refined, and used to determine the suitability of intrinsic remediation as a risk-management strategy. The validity of the conceptual model as a decision tool depends on the complexity of the actual hydrogeologic setting and contaminant distributions relative to the completeness of the characterization database. The draft USAF protocol is quite comprehensive in identifying important parameters, inputs, and procedures for data collection and analysis. The major categories of necessary data are listed in Table 1 from the draft protocol (10). Ongoing work on the protocol has revised some of the detailed guidance it provides on sampling and analytical protocols for these critical parameters; thus, recent drafts of the protocol should be even more useful to practitioners.

Typical detective monitoring data sets available prior to in-depth site characterization are more likely to contain contaminant-related information rather than the three-dimensional aquifer property, hydrogeologic, or geochemical data needed to formulate a conceptual model. A recognition of the variability inherent in these parameter distributions is critical to site characterization efforts.

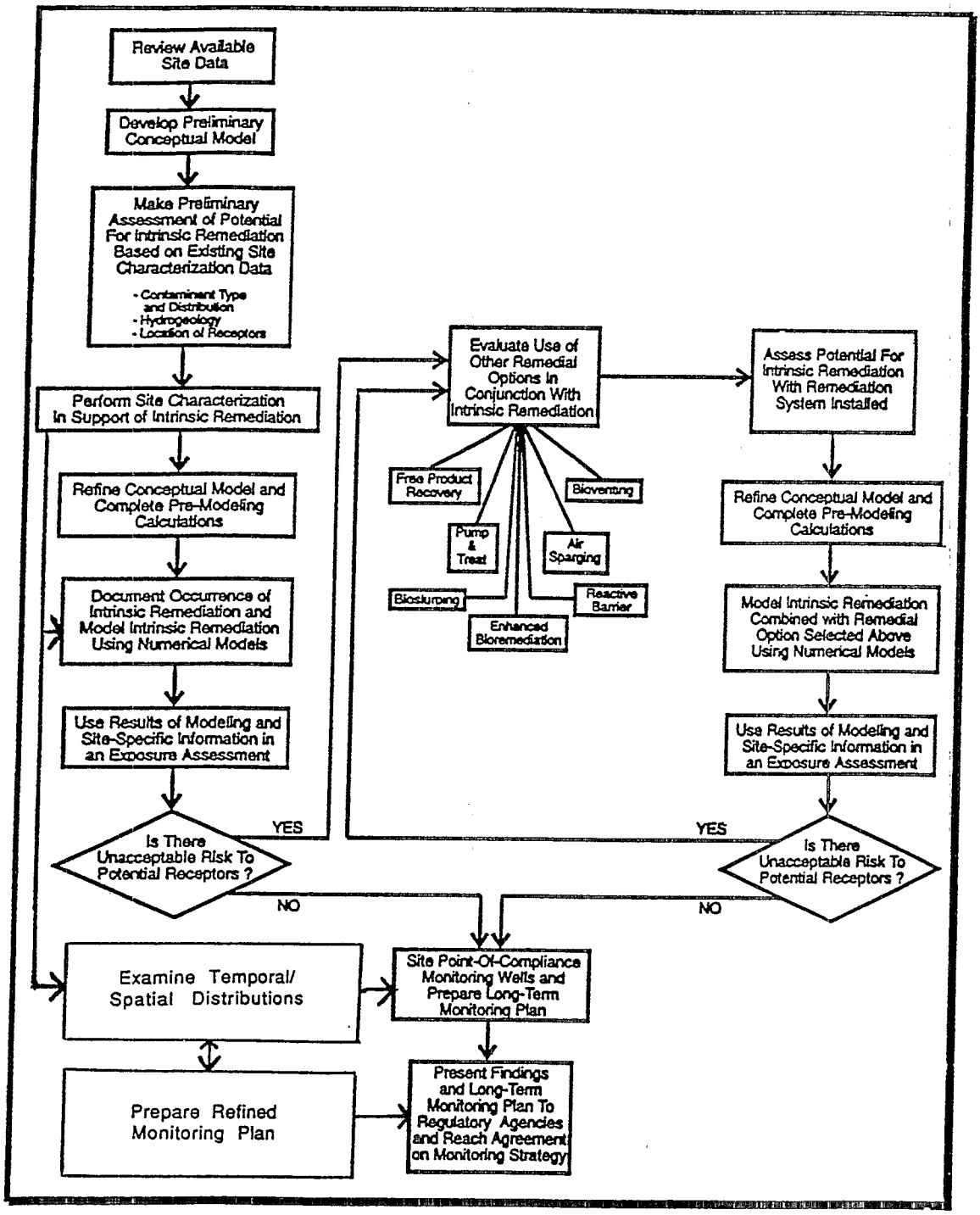


Figure 1. Intrinsic remediation flow chart.

Table 1. Site-Specific Parameters To Be Determined During Site Characterization (10)

Fractionation and Spatial Extent of Contamination	Extent and type of soil and ground-water contamination Location and extent of contaminant source area(s) (i.e., areas containing free- or residual-phase product) Potential for a continuing source due to leaking tanks or pipelines
Hydrogeologic and Geochemical Framework	Ground-water geochemical parameter distributions (Table 2) Regional hydrogeology, including: - Drinking water aquifers - Regional confining units Local and site-specific hydrogeology, including: - Local drinking water aquifers - Location of industrial, agricultural, and domestic water wells - Patterns of aquifer use - Lithology - Site stratigraphy, including identification of transmissive and nontransmissive units - Grain-size distribution (sand versus silt versus clay) - Aquifer hydraulic conductivity determination and estimates from grain-size distributions - Ground-water hydraulic information - Preferential flow paths - Location and type of surface water bodies - Areas of local ground-water recharge and discharge Definition of potential exposure pathways and receptors

Sampling in Space

The initial site characterization phase should be designed to provide spatially dense coverage of critical data over volumes corresponding to 10-yr to 100-yr travel times along ground-water flow paths. If the flow path intersects a discharge zone in less than 100 yr, then the volume should be scaled accordingly. For example, if the flow path discharges after 10 yr, the critical volume would be 1 yr of travel time. The "volume-averaged" values of the contaminants, hydrogeologic and geochemical parameters within zones along the flow path(s), should be derived from data sets that are large enough to permit estimation of statistical properties (e.g., mean, median, correlation distance, and variance). In general, this means that the data sets for

derived mass loadings of contaminants, aquifer properties, and geochemical constituents (Table 2) derived from spatial averages of data points must include approximately 30 or more data points (12-14). Indeed, this minimum data-set size strictly applies to points in a plane.

Table 2. Target Constituents for Site Characterization in Support of Intrinsic Bioremediation

Contamination Area	Apparent/ Geochemical Redox Zone	Contaminant Mixture	Inorganic Constituents	Intrinsic Constituents
Source	Reducing	Fuels	O_2, CO_2, H_2S; pH, Fe^{2+}, $HS^-/S^=$, NO_2^-, NH_3, alkalinity	Organic carbons, CH_4, organic acids, phenols
		Chlorinated solvents		As above and: chlorinated metabolites, ethylene, ethane
Downgradient	Transitional/ Suboxic	Fuels	O_2, CO_2, H_2S; pH, Fe^{2+}, alkalinity, NO_2^-, NO_3^-, NH_3, $HS^-/S^=$	Organic carbon, CH_4, organic acids, phenols
		Chlorinated solvents		As above and: chlorinated metabolites, ethylene, ethane
Upgradient/ Far-field downgradient	Oxic	Fuels	O_2, CO_2, H_2S; alkalinity, Fe^{2+}, NO_3^-, NO_2^-, NH_3	Organic carbon, CH_4, organic acids, phenols
		Chlorinated solvents		As above and: chlorinated metabolites, ethylene, ethane

Two major decisions must be made with regard to how spatially averaged masses of contaminants, electron donors (e.g., organic carbon, Fe^{2+}, $S^=$, and NH_3), and electron acceptors (e.g., O_2, NO_3^-, NO_2^-,Fe and Mn oxides, and $SO_4^=$) are to be estimated.

The first question deals with identification of the media in which the bulk of the constituent's mass resides. For aquifer properties (e.g., grain size and laboratory estimates of hydraulic conductivity), the answer is simple. In this case, the solids are clearly the media of interest. For constituents, particularly VOCs, which are sparingly water soluble, the bulk of the mass may in fact reside in the solids, though both solids and water samples must be collected carefully.

The second question pertains to the depth interval over which "planar" data points might be averaged. With fuel-related aromatic contaminants, the depth interval above and below the capillary fringe/water table interface typically exhibits order-of-magnitude differences in solid-associated concentrations. In this situation, averaging data points over depths greater than 0.5 m could easily lead to order-of-magnitude errors in estimated masses for a site. Continuous coring of subsurface solids and close interval (i.e., <1 m) sampling of water should be considered in many VOC investigations. To approach this level of depth detail in sampling, "push" technologies and/or multilevel sampling devices present very useful tools for site characterization. Push technologies rely on hydraulic or hammer-driven, narrow diameter (i.e., <2 in.) probes for solid or water sampling. These technologies have the potential to provide greater spatial coverage of the subsurface at less cost than drilling techniques.

The approach to site characterization for chlorinated hydrocarbons is significantly more difficult. Very few models of site characterization for these contaminants have estimated mass loadings in specific media. Many of the previously referenced methods may work satisfactorily. Free-phase detection, assessment, and quantitation, however, may be more a matter of luck and exhaustive sampling than intuition based on experience.

Sampling Over Time

VOC compounds (e.g., aromatic hydrocarbons and chlorinated solvents) are among the target contaminants that are considered constituents of concern in remedial investigations. Their aqueous solubility and demonstrated association with aquifer solids require sampling of these media during the site characterization phase. This suggestion also applies to organic metabolites of complex organic mixtures (e.g., ethylene, vinyl chloride, aromatic acids, and phenols). Aqueous plumes that develop subsequent to the release of these organic mixtures and byproduct compounds have received the most attention in the past. The fact that the mass of these contaminants frequently resides in the solids strongly suggests that the solids should receive the most attention in the initial site characterization effort. This should also be the case for the physical, geochemical, and microbial determinations.

Initially, conventional nested monitoring wells with screened lengths of 1 m or more will be useful for estimating the spatial extent of the dissolved plume, for delineating apparent geochemical zones, and for providing data on water level and aquifer property (e.g., slug- and pump-test derived hydraulic conductivity estimates). Semiannual or annual sampling of wells, particularly multilevels appropriately designed and completed, should be quite useful over the course of the long-term monitoring program. Sampling should track the downgradient progress of risk-associated target compounds and permit testing predictions of intrinsic bioremediation effects on risk reduction.

Proof of the effects of the net removal of specific solid-associated contaminants due to intrinsic bioremediation, however, will depend on solid sampling and analysis at annual or greater intervals, because solid-associated concentrations may be expected to change slowly. Unless biotransformation can be shown to be a major loss mechanism for contaminants mainly in solids over extended periods, it will remain an area of research rather than practice.

Because very few contamination situations have been monitored intensively for periods exceeding several years, it is difficult to define specific sampling frequencies for the range of hydrogeologic

and contaminant combinations that may be encountered. The adoption and future refinement of recently developed, technically defensible protocols will improve intrinsic remediation approaches to risk management in subsurface contamination situations.

Acknowledgements

The author would like to express his gratitude to the following individuals who aided in the preparation of the manuscript: Dr. Gary Robbins, Mr. Todd H. Wiedemeier, Dr. John T. Wilson, Dr. Fran Kramer, and Ms. Rebecca Mullin.

References

1. Scalf, M.R., J.F. McNabb, W.J. Dunlop, R.L. Cosby, and J.S. Fryberger. 1981. Manual of ground-water sampling procedures. National Water Well Association.

2. Barcelona, J.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske. 1985. Practical guide for ground-water sampling. Illinois State Water Survey, SWS Contract Report 374 U.S. Environmental Protection Agency, Ada, OK.

3. U.S. EPA. 1986. RCRA technical enforcement guidance document, OSWER-9950.1. Washington, DC.

4. Eklund, B. 1985. Detection of hydrocarbons in ground water by analysis of shallow soil gas/vapor. API Publication No. 4394. Washington, DC.

5. Plumb, R.H. 1987. A comparison of ground-water monitoring data from CERCLA and RCRA sites. Ground Water Monitor. Rev. 7:94-100.

6. Robbins, G.A. 1989. Influence of using purged and partially penetrating wells on contaminant detection, mapping, and modeling. Ground Water 2:155-162.

7. U.S. EPA. 1992. RCRA ground-water monitoring: Draft technical guidance document. EPA/530/R-93/001. Washington, DC.

8. U.S. EPA. 1994. Proceedings of the Ground Water Sampling Workshop, Dallas, TX, December 8-10, 1993. U.S. Environmental Protection Agency, Ada, OK.

9. Wilson, J.T. 1993. Testing bioremediation in the field In: National Research Council. In situ bioremediation—when does it work? Washington, DC: National Academy Press. pp. 160-184.

10. Wiedemeier T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1994. Draft technical protocol for implementing the intrinsic remediation (natural attenuation) with long-term monitoring option for dissolved-phase fuel contamination in ground water. Air Force Center for Environmental Excellence, Brooks AFB, San Antonio, TX (March).

11. National Research Council. 1993. In situ bioremediation—when does it work? Washington, DC: National Academy Press.

12. Journel, A.G. 1986. Geostatistics: Models and tools for the earth sciences. Math. Geol. 18:119-140.

13. Hoeksema, R.J., and P.K. Kitanidis. 1985. Analysis of the spatial structure of properties of selected aquifers. Water Resour. Res. 21:563-572.

14. Gilbert, R.O., and J.C. Simpson. 1985. Kriging for estimating spatial patterns of contaminants: Potential and problems. Environ. Monitor. Assess. 5:113-135.

Processes Controlling the Distribution of Oil, Air, and Water

John L. Wilson
Department of Geoscience, New Mexico Institute of Mining and Technology,
Socorro, NM

Abstract

Oils and other nonaqueous-phase liquids (NAPLs) are a major source of dissolved contamination in aquifer systems. Three major forces control the movement and distribution of NAPLs, as well as air and water, in both porous and fractured media. These are capillary, viscous, and buoyancy forces. These forces interact with the complex pattern of geological features, making fluid behavior difficult to predict and fluid distribution difficult to characterize. Intrinsic bioremediation within a NAPL-contaminated zone is probably of limited effectiveness because of mass transfer limitations, toxicity concerns, and the limited availability of other nutrients. Thus, intrinsic bioremediation is aimed at the contamination in the downgradient aqueous phase of the dissolved plume. Evaluating the effectiveness of bioremediation is impossible within the plume without knowing the distribution of the NAPL—the plume's source—or determining whether that source is still moving.

Introduction

Oil or another NAPL, such as gasoline or trichloroethylene (TCE), may be released at or near the ground surface. These liquids are primary sources for dissolved contaminant plumes in ground-water systems. Even if the NAPL has ceased to move, trapped by capillary forces as we describe below, it remains a long-term source of dissolved contamination. The limited aqueous solubility of the chemicals composing these oily liquids implies that even in small volumes they can lead to ground-water plumes of enormous dimensions. Intrinsic bioremediation is aimed at the contamination in the aqueous-phase plume, for reasons that will become clear. The plume location and concentrations depend on understanding the spatial pattern of its source, the NAPL. In the vadose zone, the problem is complicated by the presence of a third phase, air, and the propensity of the NAPL to spread at the air-water interface and to volatilize.

In this review, we first describe the three major forces controlling the movement and distribution of fluids in the subsurface, using natural processes such as infiltration to illustrate. We then add NAPLs, to relate the discussion to the contamination issue, and aquifer heterogeneity, to relate the discussion to natural hydrogeological systems. Finally, we discuss the implications for intrinsic bioremediation. Many of these issues are illustrated with photomicrographs taken of appropriate processes *in situ*.

Three Major Forces That Control Processes

Ground-water systems are composed of porous and/or fractured aquifer material containing water in the spaces between the solids (see Figure 1a). Above the water table, in the vadose

zone (see Figure 2), air is also present within this pore space (see Figure 1c). Three major forces control both the movement and distribution of each of the fluid phases: capillary forces, viscous forces, and gravity or buoyancy forces (1).

Capillarity is the result of the cohesive forces within each fluid phase and the adhesive forces between the solid phase and each of the fluids. A capillary force is proportional to the interfacial tension at the fluid-fluid interface and the strength of fluid wetting to the solid surface, and inversely proportional to the pore size. In the vadose zone, with air and water present, interfacial tension is the same as air-water surface tension. In the saturated zone, beneath the water table (see Figure 2), the only fluid is water, and capillary forces are absent (see Figure 1a). The exception occurs beneath a fluctuating water table, where gas bubbles may become entrapped by capillary forces (see Figure 1b and Figure 3; Figure 3 is a photomicrograph from a visualization experiment (see also the appendix to this paper). For most aquifer materials, water is the wetting fluid; that is, the solid aquifer material has a greater affinity for water than for air, and the air or gas is almost always the nonwetting phase (see Figures 1b and 1c). Water occurs as an interconnected film or layer of wetting liquid covering and connecting the solids in the vadose zone. The nonwetting gas phase occupies the larger pores.

Viscous or flowing forces within a fluid phase require an expenditure of potential energy. For example, in the saturated zone the ground-water flow rate is proportional to the hydraulic gradient. The flow rate is also a function of the aquifer material and the structure of its pore space, as represented by the effective permeability. If more than one fluid phase is present, as in Figures 1b and 1c, the interconnected paths in each phase are more tortuous. The permeability of each phase is reduced, with a relative permeability closer to zero than to one, the value that applies when only a single fluid occupies the pore space.

Buoyancy is a gravitational force proportional to the density difference between two fluids. The gas phase has a much lower density than water, so that gravity (buoyancy) forces play a significant role in the vadose zone. Water infiltrates downward, toward the water table, primarily under the influence of gravity. As it moves downward, water easily displaces the less dense and less viscous air phase. In the saturated zone, with only water present, gravity usually plays no direct role (although, of course, it ultimately drives the hydraulic gradient). In the saturated zone, if the chemical concentration varies enough to influence water density, gravity can again play a direct role, causing the water and its chemicals to move.

Oil and Other NAPLs

A third fluid is often present at many hazardous waste sites and most leaking underground storage tanks. NAPLs often share the pore space with both gas and water, in the vadose zone, or water alone, in the saturated zone. The NAPL may be more dense than water (a dense NAPL, or DNAPL), such as TCE, or it may be lighter than water, such as gasoline. In either case, a NAPL is heavier than air, so it easily moves downward through the vadose zone. Once it reaches the vicinity of the water table, it may continue to move deeper if it is denser than water (DNAPL), or it may remain in the vicinity of the water table if it is lighter, as illustrated in Figure 2 (2, 3); in the latter case, the term "water table" begins to lose its meaning. In either case, the NAPL leaves behind a trail of residual as it moves.

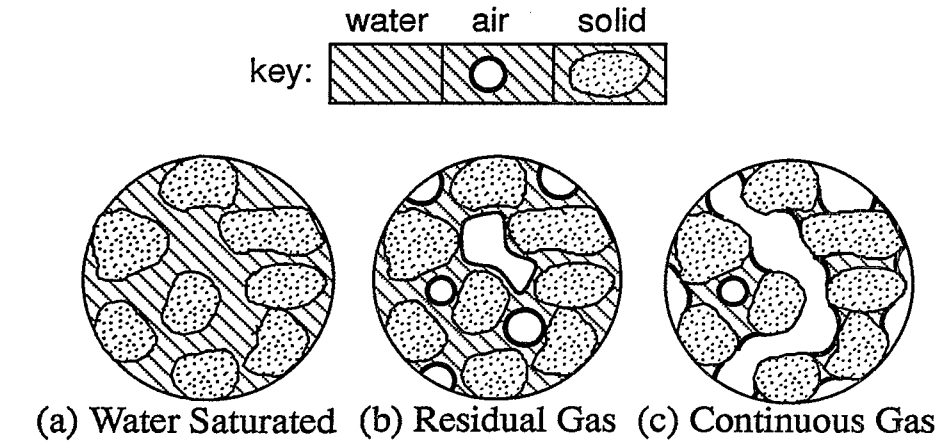


Figure 1. Diagram of fluid saturation in a porous media (4).

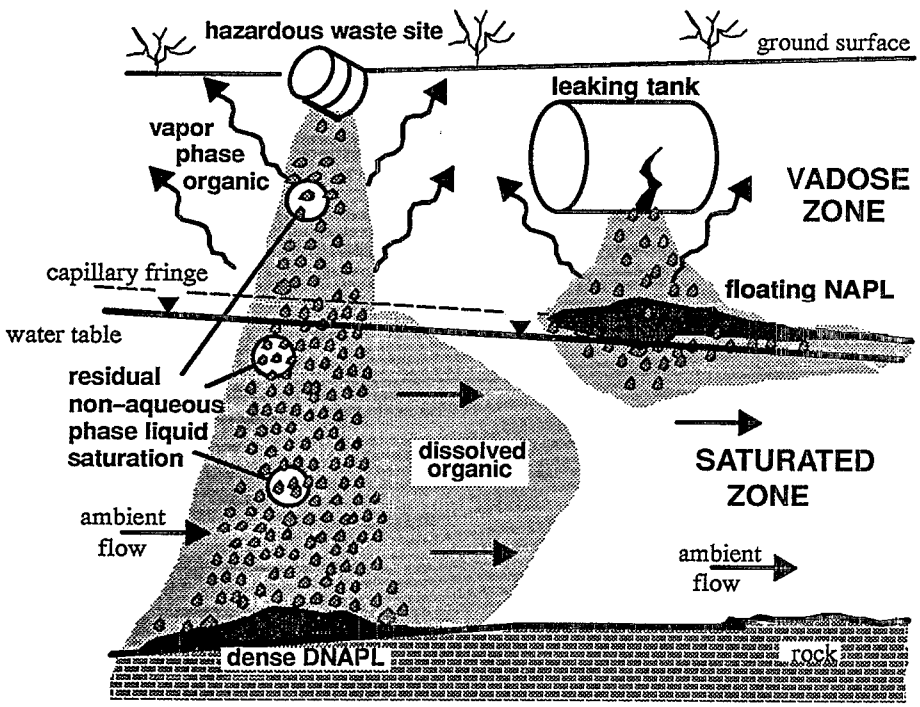


Figure 2. Diagram of the saturated and vadose zones, showing the migration pattern for a NAPL more dense than water (left), and less dense than water (right) (3).

Most NAPLs appear to be of intermediate wettability in typical aquifer materials; that is, they are nonwetting relative to water but wetting relative to gas. Thus, depending on whether it encounters gas or water, a NAPL can then display either wetting or nonwetting behavior or both. Many NAPLs, such as gasoline, also have low internal cohesion and will spread at a gas-water interface, presumably forming a film between the water phase, which because of capillarity preferentially occupies the smallest pores, and the gas phase, which preferentially fills the largest pores. In the vadose zone, this film interconnects the pockets of NAPL, which even at residual saturation should be largely continuous, as shown in Figure 4. Some NAPLs, such as TCE, have more internal cohesion and do not spread. In this case, the sum of the interfacial tensions between the NAPL and the water and air, $\sigma_{ow} + \sigma_{ao}$, exceed the surface tension between the gas and water, σ_{aw} (see Figure 5, $\theta>0$). These NAPLs will not spread as films. On a flat water surface (the gas-water interface), nonspreading liquids tend to coalesce into lenses that float on the surface (much as depicted in Figure 5), even though many of these liquids are denser than water. In porous media, this leads to complications, as shown in Figure 6.

In the saturated zone, the NAPL fills the larger pores, while water occupies the smaller pores and lies as a film between the NAPL and the solid surfaces. After the NAPL moves on, it leaves behind a residual saturation trapped by capillary forces, which occupies the larger pores. NAPL blobs occupying one or two pore bodies are shown in Figure 7. A similar process occurs in the vadose zone, when a rising water table entraps air bubbles, as shown in Figures 2b and 3. Because of lower interfacial tension, NAPL blobs are often much more complex than air bubbles, forming interconnected groups of larger pore bodies and pore throats, as shown in Figure 8.

So far we have looked at water-wet porous media. Wetting, however, may change for a variety of reasons, including the adsorption at hazardous waste sites of (polar) organic compounds onto the solid. Figure 9 shows the saturated zone residual in a pore space with altered wetting and significant wetting hysteresis. The residual NAPL is not trapped in the pore bodies, the characteristic location for a nonwetting fluid. Some of it is in the pore throats, some in the pore bodies, some has an end in both. Because of the large wetting hysteresis of this surface, water wet conditions prevailed during the invasion of the NAPL, while intermediate wet conditions prevailed when the water reentered to trap the NAPL. The NAPL-water interfaces in the figure clearly show evidence of both histories. In some locations, clearly water wet, we can infer that the interface was not disturbed as the water reentered. In other locations, the contact angle shows the recent displacement of the NAPL by water.

Heterogeneity

All of this is complicated by the geology of the ground-water system. The material composing an aquifer is always heterogeneous. For example, fluvial-deposited materials contain sand, gravel, and clay in a complex geometric pattern of geologic facies. Many formations, even those containing clay, are fractured and sometimes faulted. Heterogeneities provide preferential paths for fluid and chemical migration in an interplay of the geology with the forces of capillarity, viscosity, and gravity. For example, a DNAPL reaching the saturated zone will tend to seek out the heterogeneities with larger pore spaces such as the coarser sands or, more insidiously, fractures where its movement will be hard to trace. Heavier than water, it tends to move farther downward into the aquifer, fingering out the bottom of a sand lens or moving snakelike down the inside of a fracture.

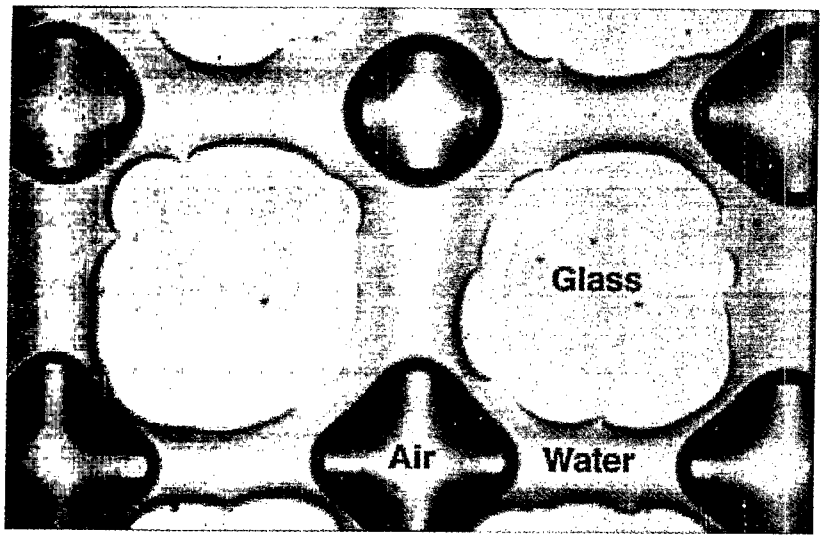


Figure 3. Photograph of a micromodel with entrapped air bubbles. The bubbles are trapped in the pore bodies, which are roughly 200 μm in diameter, while the pore throats are 50 μm in diameter (4).

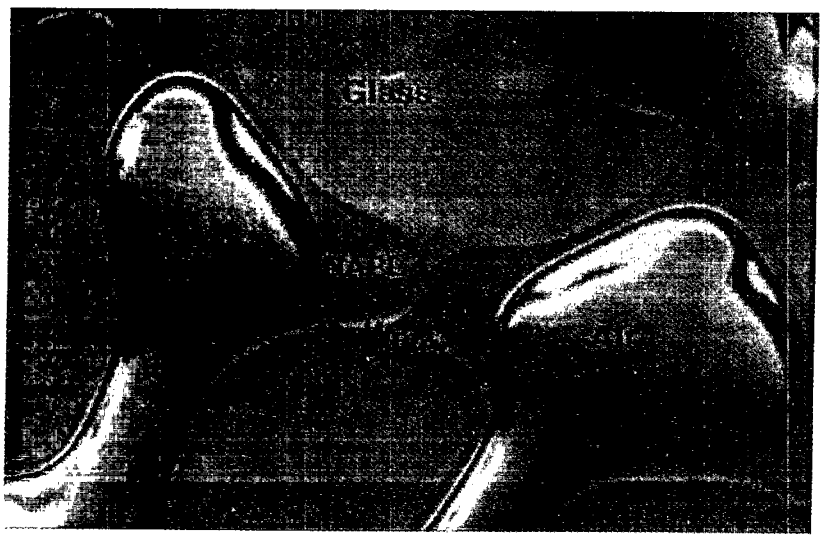


Figure 4. A micromodel after a spreading NAPL (Soltrol 130) is drained with air. Air fills the pore bodies and is interconnected through some of the pore throats. Water fills the other pore throats and some of the pore wedges and is a wetting film everywhere else. The NAPL forms a thick film filling some pore wedges and surrounding the air everywhere. This ubiquitous and interconnected film is particularly thick near the water-filled pore throats (3).

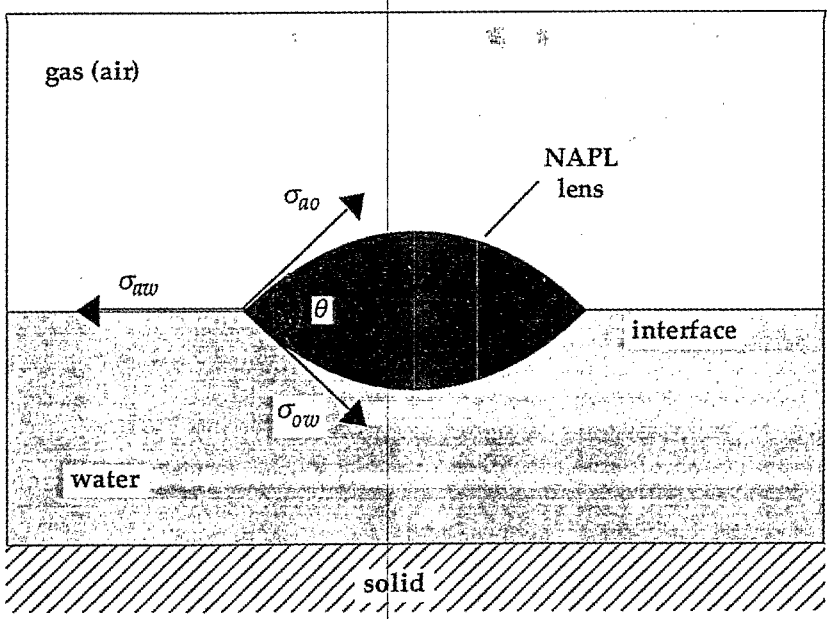


Figure 5. Cross-sectional diagram of spreading potential for a drop of NAPL floating on the air (gas)-water interface, after Adamson (10) and others. The water is wetting, the gas is nonwetting, and the NAPL is intermediate wetting.

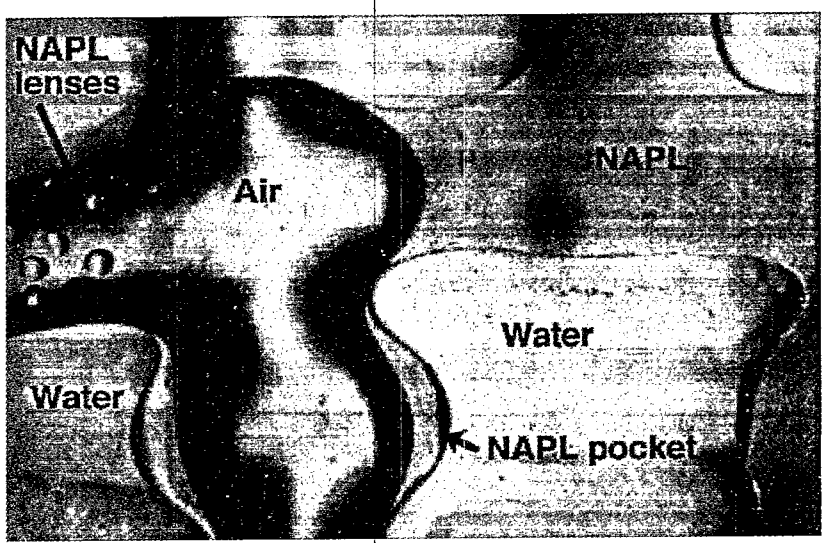


Figure 6. A micromodel after a nonspreading DNAPL (mineral oil) is drained with air. The DNAPL is not connected. As it leaves the photo at the bottom, the air is surrounded by a film of oil, similar to that seen with the spreading oil. As the air leaves to the left, the film no longer exists; it truncates somewhere in between. In this area, the air-water interface is dimpled, with small lenses of mineral oil. These lenses are not interconnected. The various pockets of oil, such as on the right side of the figure, are also generally discontinuous and not connected (11).

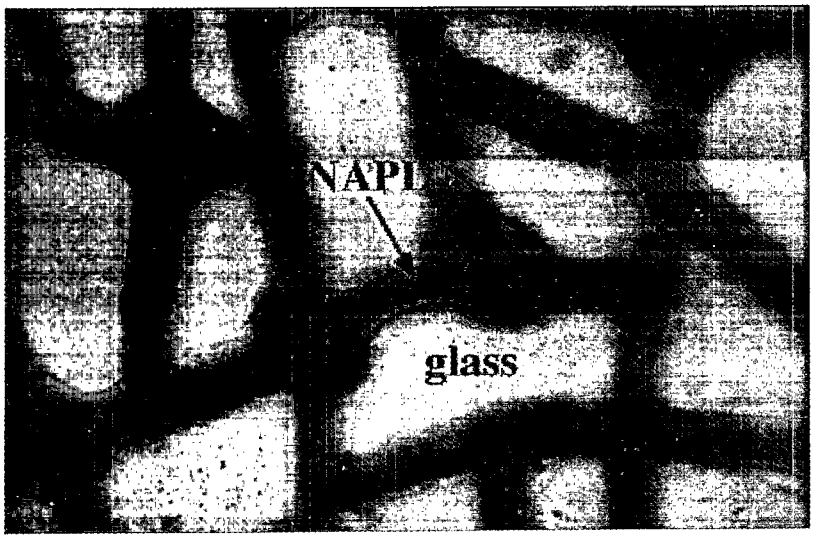


Figure 7. A micromodel with a singlet and doublet NAPL blob (dark gray) in a water-filled pore space (lighter gray) of an irregular pore network. The pore bodies are up to 1,000 μm across, and the model was 10 cm x 15 cm in area (8).

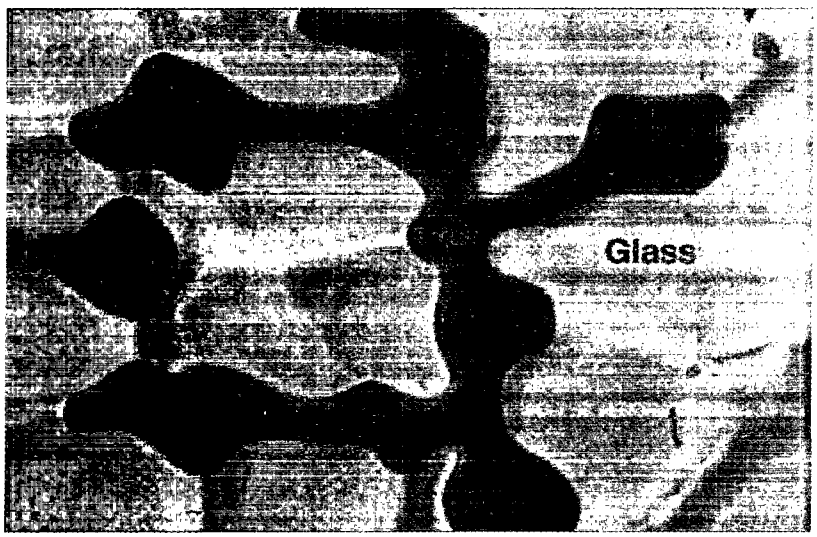


Figure 8. A micromodel with a large, branched, nonaqueous, nonwetting phase blob (dark gray) in an irregular pore network (3).

Figure 10 shows a pore system with embedded zones of larger pores surrounded by a network of smaller pores. This simulates lenses of coarse porous materials (e.g., coarse sand) embedded in a matrix of finer material (e.g., fine sand). The NAPL invaded from the side, mimicking the lateral migration of a NAPL plume along the bottom of an aquifer. Afterwards, the NAPL was displaced by water, leaving behind a residual saturation. The photograph in Figure 10 was taken at this time. The residual is dominated by the coarse lenses. In the fine material, we see the typical single- and multiple-pore body blobs, but the coarse lenses have been completely bypassed. Capillary forces are too strong, and the viscous forces in the moving water too weak, to displace the NAPL from these isolated coarser zones. Note that the zones with higher saturated permeability trap the NAPL.

This experiment was repeated at a much higher water flow rate. A photograph taken while this was occurring is shown in Figure 11. A significant amount of NAPL has been swept from the coarse lenses, even though the initial condition was essentially the same. In the swept area, on the right side, there is still some bypassed NAPL, but it is now located on the downstream end of the lenses. Sufficient viscous forces were generated to overcome the capillary forces that held NAPL in the coarse lenses. The displacement is incomplete because, as the wetting front reaches the end of a lens, it closes together and surrounds the lens. At that point, the nonwetting NAPL in the lens is no longer connected with the downstream NAPL. These two photographs suggest that in heterogeneous systems the residual nonwetting-phase saturation is a function of the structure of the heterogeneities and the fluid history. Because the residual is the source of the dissolved plume, we would like to be able to predict its location and magnitude from knowledge of the geology and the fluid flow history. We use mathematical models to assist with this kind of prediction. There is a problem, however. The current generation of multiphase flow models assumes that there is a single value of residual and, worse, that we know what it is. These models offer little assistance with the important issue of predicting the amount and distribution of residual.

These photographs were taken from experiments that simulated the movement of DNAPL parallel to stratigraphic bedding planes—for instance, as it migrates along the bottom of an aquifer. What happens as it moves perpendicular to the bedding, for example, during its movement downward from the water table toward the bottom of the aquifer? Figure 12 shows the same kind of heterogeneous lenses, except for this change in geometry. The flow is downward, across the lenses, with both gravity and viscous components. As the DNAPL encounters its first coarse lens, it tends to spread horizontally because of capillary forces. As soon as it fills a lens, it begins to spill downward, but because of the gravity instabilities—DNAPL is heavier than water—this movement occurs as fingers on the scale of a few pores. When one of these fingers encounters another, deeper coarse lens, the downward migration of the DNAPL is again arrested, until the lens is filled. In essence, the lenses promote horizontal spreading, here confined by the lateral boundaries of the model, and vertical fingering. The process leads to a very inefficient displacement, with lots of water bypassed by the DNAPL, and illustrates some of the reasons why it is difficult to directly measure DNAPLs in the field, predict their behavior, or design effective remediation measures.

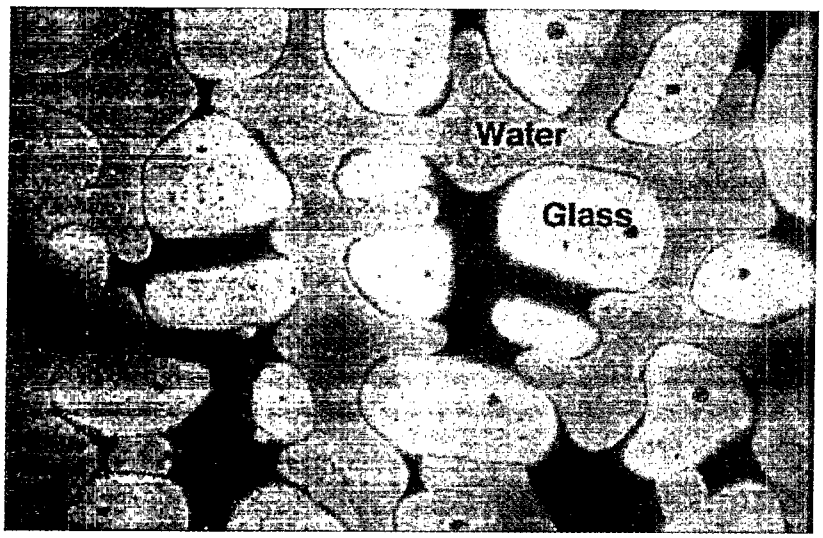


Figure 9. Residual nonaqueous-phase saturation in a micromodel treated with an alkoxysilane of proprietary composition, GlassClad 18 (Huls Americal Petrarch, Bristol, PA). This treated surface has significant contact angle hysteresis. The water is light gray, and the NAPL is darker gray in this image (9).

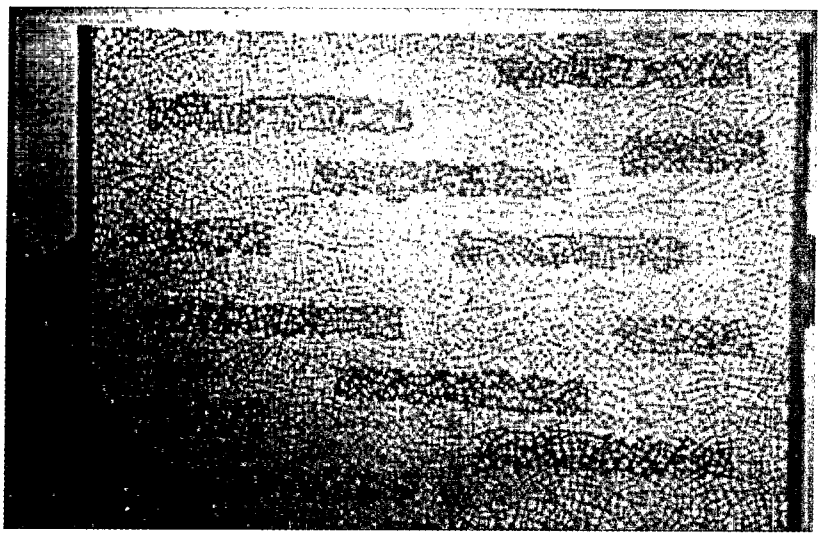


Figure 10. Water has swept through a heterogenous micromodel containing a NAPL as a nonwetting fluid and water as a residual wetting fluid. The nonwetting NAPL in the isolated coarse-grained heterogeneities has been bypassed (3).

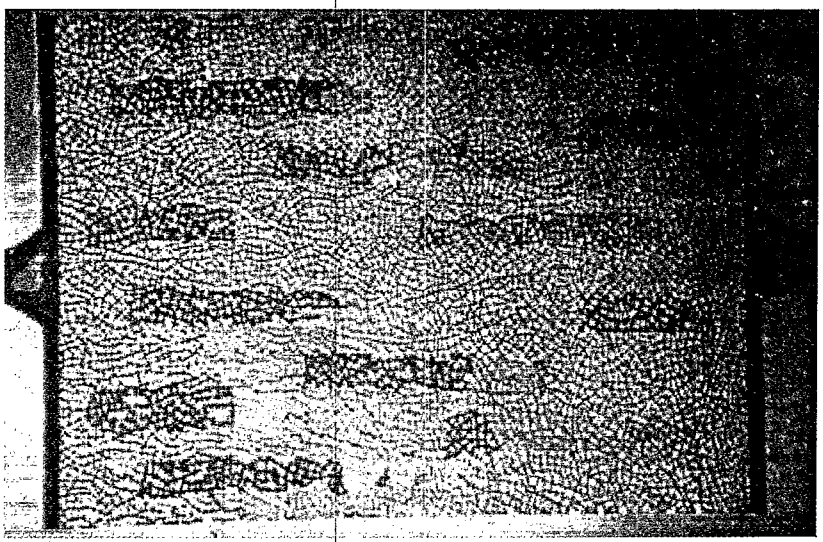


Figure 11. Water is displacing the NAPL at a higher flow rate through the same heterogeneous micromodel. The flow is from right to left. With larger viscous forces, the displacement is more efficient, and less NAPL is bypassed. This photograph was taken while the displacement was still under way. The bypassing is complete on the right side of the model and has not yet occurred at the left side (3).

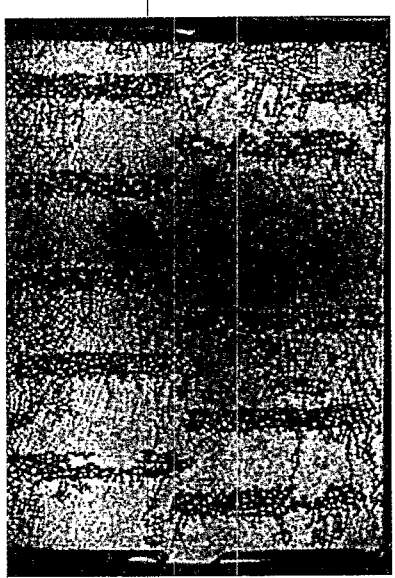


Figure 12. DNAPL is moving downward through a water-saturated heterogeneous micromodel (9).

Influence on Intrinsic Bioremediation

The distribution of fluid and solid phases controls the mass transfer and transport of chemicals and their availability for biotransformation by the microbial population. For all practical purposes, biotransformation takes place in the aqueous phase or in contact with the aqueous phase. Bacteria colonize surfaces. In water-saturated media, the only surfaces available are the solids, but in the vadose zone and in NAPL-contaminated areas there are also fluid-fluid (e.g., air-water, oil-water) interfaces that some bacteria will colonize. These colonies develop in part due to the same interfacial forces that attract abiotic colloids to solid-liquid or fluid-fluid interfaces. Figure 13 shows fluorescing colloids that are repulsed from the solid surface by electrostatic forces but that are attracted to an air-water interface by hydrophobic and capillary forces. Similar observations have been made for microorganisms (4, 5). Other important processes also lead to bacterial attachment and colonization at interfaces that are unique to living bacteria, with their complex surface chemistry and ability to produce extracellular polymers. Where NAPLs are concerned, there may also be toxicity effects repelling the bacteria, or, if the NAPL is an important nutrient source, it may be an attractant. Figure 14 shows a bacteria colony in the vicinity of a blob of iso-octane. The bacteria have colonized the solid surface and the surface of the blob, and a few were even observed to be living in the iso-octane. In a similar experiment with toluene and a toluene-degrading bacteria, the bacteria found high concentrations of toluene toxic and set up housekeeping at a distance that allowed ambient flow and mixing to dilute the concentrations many times.

The geometry of the fluid distributions have other indirect influences on intrinsic bioremediation. Consider mass transfer of chemical components between a multicomponent residual NAPL and the water phase in the saturated zone. Many spilled NAPLs—from gasoline and other fossil fuels to transformer oils containing polychlorinated biphenyls (PCBs), as well as the mixed bag of organics that are sometimes found in industrial waste pits—are mixtures having many (sometimes hundreds of) organic chemical components. The more soluble components of these mixtures can dissolve comparatively quickly, leaving behind less soluble components to leach out more slowly.

There are also cosolvency effects to consider. Interaction between components can either enhance the solubility of a given component (cosolvency) or reduce the solubility of that component (by a kind of salting-out process). Capillary-trapped residual blob size and shape influence the partitioning of NAPL components to the aqueous phase. Mass transfer coefficients used in the mathematical models of this partitioning often employ the analogy of an equivalent spherical blob. Certainly singlet blobs can be represented by a spherical model, but it is less clear that this model works for the tortuous multiple pore-body elongated or branched blobs shown in Figure 8, or in the presence of heterogeneity shown in Figure 10. Large complex blobs hold the majority of the NAPL volume, and mass transfer from them to the aqueous phase is clearly rate limited (6-8); it can take decades under natural conditions. Intrinsic bioremediation can do little to speed up this mass-transfer process, except to possibly increase concentration gradients between the NAPL and the aqueous phase, or perhaps increase the solubility of chemical components through the production of biosurfactants.

Even in the absence of toxicity effects and mass-transfer limitations, there may be little intrinsic bioremediation within the NAPL zone. The aqueous-phase flow field is complicated by the presence of the NAPL. Among other things, the effective permeability to water is lower. Consequently, it is difficult to supply the nutrients necessary for growth (3, 8).

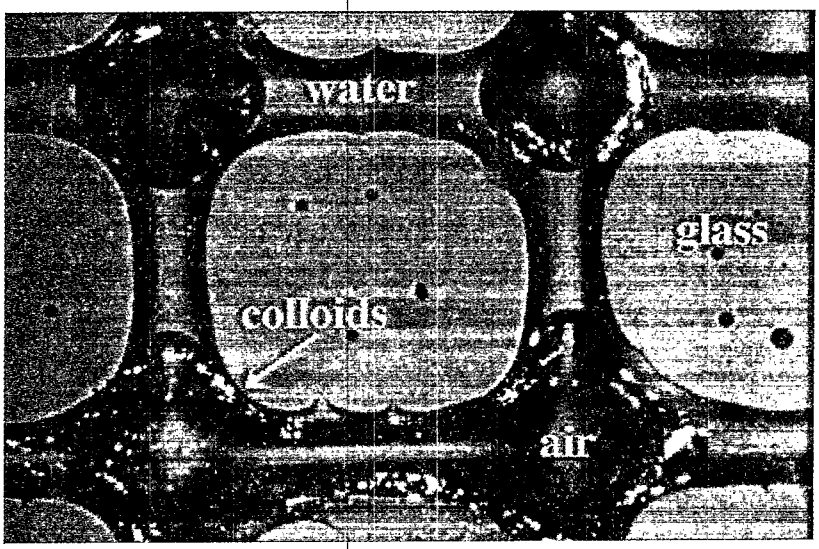


Figure 13. Negatively charged hydrophilic polystyrene particles attached to the surface of gas bubbles entrapped in a micromodel. There is almost no sorption on the glass surface at this ionic strength (4).

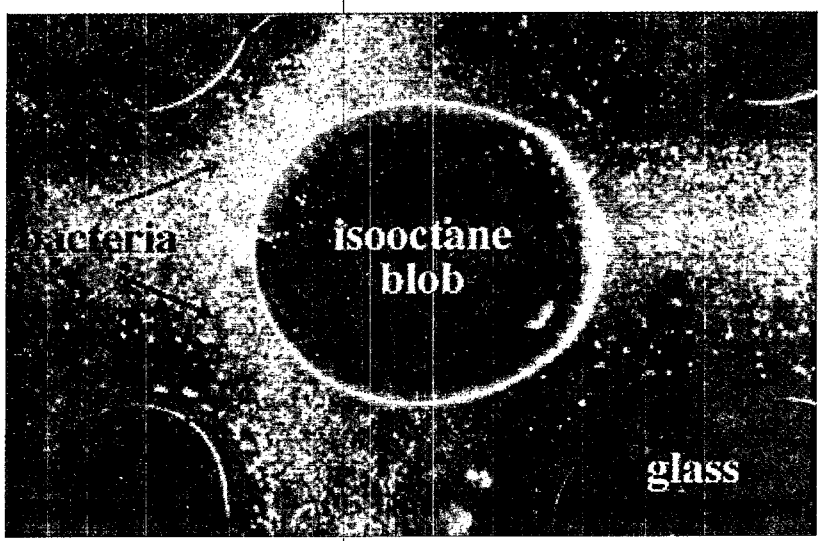


Figure 14. A colony of bacteria (*Arthrobacter* sp. ZAL001) in the vicinity of an iso-octane blob after 48 hr of growth. The blob is trapped in a pore body. The bacteria are light gray (5).

For these reasons, intrinsic bioremediation of the NAPL itself may be of limited value. If instead we consider the downgradient plume of dissolved contamination, the basic concern with the NAPL is as a source of that contamination.

To understand the plume, we must know something about the spacial distribution of the source and determine whether or not it is still moving. This both locates the source and controls the effective mass-transfer rate between the source and the ground water. If the source is a NAPL, it is obvious from some of the earlier photographs that even a small amount of liquid may be spread throughout a relatively large volume of aquifer material, and in a most complex pattern (see Figures 11 and 12). Characterization of this distribution and movement is difficult and may be beyond the current state of the art.

Summary

Three major forces control the movement and distribution of fluids in the vadose and saturated zones: capillary, viscous, and buoyancy forces. These forces interact with the complex pattern of geological features, making fluid behavior difficult to predict and fluid distribution difficult to characterize. Wetting fluids have an affinity for the solid surfaces of aquifer materials. In general, NAPLs are wetting relative to air, but nonwetting relative to water. Consequently, they tend to fill the larger pores of the saturated zone, leading to entrapment in what are usually regarded as high-permeability materials: the coarse sand but not the fine silt. This tendency, together with the propensity for gravity fingering through the finer materials, causes a complex pattern of migration and distribution in the saturated zone. In the vadose zone, behavior is further complicated by the presence of air and the question of whether or not the NAPL tends to spread at the air-water interface. Wettability can be altered by sorption processes, changing the relative roles of water and the NAPLs and leading to new pathways and fluid distributions.

Intrinsic bioremediation within a NAPL-contaminated zone is probably of limited effectiveness. Mass-transfer limitations constrain the rate at which dissolved components reach the aqueous phase. There are toxicity concerns with the high concentrations that are found nearer the NAPL blobs or films. Some other nutrients are only limited in availability because of the more complex flow patterns that water must take in this region.

Consequently, intrinsic bioremediation should probably be aimed at the contamination in the downgradient aqueous phase of the dissolved plume. It is impossible to evaluate the effectiveness of bioremediation within the plume without knowing the answer to two questions: Where is the source? and, How much contamination is entering the flowing ground water from the source? The answer to both questions requires that we know the distribution of the NAPL—the plume's source—and determine whether that source is still moving. It is a direct answer to the "where" question. The "how much" question depends on the effective mass-transfer rate between the source and the passing ground water. The trouble is that, even in a geologically simple aquifer, a small amount of nonaqueous contamination may be spread throughout a relatively large volume of aquifer material, and in the most complex pattern. Characterization of this distribution and movement is difficult and may be beyond the current state of the art.

Appendix: Visualization of Processes in Micromodels

Micromodels are transparent physical models of a pore space network, created by etching a pattern onto two glass plates which are then fused together (3, 8, 9). The resulting pores have complex three-dimensional structures, although the network is only two dimensional. The micromodel in Figure 3 shows pore bodies connected together by narrower pore throats. The fused glass located in between these connected channels represents the solid material in this model of a porous media. Glass is also at the top of the channels, toward the viewer, and below the channels. When the pore body contains a nonwetting fluid, a thin water film is attached to the top and bottom of the pore body. The film is thin enough to partially exclude the bacteria from colonizing the top surface of the iso-octane blob in Figure 14. All of the photographs in this paper can be found collected together and described in more detail in Wilson (9). Greater detail is given in the original references.

Acknowledgements

The photographs presented in this paper were taken from work sponsored by the Subsurface Science Program of the Department of Energy, or from work sponsored by the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency. M. Flinsch of New Mexico Institute of Mining and Technology assisted with the preparation of this manuscript.

References

1. Bear, J. 1972. Fluid flow in porous media. New York: Elsevier.

2. Mercer, J.W., and R.M. Cohen. 1990. A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. J. Contam. Hydrol. 6:107-163.

3. Wilson, J.L., S.H. Conrad, E. Hagan, W.R. Mason, W. Peplinski, and E. Hagan. 1990. Laboratory investigation of residual liquid organics. Report CR-813571. U.S. Environmental Protection Agency, Ada, OK.

4. Wan, J., and J.L. Wilson. 1994. Visualization of the role of the gas-water interface on the fate and transport of colloids in porous media. Water Resour. Res. 30:11-23.

5. Wan, J., J.L. Wilson, and T.L. Kieft. 1994. The gas-water interface as an influence on the transport of microorganisms through unsaturated porous media. Appl. Environ. Microbiol. 60:509-516.

6. Miller, C.T., M.M. Poirier-McNeill, and A.S. Mayer. 1990. Dissolution of trapped nonaqueous phase liquids: Mass transfer characteristics. Water Resour. Res. 26:2783-2796.

7. Powers, S.E., C.O. Louriero, L.M. Abriola, and W.J. Weber. 1991. Theoretical study of the significance of nonequilibrium dissolution of NAPLs in subsurface systems. Water Resour. Res. 27:463-478.

8. Conrad, S.H., J.L. Wilson, W.R. Mason, and W. Peplinski. 1992. Visualization of residual organic liquid trapped in aquifers. Water Resour. Res. 28:467-478.

9. Wilson, J.L. 1994. Visualization of flow and transport at the pore level. In: Dracos, T.H., and F. Stauffer, eds. Transport and reactive processes in aquifers. Rotterdam: Balkema. pp. 19-36.

10. Adamson, A.W. 1982. Physical chemistry of surfaces, 4th ed. New York: Wiley and Sons.

11. Wilson, J.L. 1992. Pore scale behavior of spreading and nonspreading organic liquids in the vadose zone. In: Weye, U., ed. Subsurface contamination by immiscible fluids. Rotterdam: Balkema. pp. 107-114.

New Tools To Locate and Characterize Oil Spills in Aquifers

Bruce J. Nielsen
Environics Directorate, Armstrong Laboratory, Tyndall AFB, FL

Abstract

The vision of the Tri-Services (Air Force, Army, and Navy) scientists is about to become reality, as a partnership between the Department of Defense (DOD), academia, and private industry evolves into a combined technology that can save millions of dollars in long-term hazardous waste site cleanup costs.

DOD has about 20,000 contaminated sites, many of which require characterization. These sites also may require monitoring for more than 30 years, at a cost of millions of dollars per year. The cost of site characterization and monitoring can be 25 percent to 30 percent of the total remediation costs.

A quick fix is needed—one that would take a "snapshot" of the type and amount of contamination, help determine the best method of remediation, monitor the effectiveness of treatment, and let technicians and engineers know when the site is clean. The vision was that of a cost-effective method that would replace the current time- and labor-intensive processes of site characterization and monitoring.

To solve the problem, the Tri-Services integrated a laser spectrometer with fiberoptics with a cone penetrometer to provide the required "snapshot" of subsurface conditions. To date, this technology has been field-tested at numerous Air Force, Army, and Navy installations. Ongoing studies will extend its sensitivities; expand its capability to other contaminants such as solvents, metals, and explosives; and make it more user-friendly for operating technicians. The end result is a technology that can significantly reduce the cost of site characterization and monitoring.

Introduction

The Air Force's Armstrong Laboratory is executing a program to demonstrate, test, and evaluate the application of cone penetrometers in support of intrinsic bioremediation (natural attenuation) demonstrations. The Air Force and its contractors, in cooperation with the U.S. Environmental Protection Agency's (EPA's) Robert S. Kerr Environmental Research Laboratory, have conducted investigations at Tinker Air Force Base (AFB), Oklahoma; Plattsburgh AFB, New York; Patrick AFB, Florida; and Dover AFB, Delaware. One objective of the investigations was to assess the subsurface conditions, obtaining parameters for input into BIOPLUME® II, a numerical model useful for determining the potential for intrinsic remediation. A second objective was to validate the cone penetrometer/laser spectrometer system by soil sampling and analysis. The demonstrations proved the cone penetrometer's capabilities to quickly locate and define the areal and vertical extent of the liquid oily-phase plume using laser-induced fluorescence (LIF), and to rapidly install monitoring points and collect soil samples to provide additional data necessary to define the dissolved-phase plume.

This paper briefly describes the Tri-Services program for developing this cone penetrometer technology and recent results of the Air Force program.

Methods

Cone Penetrometry

The Site Characterization and Analysis Penetrometer System (SCAPS), developed jointly by the Tri-Services, has proven to be an effective technology for characterizing contaminated DOD sites. The Army has provided leadership on developing SCAPS, including the concept of using a sapphire window in the cone rod and of using fiberoptics and spectroscopy to analyze the soil for contamination. The Army has patented a "Device for Measuring Reflectance and Fluorescence of In Situ Soil" and is now licensing it.

The typical cone penetrometer is mounted on a 20-ton truck and driven to the site requiring characterization, where a conical rod is hydraulically pushed into the ground to be characterized. The rod is equipped with a variety of sensors or soil and ground-water sampling tools. The cone penetrometer can characterize several aspects of the subsurface, depending on the types of sensors integrated into the penetrometer. Strain gauges measure the forces against the tip and sleeve of the cone tool, allowing determination of soil type (e.g., sand, silt, clay) and stratification. Other sensors provide electrical resistivity, pore pressure, spectral characteristics, and other properties of the soil and contamination. The sensors provide information on hydrogeology and contamination; the samplers verify it. The real-time ability to receive and assess monitoring data on site without laboratory analysis is critical, facilitating decision-making during site investigation projects while ensuring accurate and efficient completion of site investigations and optimization of remedial activities.

Laser Spectrometer System

Each of the services has significant programs for developing and demonstrating laser spectroscopy and other sensor systems. One of the key components of the cone penetrometer is a neodymium:yttrium aluminum garnet (Nd:YAG) laser, which pumps a dye laser system to induce fluorescence of fuel products as the cone penetrometer probe is advanced into soils. LIF has been shown to be useful in identifying petroleum, oil, and lubricant (POL) contamination, such as gasoline and JP-4 jet fuel. The Armstrong Laboratory's Environics Directorate, working with North Dakota State University (NDSU), has developed a tunable laser/fiberoptic spectrometer system, which uses laser-generated ultraviolet light, optical fibers, and spectroscopy for hazardous waste site monitoring. The basic detection approach takes advantage of the fact that certain substances fluoresce when a particular wavelength of light shines on them. The spectral emission, including fluorescent lifetime, is somewhat like a fingerprint and therefore is useful in identifying the contaminant. The fluorescent intensity indicates concentration of the contaminant. The transportable laser system is unique because its output may be tuned to the optimum frequency for detecting the pollutants of interest.

Optical fibers are used to transmit ultraviolet light to subsurface monitoring points and return resulting light for the spectroscopic analysis. The system can identify aromatic hydrocarbons such as benzene, toluene, and xylene (BTX) and naphthalene by their fluorescent spectra. Jet fuel, which contains naphthalene and BTX, is the most common contaminant at Air Force sites.

This technology can provide semiqualitative and semiquantitative information, on site, in minutes. The LIF response can be correlated to the total petroleum hydrocarbon (TPH) concentration within the soil. The system has been tested in the field with detection limits as low as parts-per-million levels on soil when used with a cone penetrometer and in the laboratory at parts-per-billion levels for BTX in water using fiberoptic probes. Laser spectroscopy technology could also be used to monitor the progress of site remediation and to provide baseline data for intrinsic bioremediation modeling studies.

Technology Transition

Armstrong Laboratory and Unisys Corp. signed a Cooperative Research and Development Agreement (CRADA) to commercialize the Air Force-developed laser spectrometer system. The laser spectrometer was initially developed for making ground-water measurements in monitoring wells or in implanted monitoring points. A consortia consisting of the CRADA partners, Dakota Technologies Inc., and NDSU submitted a proposal to the Advanced Research Projects Agency (ARPA), Technology Reinvestment Project (TRP). ARPA selected the proposal to receive a 2-year, $1,600,000 grant with two 1-year options for follow-on technology development. The industry partners provide in-kind contributions and matching funds.

The Rapid Optical Screening Tool (ROST) is the proposed product from the commercialization of the laser spectrometer developed for the Air Force by NDSU. ROST will build upon the previous Environics Directorate research by automating the collection and mapping of data, making equipment components smaller and more rugged, and developing a more user-friendly interface to allow use by environmental technicians involved in site characterization and cleanup. ROST also has potential for process monitoring and for medical diagnostics. Initial commercial use will be with cone penetrometers for soil characterization.

Use of the proposed ROST technology should result in substantial savings in costs associated with characterization, monitoring, and remediation of hazardous waste sites. The participants are committed to commercializing the resulting instrumentation for worldwide sales by U.S. firms or companies. In short, DOD will benefit from the technology and knowledge gained; the private sector will receive a highly transferable and profitable technology; the U.S. economy will be helped; and all will benefit from a cleaner environment.

Combined Technologies

The combined cone penetrometer and transportable laser spectrometer was demonstrated at Air Force installations having fuel-contaminated areas. To date, the laser spectroscopy system's primary function with the cone penetrometer has been to define the oily-phase plume. At Tinker AFB, the tunable laser system was configured to optimize the system for jet fuel and heating oil, the known petroleum contaminants. Laboratory fluorescence spectra from these fuels suggest that naphthalene produces the maximum fluorescence; consequently, a laser excitation wavelength appropriate for the known fuels was utilized during the field program.

The system is designed to collect data in two different modes: "push" or "static." In the push mode, laser excitation frequency is fixed, and the LIF signal is monitored as the cone penetrometer probe is advanced. Operation in the static mode, or with the probe stopped, allows collection of LIF multidimensional data sets, typically fluorescence emission wavelength, intensity, and time of decay matrices (WTM). WTMs have proven to be very useful in identifying various fuels.

Results

Studies to demonstrate site amenability towards intrinsic demonstrations were conducted at Plattsburgh, Patrick, and Dover AFBs. The sites selected for the demonstrations included closed fire-fighter training areas, gasoline service stations, and aircraft hydrant fueling systems. The old fire-fighter training areas were composed of unlined pits used to ignite fuels such as JP-4, waste oils, and other flammable substances. The service stations or hydrant fueling systems had leaking underground storage tanks or piping. Substances from these operations have percolated through the vadose zone into the unconfined aquifer. The penetrometer determined the areal extent and volume of oily-phase contamination, and obtained ground-water and soil core samples. To determine site amenability, acquired data were then fed into BIOPLUME® II, a computer model for *in situ* contaminant biodegradation. The cone penetrometer system rapidly located and defined the leading edge of the oily-phase petroleum plume. The technology proved that it can be used to provide timely and accurate data for intrinsic bioremediation modeling.

The Tri-Services conducted a series of laboratory tests, and some of the preliminary results are calibration curves with different fuels on various soil matrices. The calibration curve obtained in the laboratory for diesel fuel marine (DFM) on a sand matrix indicates a detection limit that is lower than 30 mg/kg (ppm) (Figure 1). The collection of LIF multidimensional data sets (fluorescence emission wavelength, intensity, and lifetime) or WTMs for diesel #2, JP-4, unleaded gasoline, and diesel fuel marine show how each one has a characteristic pattern. These patterns make possible reliable fuel-type identification without the need for bringing samples to the surface (Figure 2). In the field, the LIF count measurements can be correlated with collected samples and analytical results. To assist in the correlation, several WTMs were conducted at various depths. Color-coded WTMs from the North Tank Area (NTA) and Fuel Purge Area (FPA) at Tinker AFB indicate different fuel types. The shapes of these spectra identify the contaminants as fuel oil at the NTA and JP-4 at the FPA (Figure 3). The fluorescence versus depth profile from push location 84-L at Plattsburgh AFB indicates narrow bands of contamination are in the "oily phase," which rests just above the water table. Note that discrete sampling at 5-ft intervals (25, 30, 35 ft, etc.) could easily skip over the contamination (Figure 4). A series of fluorescence versus depth profiles taken across a north-south transect at the Plattsburgh AFB fire-fighter training area show the extent of contamination (Figures 5 and 6). Location 84A is upgradient, 84D is in the center of the burn pit, and the remainder are downgradient. The contamination traveled directly down from the burn pit and then along the water table.

Conclusions

Currently, these technologies are being further developed and demonstrated within numerous DOD, Department of Energy, and EPA programs. Ongoing research will develop techniques to monitor contaminants such as chlorinated solvents, metals, and explosives that do not naturally fluoresce. Refining this technology is at the heart of site remediation because it provides cost-effective characterization before, during, and after remediation. We can use it to determine if remediation is needed, what remediation technology we should apply, whether the remediation is working, and whether the cleanup effort has been successful—all with a minimum of risk, time, labor, and cost.

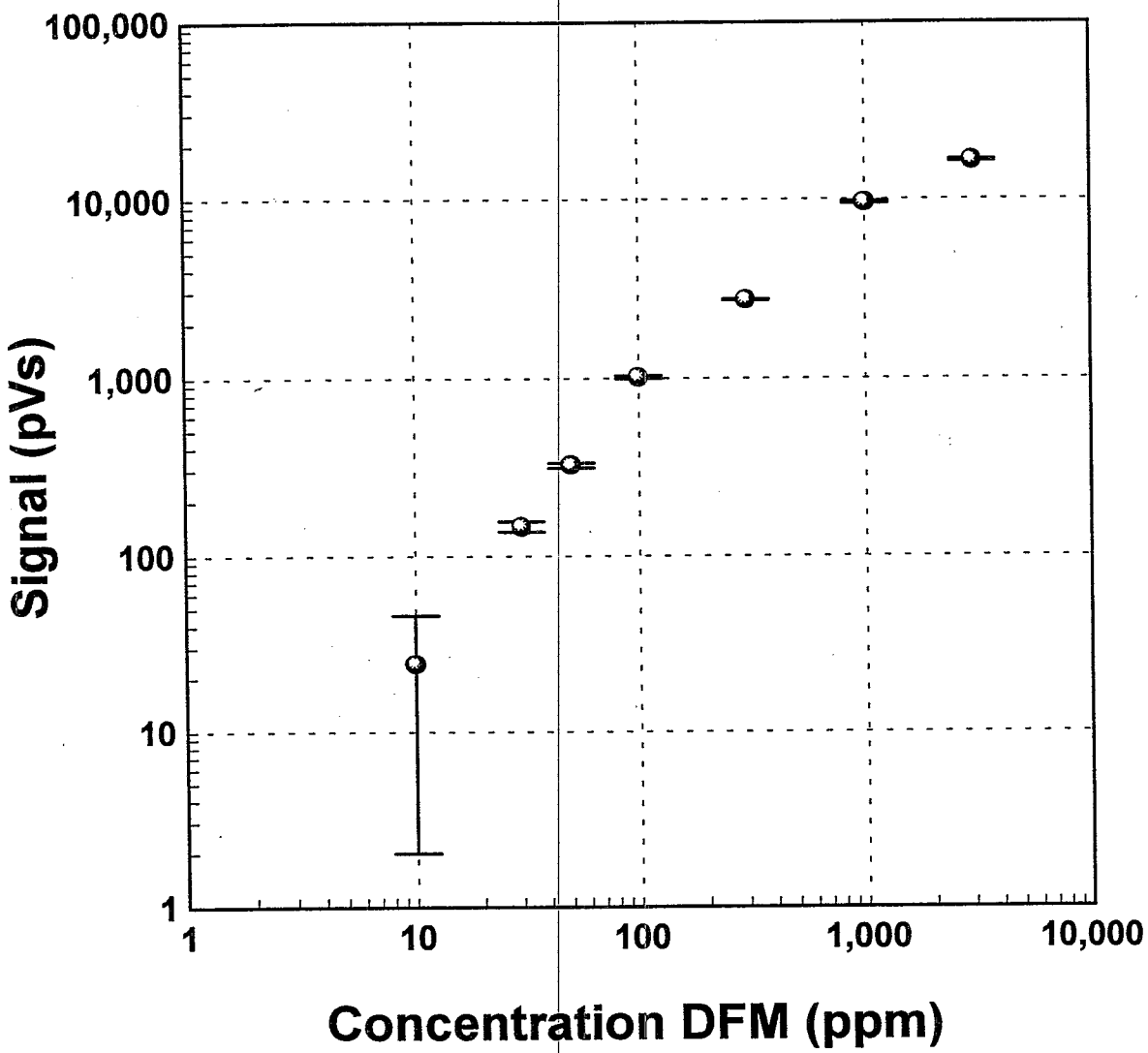


Figure 1. Calibration curve for diesel fuel marine on fisher sand.

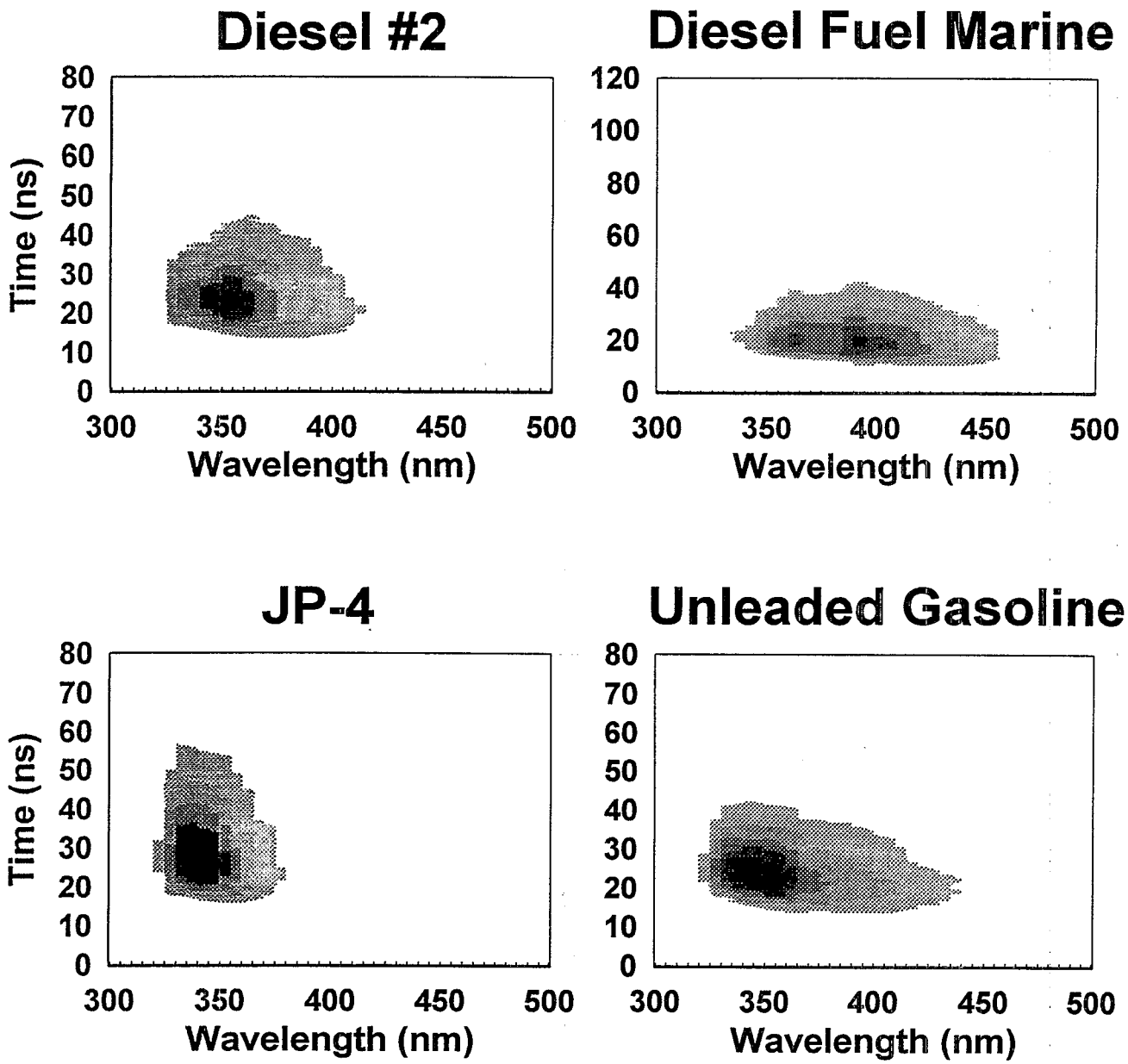


Figure 2. Wavelength time matrices of various fuels.

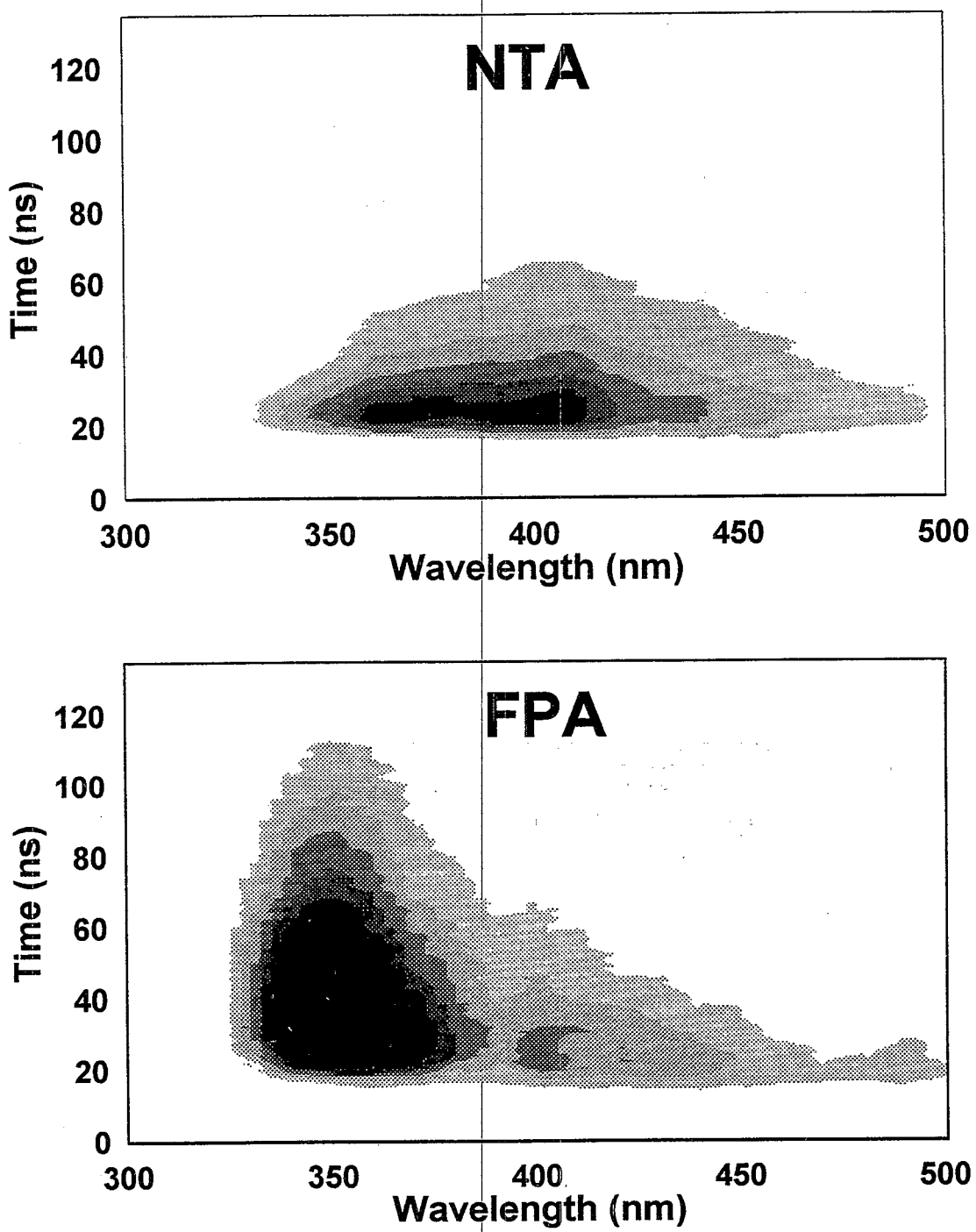


Figure 3. Wavelength time matrices at two different sites: North Tank Area versus Fuel Purge Area.

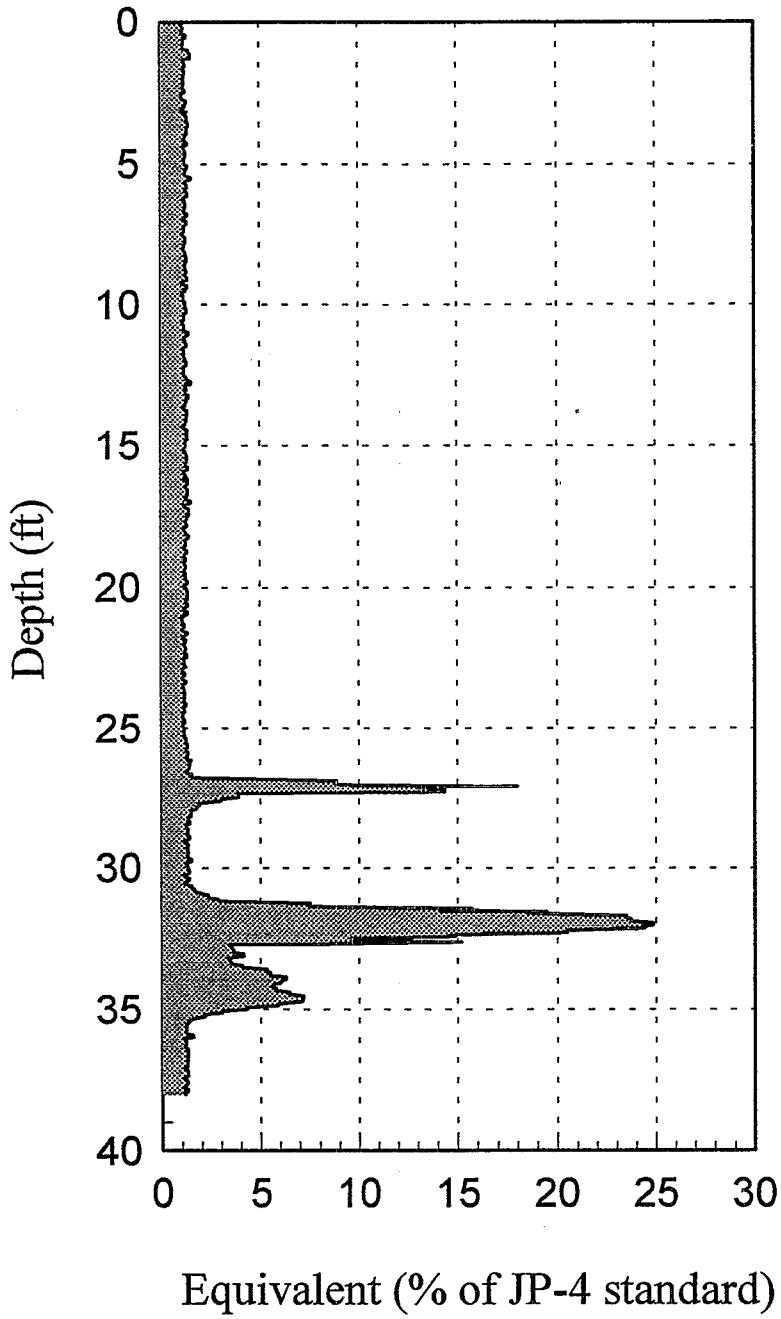


Figure 4. Fluorescent versus depth profile from fire training facility.

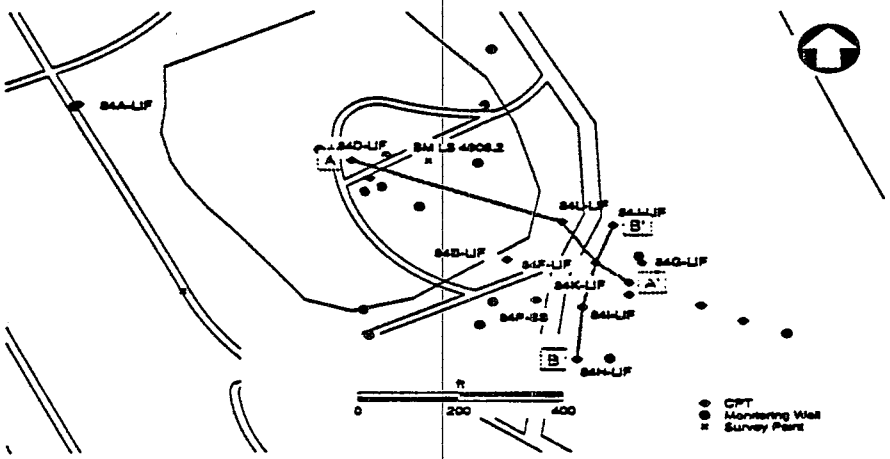


Figure 5. Base map of the fire training area showing location of CPT soundings and wells.

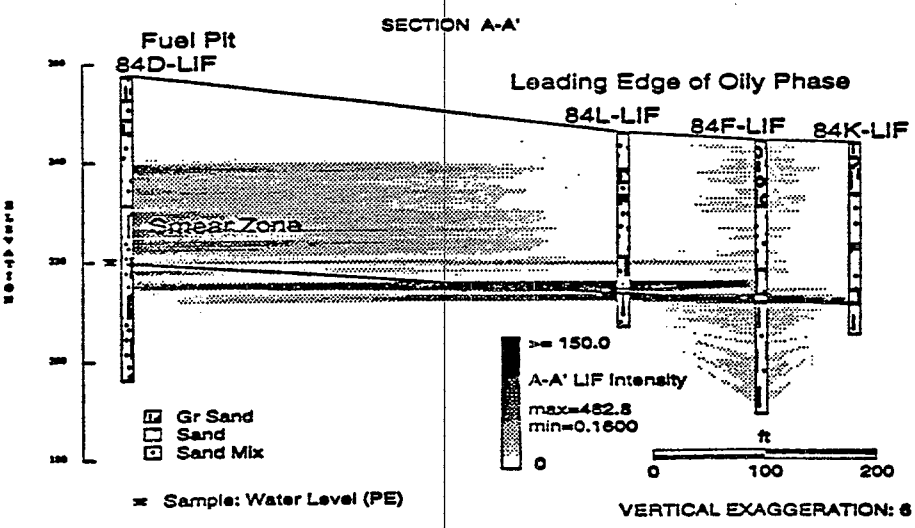


Figure 6. Cross section showing contaminated zone and water table along section A-A' in Figure 5.

References

1. Bratton, W.L., J.D. Shinn, S.M. Timian, G. Gillispie, and R. St. Germain. 1993. The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS), Vols. I-V. AL/EQ-1993-0009.

2. Gildea, M.L., W.L. Bratton, J.D. Shinn, G. Gillispie, and R. St. Germain. 1994. Demonstration of the Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS) in support of the intrinsic bioremediation (natural attenuation) option (interim report).

3. Schroeder, J.D., and S.R. Booth. 1991. Cost effectiveness analysis of the Site Characterization and Analysis Penetrometer System (SCAPS). Los Alamos National Laboratory, Los Alamos, NM.

Microbiological and Geochemical Degradation Processes

E. Michael Godsy
U.S. Geological Survey, Menlo Park, CA

Introduction

Ground-water contamination is perhaps the most dangerous and intractable environmental impact of toxic chemical spills and leaks. The prevention of ground-water contamination is of foremost importance. In terms of treatment processes, the present technology of excavation and relocation of contaminated soils to "secure landfills" (which are seldom secure) and "pump and treatment" of contaminated ground water has proven to be totally inadequate; these processes just transfer contaminants from one environmental phase to another. Bioremediation, however, achieves contaminant decomposition or immobilization by exploiting the existing metabolic potential of microorganisms with novel catabolic functions derived through selection. In response to the introduction of a toxic contaminant, an indigenous bacterial population arises that is unique from the standpoint of physiological capabilities and species diversity.

Conditions that restrict life or inactivate microbial enzymes are incompatible with intrinsic bioremediation efforts. Although the physical and chemical characteristics of the contaminants and the metabolic potential of microorganisms determine the feasibility of biotransformation reactions, actually achieving biotransformation also depends on the prevailing geochemical conditions. The ecological constraints to bioremediation can be classified as microbial, chemical, or environmental, and recognition of these constraints, as required, assesses the feasibility of intrinsic bioremediation. This article focuses on the microbiological and geochemical constraints influencing intrinsic bioremediation processes.

Bacterial Metabolic Diversity

Bacteria comprise a large and diverse group of microorganisms that obtain their energy from a variety of sources, including 1) light *(photosynthetic bacteria)*, 2) the oxidation or decomposition of reduced organic matter *(heterotrophic bacteria)*, or 3) the oxidation of reduced inorganic compounds *(autotrophic bacteria)*. Some bacteria derive energy from more than one source, such as combinations of light and reduced inorganic or organic compounds; however, heterotrophic bacteria are the major group responsible for the biodegradation of organic compounds.

All living organisms must generate reducing power for the purpose of replenishing enzymatic systems and maintaining the oxidation-reduction power cycle. This involves the reduction of oxidized compounds by the addition of electrons released from compounds oxidized during energy production. The electron acceptor can be either an organic or an inorganic compound. For many bacteria, most fungi, and all higher organisms, the final electron acceptor is O_2 in the process termed *aerobic respiration*. The final reduced substrate in aerobic respiration is H_2O, and the final oxidized compound respired from energy production is CO_2.

In the absence of O_2, certain bacterial populations respire other less oxidized inorganic compounds *(inorganic respiration)* or use only organic compounds *(fermentation)*. Denitrification is a process promoted by bacteria that can thrive under either aerobic or anaerobic conditions *(facultative anaerobes)* by using O_2 as the terminal electron acceptor, when available, or, in the absence of O_2, by using NO_3^- as the terminal electron acceptor *(inorganic respiration)*. When oxidation-reduction potentials within soils are even lower, other inorganic compounds are used by specific groups of bacteria as terminal electron acceptors. Because O_2 is toxic to these bacteria, they are called *obligate anaerobes*. Several common alternative electron acceptors and associated bacterial groups include ferric iron *(iron reducers)*, SO_4^{2-} *(sulfate reducers)*, and CO_2 *(methanogens)*.

Incorporating Contaminants Into Bacterial Ecosystems

The ecosystem as a whole can be thought of as a series of integrated oxidation-reduction (redox) reactions driven ultimately by the radiant energy of the sun. Microorganisms catalyze many of these reactions and play an essential role in maintaining the electron balance of complex ecosystems. For a contaminant to be incorporated into these redox reactions, it must be able to serve as either an electron donor or an electron acceptor. Moreover, its tendency to either donate or accept electrons—and thus be oxidized or reduced—depends on the chemistry of the compound. For example, many halogenated organic compounds are highly oxidized relative to their nonhalogenated counterparts, and thus tend to accept electrons and to be reductively dehalogenated. The halogenated compounds must compete with other physiological electron acceptors in order to be incorporated into microbial energy cycles. Thus, the effectiveness of reductive dehalogenations is often influenced by the presence of other electron acceptors, such as NO_3^- or SO_4^{2-}. This effect would explain why reductive dehalogenations are more frequently observed under methanogenic conditions, where generally a paucity of these anions exist.

Bacteria-Contaminant Interactions in Aquifer Material

A minimum of three conditions must be met before a contaminant can be degraded or transformed by bacteria: 1) the bacteria must be in the immediate vicinity of the contaminant; 2) the contaminant must be available to the bacteria; and 3) the bacteria must have the capacity to participate in some part of the degradation or transformation process. Specific bacterial populations prefer or require particular environmental conditions. If these conditions do not exist, these populations tend to become quiescent until more ideal conditions return or develop, or in some cases they may even die off. The nature of limiting environmental factors often dictates which bacterial populations exist. While the subsurface environment can be modified, modification is often accomplished with great difficulty and always at great expense.

Bacterial Nutrition

Bacteria are composed of combinations of elements that are the components of their genetic material, structural molecules, enzymes, and intracellular plasma. Because of the great diversity among bacteria, the proportion of nutrient elements required for growth varies widely; however, the major required elements that make up bacteria are carbon, hydrogen, sulfur, nitrogen, and phosphorus. In soils and aquifer materials contaminated with most organic compounds, carbon and hydrogen are not typically limiting because they are the major components of organic

compounds, and sulfur is generally available in sufficient quantities for growth. Thus, the major limiting elements for growth are nitrogen and phosphorus. The carbon/nitrogen/phosphorus ratio (C/N/P) usually considered ideal is 300 to 100:10:1 to 0.05 (1); however, this ratio can vary depending the nature of the contaminant(s).

pH and Redox Potential

Near-neutral aquifer pH values are usually optimum for the biodegradation of contaminant organic material. The hydrogen ion concentration of the ground water is governed by the types of compounds produced by bacterial activity, and is controlled especially by CO_3^{2-}:HCO_3^-:CO_2 equilibrium rates (2). Because hydrogen ion transfer is commonly involved in electron transport, pH and redox potential are interdependent (3).

The redox potential, termed E_h, is extremely important in the biotransformation schemes of both organic and inorganic contaminants. Usually, a heavily contaminated site is anoxic because ongoing bacterial respiration has depleted all available O_2. The resulting anoxic conditions tend to favor different electron acceptors, with the most oxidized compounds (higher E_h) being used first. The resultant scheme is NO_3^- (denitrification) utilization after O_2 depletion, Fe^{3+} (iron reduction) utilization after NO_3^- depletion, SO_4^{2-} (sulfate reduction) utilization after Fe^{3+} depletion, and finally CO_2 reduction to CH_4 after depletion of the available SO_4^{2-} . As a result, bacterial populations having different degradative potentials can be operative at different times at the same contamination site as the redox potential varies.

Although E_h measurements can provide valuable clues about the functioning of geochemical systems in aquifer material, they alone will not give definite information about the chemical species present. These measurements indicate that a potential exists for certain redox reactions, such as those involving bacterial respiration. Various organic and inorganic redox reactions cannot be predicted because of their complexity and different interdependent reaction rates (2).

Temperature

Ground-water temperature is often one of the most important factors controlling microbial activity and rates of organic matter decomposition. Generally, rates of enzymatic degradation and bacterial metabolism double for every 10°C increase in temperature until close to inhibitory temperatures, which are usually around 40°C to 50°C for most bacteria. Except for subfreezing temperatures, however, bacteria are generally capable of degradation at most ambient temperatures (4). Perhaps more importantly, temperature can influence biodegradation of a compound or contaminant mixture by changing its physical properties, bioavailability, or toxicity to bacteria. For example, an increase in temperature usually increases the equilibrium vapor concentration, resulting in an increased volatilization rate, but it can at times also increase sorption to aquifer particles (5).

Physical Deterrents to Biodegradation

Physical or physicochemical factors can also affect the biodegradation of contaminants. Some molecules are recalcitrant to degradation because they are too large to enter bacterial cells, which is usually required for complete degradation by membrane-bound enzymes. Some substances are difficult to biodegrade because the number, length, or location of functional groups impede enzyme attack. Strong sorption on aquifer material can greatly hinder the ability of bacteria to attach to, absorb, or enzymatically attack the molecule (6).

Sorption and solubility of organic contaminants are complex interdependent phenomena that vary with the composition of the aquifer material and complex contaminant mixtures. For example, aromatic hydrocarbon concentrations in water extracts of 31 gasoline samples varied over an order of magnitude (7). Although gasoline variability could account for this, the solubility of each component of mixtures can vary from ideal conditions, with each compound acting as a cosolvent to increase hydrophobic hydrocarbon solubilities (8). Organic solvents can also affect the sorption of organics on soils in general (9).

Contaminant Metabolism: Aerobic Versus Anaerobic

A common misconception is that all organic contaminants are biodegraded most rapidly and thoroughly under aerobic conditions. Although this is commonly the case, anaerobic conditions promote some very important degradative processes. For example, compounds that are highly oxidized, such as polychlorinated biphenyls or chlorinated solvents, are more susceptible to reductive processes than to oxidative processes (10) during the initial stages of mineralization.

Most organic compounds found in crude oil, refined oils, and fuels are known to degrade under aerobic conditions (4); however, current research efforts have shown that the biodegradation of many monoaromatic compounds common to most fuels also occurred in the laboratory under anaerobic conditions. This biodegradation readily occurs not only with NO_3^- serving as the terminal electron acceptor (11) but also under SO_4^{2-} reducing conditions (12), Fe^{3+} reducing conditions (13), and methanogenic conditions (14,15).

Benzene has been especially recalcitrant to anaerobic biodegradation in laboratory studies under denitrifying and sulfate-reducing conditions (10,12). Yet some laboratory (16) and field studies (17) have shown the depletion of all common monoaromatic hydrocarbons found in gasoline under denitrifying conditions. In 1986, Vogel and Grbić-Galić (18) demonstrated that benzene and toluene were degradable to CH_4 and CO_2 in laboratory microcosms; however, the confirmation of the degradation of benzene in field situations under methanogenic conditions has been rather elusive. One of the few well-documented instances of the methanogenic degradation of benzene in the field is a crude oil spill in Bemidji, Minnesota (19), where many of the water-soluble monoaromatic hydrocarbons present in crude are undergoing intrinsic bioremediation.

Conclusion

Although bioremediation in general has gained considerable attention, obstacles remain before bacteria can be used effectively for detoxifying wastes affecting ground water. A lack of knowledge or misunderstanding concerning what can and cannot be done with bioremediation has resulted in unrealistic expectations, leading in turn to disappointments and ultimate failures. Continued research into and application of sound bioremediation schemes will undoubtedly prove the viability of intrinsic bioremediation in the overall remediation efforts of contaminated ground water.

References

1. Torpy, M.F., H.F. Stroo, and G. Bruebaker. 1989. Biological treatment of hazardous wastes. Poll. Eng. 21:80-86.

2. Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry. New York, NY: John Wiley & Sons.

3. Grundi, T. 1994. A review of the current understanding of redox capacity in natural, disequilibrium systems. Chemosphere 28:613-626.

4. Leahy, J.G., and R.R. Colwell. 1990. Microbial degradation of hydrocarbons in the environment. Microbiol. Rev. 54:305-315.

5. Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1982. Handbook of chemical property estimation methods: Environmental behavior of organic chemicals. New York, NY: McGraw-Hill.

6. Cheng, H.H., K. Haider, and S.S. Harper. 1983. Catechol and chlorocatechols in soil: Degradation and extractability. Soil Biol. Biochem. 15:311-317.

7. Cline, P.V., J.F. Delfino, and P.S.C. Rao. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. Environ. Sci. Technol. 25:914-920.

8. Groves, F.R. 1988. Effect of cosolvents on the solubility of hydrocarbons in water. Environ. Sci. Technol. 22:282-286.

9. Fu, J.-K., and R.G. Luthy. 1986. Effect of organic solvent on sorption of aromatic solutes onto soils. J. Environ. Eng. 112:346-366.

10. Kuhn, E.P., and J.M. Sulflita. 1989. Dehalogenation of pesticides by anaerobic microorganisms in soils and ground water: A review. In: Sawhney, B.L., and K. Brown, eds. Reactions and movement of organic chemicals in soils. Special Publication 22. Madison, WI: Soil Science Society of America. pp. 111-180.

11. Evans, P.J., D.T. Mang, and L.Y. Young. 1991. Degradation of toluene and *m*-xylene and transformation of o-xylene by denitrifying enrichment cultures. Appl. Environ. Microb. 57:450-454.

12. Edwards, E.A., L.E. Wills, D. Grbić-Galić, and M. Reinhard. 1991. Anaerobic degradation of toluene and xylene: Evidence for sulfate as the terminal electron acceptor. In: Hinchee, R.E., and R.F. Olfenbuttel, eds. *In situ* bioreclamation: Applications and investigations for hydrocarbon and contaminated site remediation. Boston, MA: Butterworth-Heinemann. pp. 463-471.

13. Lovely, D.R., and D.J. Lonergan. 1990. Anaerobic oxidation of toluene, phenol, and *p*-cresol by the dissimilatory iron-reducing organism, GS-15. Appl. Environ. Microb. 56:1,858-1,864.

14. Grbić-Galić, D., and T.M. Vogel. 1987. Transformation of toluene and benzene by mixed methanogenic cultures. Appl. Environ. Microb. 53:254-260.

15. Wilson, B.H., G.B. Smith, and J.F. Rees. 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosms study. Environ. Sci. Technol. 20:997-1,002.

16. Major, D.W., C.I. Mayfield, and J.F. Barker. 1988. Biotransformation of benzene by denitrification in aquifer sand. Ground Water 26:8-14.

17. Berry-Spark, K.L., J.F. Barker, D. Major, and C.I. Mayfield. 1986. Remediation of gasoline-contaminated ground-waters: A controlled experiment. In: Proceedings of petroleum hydrocarbons and organic chemicals in ground water: Prevention, detection, and restoration, NWWA/API. Dublin, OH: Water Well Journal Publishing.

18. Vogel, T.M., and D. Grbić-Galić. 1986. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. Appl. Environ. Microb. 52:200-202.

19. Cozzarelli, I.M., R.P. Eaganhouse, and M.J. Baedecker. 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground-water environment. Environ. Geol. Water Sci. 16:135-141.

Field and Laboratory Results: Getting the Whole Picture

Mary Jo Baedecker
U.S. Geological Survey, Reston, VA

Abstract

Concern over contamination of ground water in the last decade has led to an increased awareness of the need to understand the transport and fate of organic contaminants and the geochemical processes that result from their presence in the subsurface. A large number of contaminated sites contain petroleum-derived hydrocarbons. Many of the hydrocarbons are biodegraded in ground-water environments, and the extent of their removal by natural processes has been evaluated in field and laboratory investigations. Both types of investigations demonstrate that natural biodegradation can be an important component in remediation strategies for some contaminated sites.

Results and Discussion

The processes that control the attenuation of organic compounds in the subsurface are complex, and many investigations have been undertaken in the field and in laboratories to understand better the factors that control degradation reactions. Parts of contaminant plumes often become anoxic, and the fate of contaminants at anoxic field sites has been reported in several studies (1-5). One of the most widespread types of contaminants is petroleum-derived hydrocarbons from pipeline breaks, leaking storage tanks, spills, and disposal of wastes. Many of these sites, such as those contaminated by leaking small underground storage tanks, are easier to remediate than sites with contaminants such as chlorinated compounds. The number of such sites is large, however, and much effort has been spent trying to understand processes and to develop effective remediation strategies to deal with petroleum-derived hydrocarbons. Several research efforts have been undertaken in the field and laboratory to determine processes that affect the fate and transport of individual hydrocarbons. In field investigations, degradation of soluble aromatic hydrocarbons has been shown to occur downgradient from source areas (6-10). Hydrocarbon-degrading bacteria were found and quantified in soil and ground water at a fuel-oil contaminated site (11). Degradation of petroleum-derived hydrocarbons is generally considered to occur more rapidly in aerobic or suboxic environments, where oxygen or nitrate is available as an electron acceptor (7, 12-13), but anaerobic biodegradation also may remove significant amounts of hydrocarbons from ground water (14-17).

An investigation of the effects of a crude-oil spill on an aquifer was undertaken near Bemidji, Minnesota, as part of the Toxic Substances Hydrology Program of the U.S. Geological Survey. An underground pipeline carrying crude oil ruptured and sprayed oil over land surface. Part of the oil was removed during remediation, but part of it infiltrated through the unsaturated zone and accumulated as an oil body floating on the ground water. A more detailed description of the processes that occurred at the site is available in Baedecker et al. (5), Bennett et al. (18), Eganhouse et al. (9), Baedecker and Cozzarelli et al. (19), Cozzarelli et al. (20), and Eganhouse et al. (21).

The concentrations of benzene, toluene, ethylbenzene and o-, m-, and p-xylene (BTEX) in the upper 1.5-m thickness of the aquifer downgradient from the oil body are shown in Figure 1. The concentrations of BTEX decreased with increasing distance from the oil body and were attenuated under anoxic and oxic conditions. Where oxygen was encountered, concentrations decreased by several orders of magnitude (56 m to 137 m). The mass of BTEX lost near the oil body (26 m to 56 m), however, was as high as that lost farther downgradient. The decrease in concentrations of BTEX near the oil body (26 m to 56 m) was in the anoxic part of the plume, where no oxygen was detected in the ground water over an 8-yr period. Another indicator that this part of the aquifer was anoxic is that ferrous iron concentrations were 1.8 mg/L at the water table and 71 mg/L at only 0.3 m deeper in the aquifer (22). Ferrous iron precipitates where it encounters trace quantities of oxygen. Thus, the high concentrations of ferrous iron near the oil body indicate that dissolved oxygen was not transported to the water table. Degradation of hydrocarbon vapors in the unsaturated zone most likely consumed the oxygen by aerobic respiration (23). The downgradient movement of the BTEX plume averaged about 8 m/yr from 1987 to 1992, but movement has not been at a steady rate. Near the oil body, microbial degradation is the primary process of hydrocarbon attenuation. As the hydrocarbons are transported farther from the oil body, additional processes such as dispersion, mixing (24), and sorption become more important.

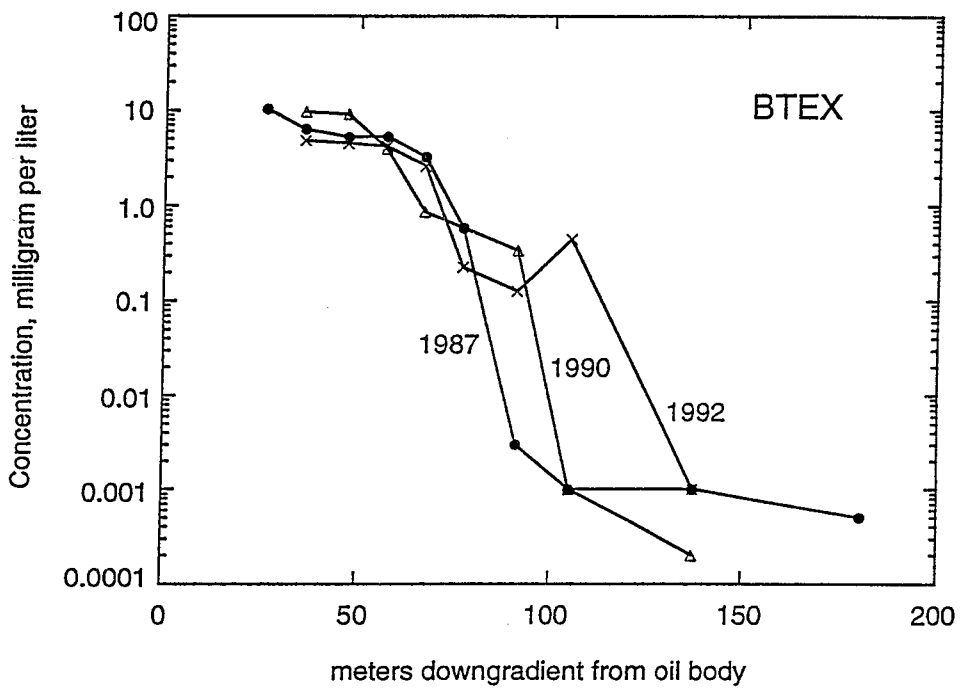


Figure 1. Concentrations of benzene, toluene, ethylbenzene, and o-, m-, and p-xylene (BTEX) in the upper 1.5-m thickness of an aquifer contaminated with crude oil (19).

Laboratory experiments demonstrated that these hydrocarbons can degrade under controlled laboratory conditions. To verify that the hydrocarbons were degrading under anoxic conditions, microcosm experiments were undertaken with sediment and water from the anoxic part of the plume (5, 20). In two separate experiments, benzene and a mixture of toluene and naphthalene were added to microcosms under anaerobic conditions. These compounds were also added to microcosms that were poisoned and sterilized for controls. In the microbially active microcosms, benzene decreased in concentration by 98 percent in 125 d, and toluene decreased by 99 percent in 45 d (5). No loss of naphthalene was observed during the same period. For the controls, no loss of benzene, toluene, or naphthalene was observed. These laboratory experiments and field results provide strong evidence that hydrocarbons are degrading in an anoxic environment. By comparing the results from the microbially active microcosms with results from controls, sorption and abiological chemical oxidation were eliminated as possible explanations for the loss of benzene and toluene.

Field and laboratory studies of anaerobic biotransformation or aromatic hydrocarbons were reviewed by Barker and Wilson (25) who found evidence at five methanogenic sites for biodegradation of benzene, toluene, ethylbenzene, and the xylenes. The estimated half-lives were 0.5 yr and 3.8 yr. The longest half-lives were for benzene. Laboratory experiments also have indicated biodegradation by several pathways (26); however, for benzene the results have been contradictory. Large concentrations of benzene are biodegraded in the subsurface (27), yet in some ground-water environments benzene is the most persistent hydrocarbon among the monoaromatics.

Natural processes can remove significant concentrations of hydrocarbons and prevent the spreading of a plume. At sites where the rates of solubilization, volatilization, and biodegradation of hydrocarbons are such that the plume is either contained or spreading at a slow rate, these natural processes can be considered in the design of a site remediation program. Even at sites where plumes are spreading at a fast rate, knowledge of the natural processes that are attenuating contaminants provides information that can be used to accelerate biodegradation processes.

Note

The data and interpretation in this report were previously published in Baedecker and Cozzarelli (19) and Baedecker et al. (5).

References

1. Baedecker, M.J., and W. Back. 1979. Hydrogeological processes and chemical reactions at a landfill. Ground Water 17:429-437.

2. Nicholson, R.V., J.A. Cherry, and E.J. Reardon. 1983. Migration of contaminants in ground water at a landfill: A case study 6. Hydrogeochemistry. J. Hydrol 63:131-176.

3. Lesage, S., R.E. Jackson, M.W. Priddle, and P.G. Riemann. 1990. Occurrence and fate of organic solvent residues in anoxic ground water at the Gloucester landfill, Canada. Environ. Sci. Technol. 24:559-566.

4. Godsy, E.M., D.F. Goerlitz, and D. Grbic-Galic. 1992. Methanogenic biodegradation of creosote contaminants in natural and simulated ground-water ecosystems. Ground Water 30:232-242.

5. Baedecker, M.J., I.M. Cozzarelli, R.P. Eganhouse, D.I. Siegel, and P.C. Bennett. 1993. Crude oil in a shallow sand and gravel aquifer, III. Biogeochemical reactions and mass balance modeling in anoxic ground water. App. Geochem. 8:569-586.

6. Barker, J.F., J.S. Tessman, P.E. Plotz, and M. Reinhard. 1986. The organic geochemistry of a sanitary landfill leachate plume. Contam. Hydrol. 1:171-189.

7. Major, D.W., C.I. Mayfield, and J.F. Barker. 1988. Biotransformation of benzene by denitrification in aquifer sand. Ground Water 26:8-14.

8. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground-water environment. Environ. Geol. Water Sci. 16:135-141.

9. Eganhouse, R.P., M.J. Baedecker, I.M. Cozzarelli, G.R. Aiken, K.A. Thorn, and T.F. Dorsey. 1993. Crude oil in a shallow sand and gravel aquifer, II. Organic geochemistry. Appl. Geochem. 8:551-567.

10. Davis, J.W., N.J. Klier, and C.L. Carpenter. 1994. Natural biological attenuation of benzene in ground water beneath a manufacturing facility. Ground Water 32(2):215-226.

11. Kämpfer, P., M. Steiof, and W. Dott. 1991. Microbiological characterization of a fuel oil-contaminated site including numerical identification of heterotrophic water and soil bacteria. Microb. Ecol. 21:227-251.

12. Kuhn, E.P., J. Zeyer, P. Eicher, and R.P. Schwarzenback. 1988. Anaerobic degradation of alkylated benzene in denitrifying laboratory aquifer columns. Appl. Environ. Microb. 54:490-496.

13. Hutchins, S.R., G.W. Sewell, D.A. Kovacs, and G.A. Smith. 1991. Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions. Environ. Sci. Technol. 25:68-76.

14. Wilson, B.H., G.B. Smith, and J.F. Rees. 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. Environ. Sci. Technol. 20:997-1,002.

15. Grbić-Galić, D., and T.M. Vogel. 1987. Transformation of toluene and benzene by mixed methanogenic cultures. Appl. Environ. Microbiol. 53:254-260.

16. Lovley, D.R., M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.P. Phillips, and D.I. Siegel. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. Nature 339:297-299.

17. Haag, F.M., M. Reinhard, and P.L. McCarty. 1991. Degradation of toluene and p-xylene in anaerobic microcosms: Evidence for sulfate as a terminal electron acceptor. Environ. Toxicol. Chem. 10:1,379-1,390.

18. Bennett, P.C., D.I. Siegel, M.J. Baedecker, and M.F. Hult. 1993. Crude oil in a shallow sand and gravel aquifer, I. Hydrology and inorganic geochemistry. Appl. Geochem. 8:529-549.

19. Baedecker, M.J., and I.M. Cozzarelli. 1994. Biogeochemical processes and migration of aqueous constituents in ground water contaminated with crude oil. In: Toxic substances and the hydrologic sciences. American Institute of Hydrology. pp. 69-79.

20. Cozzarelli, I.M., M.J. Baedecker, R.P. Eganhouse, and D.F. Goerlitz. 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in ground water. Geochim. Cosmochim. Acta 58(2):863-877.

21. Eganhouse, R.P., M.J. Baedecker, and I.M. Cozzarelli. 1994. Biogeochemical processes in an aquifer contaminated by crude oil: An overview of studies at the Bemidji, Minnesota, research site. Presented at the U.S. EPA Symposium on Intrinsic Bioremediation of Ground Water, Denver, CO (August 30 to September 1).

22. Cozzarelli, I.M., M.J. Baedecker, G. Aiken, and C. Phinney. 1994. Small-scale chemical heterogeneities in a crude-oil-contaminated aquifer, Bemidji, Minnesota. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

23. Hult, M.F., and R.R. Grabbe. 1988. Distribution of gases and hydrocarbon vapors in the unsaturated zone. In: Ragone, S.E., ed. U.S. Geological Survey toxic waste/ground water contamination study. Proceedings of the Technical Meeting of the U.S. Geological Survey, Cape Cod, MA (October 21-25, 1985). Open-File Report 86-481. pp. C21-C26.

24. Essaid, H.I., M.J. Baedecker, and I.M. Cozzarelli. 1994. Use of simulation to study field-scale solute transport and biodegradation at the Bemidji, Minnesota, crude-oil spill site. In: Morganwalp, D.W., and D.A. Aronson, eds. U.S. Geological Survey toxic substances hydrology program. Proceedings of the Technical Meeting of the U.S. Geological Survey Water Resources, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

25. Barker, J.F., J.T. Wilson. 1992. Natural biological attenuation of aromatic hydrocarbons under anaerobic conditions. Proceedings of the Subsurface Restoration Conference, Dallas, TX. pp. 57-58.

26. Grbic-Galic, D. 1990. Anaerobic microbial transformation of nonoxygenated aromatic and alicyclic compounds in soil, subsurface, and freshwater sediments. In: Bollag, J.M., and G. Stotzky, eds. Soil Biochemistry, Vol. 6. New York, NY: Marcel Dekker, Inc. pp. 117-189.

27. Hadley, P.W., and R. Armstrong. 1991. Where's the benzene? Examining California ground-water quality surveys: Ground Water 29(1):35-40.

In Situ Bioremediation at the Seventh Avenue Site in Denver: Remediation of Soils and Ground Water

Christopher Nelson
Groundwater Technology, Inc., Englewood, CO

In situ bioremediation is a cost-effective method for the remediation of soils and ground waters contaminated with petroleum hydrocarbons. This paper presents a case study of the successful application of *in situ* bioremediation at a public utility site in Denver, Colorado.

The site was used as a truck maintenance facility for almost 30 years. During that time, nonvolatile petroleum hydrocarbons from used motor oil, diesel, gasoline, and other automotive fluids were released to a used oil sump at the site. The local geology of the site includes claystone and sandstone bedrock, covered with recent deposits of interbedded alluvial sands and gravels, as well as silty sands and clays. The principal aquifer at the site lies within the interbedded alluvial sands and gravels.

Soil and water sampling confirmed the presence of petroleum hydrocarbons in both the vadose and saturated zones. Laboratory studies showed that the chemical, microbiological, and hydrogeological characteristics of the site were conducive to bioremediation.

Site Assessment/Treatability Study

An extensive site assessment and treatability study was conducted at the site to determine physical, chemical, microbiological, and hydrogeological characteristics controlling the biodegradation of contaminants and the mass transport of nutrients and oxygen. Nine monitoring wells were installed at depths of about 7.6 m, using a 3-m screen interval. The site assessment indicated that the primary contaminant at the site was waste oil located in the saturated and unsaturated sediments beneath the former used oil sump. Samples showed high levels of benzene, toluene, ethylbenzene, and the xylenes (BTEX); total petroleum hydrocarbons (TPHs); and total organic carbon (TOC) in ground water, with localized but detectable levels of chlorinated organics. A relatively large population of bacteria was found within the contamination zone; however, its growth appeared to be restricted by nutrient and oxygen conditions.

Feasibility studies were performed on soil and sediment samples to determine the biodegradability of contaminants under various nutrient loads and aerobic conditions. Aerobic testing was performed to simulate optimal conditions for the bioremediation of hydrocarbons. Column studies also were conducted to determine how nutrient and hydrogen peroxide loading would affect the hydraulic conductivity of sediments in the subsurface above the ground-water table.

The results showed that the loading of nutrients and hydrogen peroxide would be critical to the success of *in situ* bioremediation at this site and that the loading should be minimized in the silty sand zone because of high reactivity. A nutrient adsorption test indicated that ammonia and phosphate loading was feasible in the soil at the site.

System Design and Installation

After reviewing several remedial operations, *in situ* bioremediation was selected. The conceptual design included stimulating indigenous bacterial populations through the introduction of oxygen and inorganic nutrients. The primary functions of the remediation system included ground-water recovery, treatment, and reinjection; vapor extraction and discharge; stimulation of *in situ* bioremediation by subsurface inorganic nutrient and oxygen additions; and phase-separated hydrocarbon recovery.

Laboratory tests showed that hydrogen peroxide and nutrient loading worked best in sediments from the coarse sand interval. Nutrient injections and the addition of atmospheric oxygen from the vapor extraction system stimulated bioremediation in the unsaturated zone and enhanced the desorption of adsorbed hydrocarbons for recovery in the monitoring wells.

Operation, Monitoring, and Results

Once the bioremediation system was installed, it was inspected weekly to adjust and maintain the water-table depression pump, the hydrogen peroxide and nutrient injection equipment, and the soil vapor extraction system. Crews conducted field analyte tests, sampled ground water, and gauged monitoring wells. The bioremediation system began operating in July 1989 and continued through March 1992.

Approximately 36,000 lb of hydrocarbons have been removed. Nearly 94 percent of the contaminant mass was degraded biologically, as evidenced by the low concentrations of dissolved oxygen and the relatively high concentrations of background heterotrophs and hydrocarbon-utilizing bacteria. Approximately 9 million gal of ground water were recovered, amended with nutrients, and reinfiltrated. The site is currently undergoing closure with the Colorado Department of Health.

Reference

For more information about the Denver site and supporting data, refer to:

Nelson, C.H., R.J. Hicks, and S.D. Andrews. 1994. An integrated system approach for *in situ* bioremediation of petroleum hydrocarbon contaminated soil and ground water. In: Flathman, P.E., D.E. Jerger, and J.H. Exner, eds. Bioremediation: Field experience.

The Role of Intrinsic Bioremediation in Closure of Sites After Cleanup Through In Situ Bioremediation: The Regulator's Perspective

Mark E. Walker and Lisa C. Weers
Colorado Department of Health, Denver, CO

Because staff are assigned such a large number of sites, reviewing all of the hard data for each and every site is not conceptually possible. Therefore, we do not want to receive all of the technical information and correspondence generated at every site; instead, we prefer the technical interpretation. Our approach to site evaluation is to review this interpretation, reserving the right to request any and all hard data generated during the course of the investigation.

Although the technical staff at the Colorado Department of Health (CDH) review an abridged version of the total information generated at a particular site, our version of the file on the Public Service Company of Colorado (PSCo) occupied 6 feet of shelf space. Even a review of the abridged version of this site presented a daunting task.

I needed to get up to speed quickly on the file to consider this site for closure. My first task was to verify if an approved corrective action plan was in place and to determine what conditions had been placed on this approval, if any. In any case where ground-water contamination has been documented, we check to see if the point of compliance (POC) wells have been affected in excess of state maximum contaminant levels (MCL). The second task was to conduct an evaluation of the existing monitoring program to determine if the program was adequate for detecting contamination emanating from the release. Based on the calculated ground-water velocity, was the monitoring period long enough to detect contamination from the source? With respect to monitoring well construction and location, were these wells placed downgradient? (Has direction changed with the seasons?)

After the monitoring plan was completed and the closure borings had been drilled and analyzed, the next topic for examination prior to closure was the extent of the remaining contamination and its potential for adversely affecting the environment. This information is considered with the identified receptors in the immediate vicinity and the potential for these receptors to be affected by the remaining contamination.

After closure is complete, one might ask, "Well, where does this site stand now, from a regulatory point of view?" The following items should be considered: 1) after closure is complete, CDH does not release the owner/operator from any liability regarding the contamination remaining in the subsurface; 2) the closure decision is based solely on the information submitted; 3) similar to the owner's liability issue, the CDH wants to be informed of any developments that could increase the potential for this site to affect human health and the environment adversely, at which point we assess the need for additional work/remediation.

In conclusion, CDH is willing to consider innovative remedial technologies. Those who are proposing such technologies should be prepared to demonstrate that these technologies can be implemented in a manner that does not adversely affect human health and the environment. Proposal of an innovative technology should be approached from the viewpoint of a regulator:

consider receptors and aspects of the technology that might be detrimental to the environment, and address these concerns in a responsible, forthright manner.

The Importance of Knowledge About Intrinsic Bioremediation for Cost-Effective Site Closure: The Client's Perspective

Harry E. Moseley
Public Service Company of Colorado, Denver, CO

Public Service Company of Colorado (PSCo) is Colorado's largest electric and gas utility. During an underground storage tank removal and replacement project in 1987 at PSCo's Seventh Avenue Service Center, a facility used for automotive maintenance, an oil sump was discovered. Because the sump did not have a concrete bottom or other type of platform, the soil beneath the sump was saturated with used oil.

After an extensive study to determine the nature and extent of the contamination beneath the facility, PSCo officials decided that *in situ* bioremediation of the site would be more cost effective than removing the building that housed the center. Construction of a new facility would cost at least $1 million, excluding demolition of the existing facility and removal or remediation of the contaminated soil and ground water. After discussions with the Colorado Department of Health and 18 months of ground-water monitoring, the site received approval for final closure in March 1994, 7 years after discovery of the contamination.

PSCo, a business without extensive expertise in environmental restoration, undertook the project with a fairly direct goal: to remediate the site as efficiently and cost-effectively as possible. Intrinsic bioremediation was found to be a key element of the project's success. In 1988, little was known about intrinsic bioremediation, and some opportunities may have been lost; indeed, additional knowledge of these fields might have reduced costs.

For example, in investigating whether bioremediation was feasible, emphasis was placed on enhancing the activities of the bacteria that would perform the remediation, rather than on determining how long the enhancement could sustain bacterial growth, which might have revealed a more effective strategy for delivering nutrients. Once the nutrients penetrated across the site, batch feeding of the nutrients may have been more effective for the sustained growth of the bacteria than the continuous recirculation of the enriched ground water. If this fact had been considered before the start of the project, operation and maintenance costs incurred during the project's life cycle could have been reduced.

The risk assessment and ground-water data suggested that the chance of any contaminants appearing in any ground water being consumed or used by humans was minimal. The natural ground-water flow across the site was very slow, and the site might have remediated itself with the help of a small amount of oxygen and other nutrients.

To evaluate the progress of the project and to adhere to Underground Injection Control regulations, many tests were required that monitored the concentration of the injected chemicals, or "nutrients"; these tests necessitated costly site visits and report submissions. The chemicals were not injected at harmful levels, however, nor was the risk of human exposure significant due to the location of the injections and the velocity of the ground water. Three years into the project, the reporting requirements were reduced to quarterly, but a better understanding of the bioremediation process would have reduced these requirements earlier.

The bioremediation process came in on budget and successfully removed all threat to human health and the environment (see Table 1).

Table 1. Resources Used at the Seventh Avenue Bioremediation Project

1990	Labor hours	2,024 hours total 168 hours per month average
	Activities	O&M costs Quarterly and monthly reporting
	Testing cost	$12,778
	Materials cost	$16,473
1991	Labor hours	1,746 hours total 145 hours per month average
	Activities	Onsite inspections (once or twice a week) Risk assessment formulation O&M costs Quarterly and monthly reporting
	Testing cost	$13,451
	Materials cost	$12,000
1992	Labor hours	551 hours total 46 hours per month average
	Activities	Quarterly reports Monthly site visits Closure report submittal
	Testing cost	$11,539
1993	Labor hours	94.25 hours total 7.85 hours per month average
	Activities	Closure monitoring
	Testing (quarterly)	$8,420

Information from past projects, sound scientific judgment, and risk analyses will provide an understanding of intrinsic bioremediation that could increase the number of cleanups, speed up the closure process, and reduce testing and reporting requirements, thereby substantially reducing costs to industry.

The Role of Intrinsic Bioremediation in Closure of Sites After Cleanup Through In Situ Bioremediation: The Role of Mathematical Models

Tissa H. Illangasekare and David C. Szlag
Department of Civil, Environmental, and Architectural Engineering,
University of Colorado, Boulder, CO

John T. Wilson
Robert S. Kerr Environmental Research Laboratory,
U.S. Environmental Protection Agency, Ada, OK

Abstract

This paper discusses the important processes in developing mathematical models to be used as tools for the design and evaluation of ground-water remediation schemes in aquifers contaminated with nonaqueous phase organic chemicals. The paper also presents the application of a mathematical model that considers these processes in developing a methodology for retrospective evaluation of bioremediated sites.

Introduction

Mathematical models of water flow and chemical transport have been extensively used in ground-water quantity and quality management. Some of the applications of these models involve bioremediation. The basic processes of flow of water and transport of dissolved substances are fairly well understood, and numerical models for the solution of the governing equations have been developed. Field applications of models as prediction and design tools, however, have not been very successful for many reasons, including the complexities associated with natural heterogeneities and the inadequacy of available field techniques for physical and chemical characterization; this is especially true in ground-water contamination situations involving chemicals in the form of separate phase organics. The models that have been developed to simulate the transport and entrapment behavior of nonaqueous phase chemicals and waste products have not been adequately validated due to the scarcity of laboratory and field data. These models sometimes fail to simulate flow and entrapment behavior under heterogeneous soil conditions that are commonly encountered in the field. Accurate calibration and prediction become difficult due to the limitations of field and laboratory techniques that are used to obtain model parameters. Some of the scaling issues related to multiphase flow model parameters are not very well understood. The assumptions that are made in modeling mass transfer from entrapped chemicals to the aqueous phase become questionable under some conditions of ganglia formation and macroscale entrapment.

The movement of nonaqueous phase liquids (NAPLs) in the subsurface is a complicated process leading to large amounts of NAPLs becoming trapped in the soil. Most of the common organic wastes in the form of NAPLs are only sparingly soluble in water and thus act as long-term sources of ground-water contamination. In a case study presented in this paper, we will show that after bioremediation, pockets of NAPLs remained in the soil. These entrapped fluids have

the potential to contribute to ground-water pollution after active remediation has been discontinued.

In our research, we have identified two modes of entrapment: microscale and macroscale. Microscale entrapment, which occurs at residual levels, is primarily governed by fluid properties and pore characteristics (1). Macroscale entrapment is defined as entrapment at saturations higher than residual (or irreducible) due to heterogeneities in the soil (2).

Many models employed in remediation design make use of the local equilibrium assumption (LEA); in other words, any water exiting a zone of entrapped NAPL will be completely saturated with the contaminant, regardless of the system parameters. The LEA is conservative in predicting the maximum concentration observed in ground water but may lead to gross underprediction of the contaminant source lifetime. It is our hypothesis that entrapment itself will change the system parameters controlling mass transfer into the flowing water, and the LEA assumption is not a physically realistic way to quantify mass transfer.

Laboratory experiments were conducted to obtain a fundamental understanding of the processes that govern the transport and distribution of organic chemicals in soils and to generate data for validation of models that will be used as tools for the design of remediation schemes and monitoring systems. A detailed investigation of these processes under controlled conditions was done in small soil cells, columns, and large flumes.

In our ongoing research, new models and modeling approaches have been developed. To improve these models, we have focused on issues related to entrapment, mobilization, and mass transfer associated with organic waste chemicals in heterogeneous aquifers. The effectiveness of models as tools to design and evaluate treatment and remediation technologies depends on their ability to accurately represent the above processes. A case study conducted in Colorado identifies some of these basic processes that are of importance in remediating and monitoring sites contaminated with organic fluids, and demonstrates the use of a mathematical model.

Study Objectives

Conventional methods for determining the extent of cleanup at a bioremediation site can often be misleading. Monitoring wells may show very low or zero levels of contaminants after active bioremediation, but levels may increase over time. In most cases, regulatory authorities require a direct measure of the residual NAPLs after bioremediation in addition to monitoring well data. Often the relative composition of the oily phase is assumed to remain constant during bioremediation. This is a conservative assumption and generally leads to target levels of total petroleum hydrocarbon (TPH) concentrations on the order of 10 to 100 mg/kg aquifer material. Many bioremediation schemes, however, may preferentially degrade the compounds of regulatory concern, leaving relatively high TPH levels in the soil that pose a minimal risk. This modeling study focuses on developing a methodology to evaluate the possible risk, if any, associated with benzene, toluene, ethylbenzene, and xylene (BTEX) sources left in soils after the implementation of a bioremediation scheme. This developed methodology will assist in providing answers to the following questions: 1) Will BTEX reappear in ground water? 2) How long will it take the plume to reappear? 3) What concentration level may be expected? The results of the case study will also assist in providing a technical basis for implementing monitoring schedules, locating compliance wells, and constructing rational criteria for site closure.

Problem Description

A temporary holding tank under a garage in an industrial area in Denver, Colorado, leaked used crank case oil, diesel fuel, gasoline, and other material into a shallow water table aquifer.

Remediation involved removal of separate oily phases, *in situ* bioremediation with hydrogen peroxide and mineral nutrients, and bioventing. An estimated 2,147 lb of hydrocarbons have been removed by pumping hydrocarbon emulsion from monitoring wells or by volatization through soil aeration. In the treatment system, the ground water pumped from a downgradient recovery well was treated and amended with organic nutrients and hydrogen peroxide. The solution was then injected into the subsurface system upgradient of the contaminated site. The system operated from October 1989 to March 1992. Table 1 compares the reduction in concentration of benzene and total BTEX compounds in ground water achieved by this remediation scheme (3, 4).

Table 1. Reduction in Concentration (μg/L) of Hydrocarbon Contaminants in Ground Water Achieved by *In Situ* Bioremediation

Well	Benzene			Total BTEX		
	Before	During	After	Before	During	After
MW-1	220	<1	<1	2,030	164	<6
MW-8	180	130	16	1,800	331	34
MW-2A	—	11	0.8	—	1,200	13
MW-3	11	5	2	1,200	820	46
RW-1	<1	2	<1	<1	2	<1

Water from the monitoring wells and the recirculation well contained low concentrations of contaminants by March 1992. Active remediation was terminated, and the site entered a period of postremediation monitoring. In June 1992, core samples were taken from the aquifer to determine the extent of hydrocarbon remaining and to determine whether a plume of contamination could return once active remediation ceased. The site was cored along a transect downgradient of the release. The cores were extracted and analyzed for total petroleum hydrocarbons and for the concentration of individual BTEX compounds. Data from one of the boreholes with the highest concentrations of hydrocarbons are given in Table 2. At the time of sampling, the elevation of the water table was 5,280.5 ft above mean sea level (AMSL).

Table 2. Vertical Extent of Total BTEX and TPH (mg/kg) at a Borehole

Elevation (Feet AMSL)	TPH	BTEX	Benzene	Color and Texture
281.14-5,280.31	<44	<1	<0.02	Brown sand
5,280.31-5,279.97	227	5.1	<0.2	Brown sand
5,279.97-5,279.56	860	101	<0.2	Brown sand
5,279.56-5,279.14	1,176	206	4.3	Brown sand
5,279.14-5,278.97	294	27	0.68	Brown sand
5,278.97-5,278.64	273	7.4	0.26	Brown sand
5,278.64-5,278.22	<34	<1	<0.2	Brown sand
5,278.22-5,277.14	<24	<1	<0.2	Brown/yellow sand

To hydraulically characterize the aquifer, selected soil cores that had previously been used to measure hydrocarbon saturations were reconstructed in a load cell, and hydraulic conductivity was determined with a constant flux apparatus. The hydraulic conductivity varied two orders of magnitude across the site, with some highly permeable channels evident.

The results of this field investigation suggest that hydrocarbon in the form of nonaqueous fluids moved into preferential flow channels created by the local heterogeneities. After direct recovery, the fluids remained entrapped at saturations that may be higher than residual. During remediation, the treating agents did not reach some of the locations where the chemicals were entrapped.

A modeling study was conducted at the site to make a retrospective evaluation of the effectiveness of the remediation scheme. The results of this study are reported in Szlag et al. (3).

Model Selection

The following observations at the site and in the laboratory indicated the need for three-dimensional simulation: 1) visual inspection of aquifer material indicated the presence of coarse gravel lenses, clayey sands, and sands of varying gradation; 2) light nonaqueous phase liquid (LNAPL) plumes are inherently three-dimensional, forming thin, pancake-like plumes in the capillary fringe and just beneath the water table; 3) LNAPL can become entrapped in coarse lenses that act as preferential flow channels well beneath the water table; 4) solute plumes are not vertically homogeneous, and biological activity will not be uniformly distributed vertically. Bypassing due to the lowered hydraulic conductivity of the central part of the LNAPL plume by nutrients and electron acceptors resulted in high TPH and BTEX levels in some cores. Coupled with the clear need for a three-dimensional model are other criteria such as availability, ease of use, reliability, and cost. We have selected MODFLOW, a three-dimensional ground-water flow model developed by the U.S. Geological Survey (USGS), to simulate ground-water flow. Solute transport is simulated with a three-dimensional random walk called RAND3D.

Modeling Approach

The problem domain was modeled as a rectangular area 300 ft long and 200 ft wide. Two wells outside of the modeled domain were used as reference head locations for general head boundaries. The NAPL contaminant zone covers approximately 1,600 ft^2 of area and a soil depth of approximately 1.7 ft. To accurately assess the mass flux from the LNAPL contaminant source, three layers were chosen in the model. The upper two layers are 1 ft thick, and the bottom layer is 18 ft thick. The LNAPL organic contaminant is confined to the upper two layers.

Data for the period June 8, 1989, to April 1, 1990, were used for calibration. The goodness of fit between the model and measured well data was characterized by a mean residual and standard deviation of the mean residual. The best fit model was obtained by assigning the pump test average hydraulic conductivity to the bottom layer, which carried the majority of water.

The main focus of this modeling effort is to determine how much contaminant mass will be transported from the remaining residual and whether it will generate a plume of regulatory concern. A monitoring well screened in only the upper two layers would see the highest contaminant concentrations. A pumping well screened over the entire aquifer thickness is also being considered; in this case, however, dilution will play a major role in reducing the maximum concentrations. Two significant assumptions are used in the solute transport modeling: 1) the concentration of BTEX in the source zone remains constant, and 2) water flowing from the contaminated cells is in equilibrium with the residual NAPL. Using the heads generated by MODFLOW, ground-water velocity through each source cell was calculated. The known NAPL BTEX concentration was then used to calculate the equilibrium concentration and, consequently, the mass flux. Estimated benzene mass fluxes were converted into particle inputs for each layer. The particle tracking model was used to simulate solute transport using the velocity field generated from MODFLOW.

Results and Discussion

Any simulation of solute transport requires specification of the contaminant source. For the case of a NAPL spill, the source function will consist of a continuous mass flux of solute from the residual NAPL phase to the aqueous phase. Many researchers have shown that equilibrium is quickly reached in spill scenarios if ground-water velocity is low and the "residence time" of the water in contact with NAPL is "long enough." From a regulatory standpoint, the assumption of equilibrium is conservative, as greater mass fluxes cannot be achieved. The water flux can vary significantly in the source zone, which often gives misleading indications that the contaminant transport is rate-limited. This primary problem has been the focus of our work. Preferential flow paths often develop within the source zone in areas with low BTEX and TPH concentrations, allowing water flow to bypass the more highly contaminated areas. Laboratory determination of the hydraulic conductivity in the samples containing high amounts of TPH confirms this observation.

A key result of the modeling study is that the solute plume emanating from a NAPL source is not homogeneous. In general, the solute plume will consist of subplumes at different depth intervals and widely different concentrations, and moving at different velocities. A regulatory question posed earlier in this paper is, "How long should the compliance wells be monitored?" The answer is when all the subplumes have reached steady-state. The plumes in the middle and

bottom layer have reached or are close to equilibrium by 330 days. The plume in the top layer, which has the highest benzene concentration, has not reached equilibrium at 420 days.

The design of the compliance wells will have tremendous impact on the actual sampled concentration. If the wells are bailed or pumped so that the well volume is completely mixed, significant dilution will occur. The existing monitoring wells at the site are screened over the top 5 ft of the aquifer. The maximum concentration achieved in the well screened over a 5-ft interval reaches a steady-state concentration of 26 ppb. If that well is screened over the entire saturated thickness, a concentration of 15 ppb is achieved. Even greater dilution will occur if the well is pumped.

Several operational considerations for risk assessment and compliance well monitoring can be made from the modeling study: 1) a benzene plume will reestablish itself at the site, but it will be three orders of magnitude lower than the federal maximum contaminant level—new standards may be set, however, and the risk from this plume may be deemed significant; 2) local hydraulic conductivity plays a significant role in determining the contaminant mass flux and in creating subplumes of different concentration and velocity; 3) compliance well monitoring will have to be continued past August 1993 so that solute plumes in all levels will reach steady-state; 4) retardation coefficients and effective porosity data would significantly improve the time of arrival estimate of the solute plume; 5) compliance well design should be carefully considered when sampling a three-dimensional plume because well design can lead to significant contaminant dilution.

Conclusions

A modeling methodology for the retrospective evaluation of bioremediated aquifers contaminated with organic chemicals was developed. The primary hypothesis on which the methodology was based is that during a spill, NAPL contaminant becomes entrapped preferentially in coarse formations in the saturated zone and fine formations in the unsaturated zone. This hypothesis is supported by laboratory experimental (2) and field data. Flow channels created by naturally occurring aquifer soil heterogeneities as well as macroscale entrapment of the NAPL will also produce preferential paths for the treating agents. The proposed methodology requires that these local heterogeneities in the contaminant zone of the spill be captured. Standard pump tests, which provide regional values for transmissivity, will not have adequate resolution to capture these spill-site-scale heterogeneities. Even though hydraulic conductivity values determined in the laboratory on disturbed soil samples were used in this study, a more appropriate characterization method would be well-designed bail tests (or slug tests) that capture the local layered heterogeneities more accurately. These local hydraulic conductivity values allow us to obtain the velocity field in the contaminant zone and to subsequently determine the contaminant mass flux. Solute breakthrough curves determined by this method can then be used to conduct risk analysis and to provide a rational basis for postremediation well monitoring.

References

1. Szlag, D., and T.H. Illangasekare. 1994. Quantification of residual entrapment of nonaqueous phase organic fluids in soils. Ground Water. In review.

2. Illangasekare, T.H., D. Szlag, J. Campbell, J. Ramsey, M. Al-Sherida, and D.D. Reible. 1991. Effect of heterogeneities and preferential flow on distribution and recovery of oily wastes in aquifers. Proceedings of the Conference on Hazardous Waste Research, Manhattan, KS. Manhattan, KS: Kansas State University.

3. Szlag, D.C., T.H. Illangasekare, and J.T. Wilson. 1993. Use of a three-dimensional ground-water model for retrospective evaluation of a bioremediated aquifer contaminated with organic chemicals. Proceedings of the Ground-Water Modeling Conference, Golden, CO (June 10).

4. Wilson, J. 1993. Retrospective performance evaluation on *in situ* bioremediation: Site characterization. In: U.S. EPA. Symposium on bioremediation of hazardous wastes: Research, development, and field evaluations (abstracts). EPA/600/R-93/054. Washington, DC (May).

Acknowledgments

The support of the U.S. Environmental Protection Agency through the Hazardous Substance Research Center at Kansas State University (agreement R-815709) is gratefully acknowledged. We would also like to thank Ms. Lisa Weers of the Colorado Department of Health for her assistance.

Intrinsic Bioremediation of JP-4 Jet Fuel

John T. Wilson, Fredrick M. Pfeffer, James W. Weaver, and Don H. Kampbell
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK

Todd H. Wiedemeier
Engineering Science, Denver, CO

Jerry E. Hansen and Ross N. Miller
Air Force Center for Environmental Excellence, Brooks AFB, TX

Introduction

Intrinsic bioremediation is a risk management option that relies on natural biological processes to contain the spread of contamination from spills. The option is most appropriate when the concentration of contaminants is reduced to regulatory limits before ground water discharges to surface water or is collected by a pumped well.

In the past, remedial action plans have proposed the intrinsic remediation option based solely on the apparent attenuation of contamination in water from monitoring wells that are distant from the spill. These plans were often criticized because it was impossible to distinguish attenuation due to contaminant destruction from attenuation due to simple dilution in the aquifer or in the monitoring well. Convincing regulators that the wells with low concentrations of contaminants actually sample the plume of contaminated ground water has been difficult. This lack of credibility has led to the "one-more-well" syndrome, with excessive investment in a monitoring approach that focuses on the compounds of regulatory concern but fails to earn the confidence of the regulatory community.

During characterization of JP-4 jet fuel spills at Eglin Air Force Base (AFB), Florida, and Hill AFB, Utah, three approaches were used to distinguish contaminant attenuation due to destruction from attenuation due to dilution or sorption.

To distinguish attenuation due to biological destruction of the contaminants from attenuation due to dilution, the attenuation of the compounds of regulatory concern—benzene, toluene, ethylbenzene, and the xylenes (BTEX)—was compared with the attenuation of other components of the fuel that were relatively recalcitrant. Tracers have been used successfully to correct for dilution and sorption of hydrocarbons in ground water. Cozzarelli et al. (1) used 1,2,3,4-tetramethylbenzene to normalize the concentrations of other alkylbenzenes and their anaerobic degradation products in ground water that had been contaminated by a spill of light crude oil. Wilson et al. (2) used 2,3-dimethylpentane to normalize the concentrations of BTEX compounds in ground water contaminated with gasoline from an underground storage tank. In both cases, the tracer was a component of the spilled fuel.

To distinguish attenuation due to biological destruction from attenuation due to sorption, core samples were analyzed for the total quantity of individual BTEX compounds and for total petroleum hydrocarbons. Partitioning theory was used to predict the concentration of individual

hydrocarbons in ground water in contact with the core material. The predicted concentrations were compared with concentrations in water from monitoring wells to determine if the ground water in the plume was in sorptive equilibrium with the spilled fuel.

To prove that the attenuation was due to biological activity, the geochemistry of the ground water was examined. Microbial metabolism of petroleum hydrocarbons has predictablegeochemical consequences. The hydrocarbons can be respired, resulting in the consumption of oxygen, nitrate, sulfate, or iron II minerals in the aquifer matrix and in the production of water, dinitrogen, sulfide, or iron II. Microbiologist often refer to the substrates for microbial respiration as electron acceptors. Alkylbenzenes can be fermented, resulting in the production of methane. Simple stoichiometry can be used to predict the quantity of electron acceptors consumed or the quantity of methane produced during biotransformation of a given concentration of petroleum-derived hydrocarbons.

Intrinsic Bioremediation of Ground Water at Eglin AFB, Florida

Leaking distribution pipes from an underground storage tank released JP-4 jet fuel to the water table aquifer under the petroleum, oil, and lubricants storage depot (POL) at Eglin AFB. The POL is located over sands and silty peats characteristic of a barrier island complex. At the time of the study, a plume of contaminated ground water moved away from the residual JP-4 and discharged to a small creek approximately 300 ft downgradient (Figure 1). The elevation of the water table is approximately 8.4 ft above sea level in the area with residual JP-4. The water table in the creek is 1.4 ft above mean sea level. Hydraulic conductivity determined by pumping tests in monitoring wells varied from 48 ft to 102 ft per day. Based on these data, and assuming an effective porosity of 30 percent, the residence time along the flow path from the spill to the creek is on the order of 10 wk. Water samples were acquired with a geoprobe, using an 18-in. screen. Seasonally, the temperature of ground water at the site varies from 19°C to 28°C, and the pH varies from 5.6 to 6.7. Samples producing the data in Table 1 were taken in August 1993, when ground-water temperatures varied from 24°C to 28°C.

Correcting for Dilution at Eglin AFB

Table 1 presents the changes in concentrations of BTEX compounds and the three trimethylbenzenes (TMB) along the flow path from the spill to the creek (Figures 1 and 2). Sample 80H-3 is from a location just outside the JP-4 spill and appears to be in chemical equilibrium with the weathered residual fuel. Samples 83H-1 and 83Z-2 are from locations approximately 150 ft and 300 ft downgradient from the spill. Samples 83U-2 and 83U-3 were taken 0.5 ft and 4.1 ft below the sediments of the creek receiving discharge from the plume. Sample 83U-1 is water from the creek at the sediment boundary, taken when the tide was going out and the plume was actively discharging to the creek.

When trimethylbenzene concentrations in samples 80H-3 and 83U-3 were compared, the reduction in the concentration of these compounds was found to be remarkably uniform. Concentrations under the creek were 36, 27, and 46 percent of the concentrations near the spill, while the concentrations of toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene were 0.02, 0.08, 0.44, 0.20, and less than 0.02 percent of the initial concentrations.

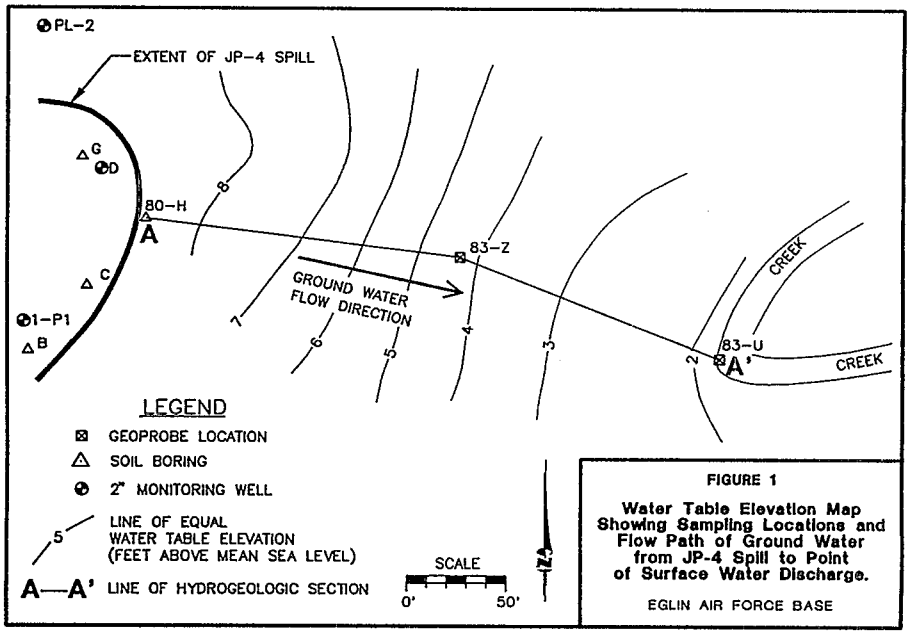


Figure 1. Flow path of ground water from a JP-4 spill at Eglin AFB to the point of discharge to surface water: plan view.

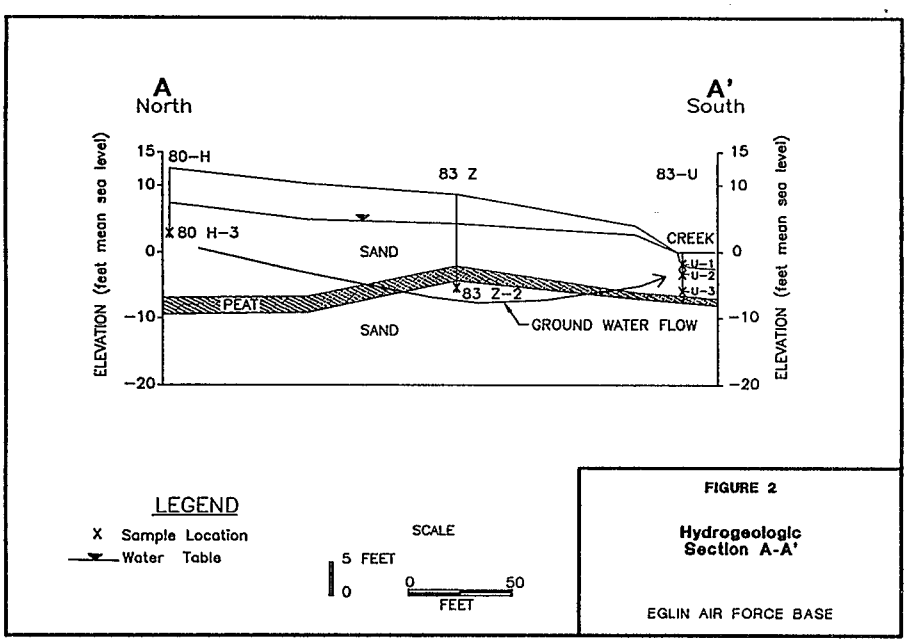


Figure 2. Flow path of ground water from a JP-4 spill at Eglin AFB to the point of discharge to surface water: cross section.

Table 1. Bioattenuation in Methanogenic Ground Water: Changes in Ground-Water Chemistry Along a Flow Path From a JP-4 Spill to the Point of Discharge to Surface Water

	Location Along Flow Path to Surface Water				
Compound	80H-3	83Z-2	83U-3	83U-2	83U-1
			(μg/L)		
Benzene	100	153	198	6.9	<1
Toluene	5,150	18.3	1.1	<1	<1
Ethylbenzene	1,700	227	1.4	1.4	<1
p-Xylene	3,120	594	13.8	25.1	<1
m-Xylene	6,750	1,270	13.5	39.8	<1
o-Xylene	5,480	<1	<1	<1	<1
1,3,5-TMB	327	114	70.9	119	2.3
1,2,4-TMB	1,090	420	172	299	<1
1,2,3-TMB	406	182	115	187	<1
			(mg/L)		
BTEX and TMB	24.1	2.97	0.59	0.68	0.002
Oxygen	0.4	0.2	0.3	0.6	3.8
Nitrate + Nitrite - N	0.14	0.12	<0.05	<0.05	<0.05
Sulfate	1.6	0.62	5.6	1.76	<0.5
Methane	3.7	16.8	12.5	14.2	0.7
Iron II	2.3	7.8	3.3	2.8	<0.5

Apparently, concentrations were reduced from one-half to one-fourth of the initial concentration due to dilution, with further reductions due to biological activity. Benzene was not degraded in the anaerobic portion of the flow path.

As the plume moved up into the sediments of the creek, the concentration of benzene was reduced more than 20-fold (compare 83U-2 with 83U-3 in Table 1). If we assume that the trimethylbenzenes are recalcitrant, the dilution of 1,2,4-trimethylbenzene can be used to correct for the dilution of benzene and determine the true removal due to biodegradation. The corrected concentration of a biologically transformed compound in a downgradient well would be the measured concentration in the downgradient well, multiplied by the measured concentration of 1,2,4-trimethylbenzene in the upgradient well, and divided by the measured concentration of 1,2,4-trimethylbenzene in the downgradient well.

The concentration of benzene measured in sample 83U-2 was 6.9 μg/L. Compared with sample 83Z-2, the concentration corrected for dilution would be 9.7 μg/L. Compared with 153 μg/L in 83Z-2, there was a 15-fold attenuation in benzene concentration between 83Z-2 and 83U-2. The benzene attenuation at 83U-2 compared with 83U-3 would be 50-fold.

The concentration of oxygen in the sample 83U-2, taken 0.5 ft below the sediment surface, was higher than the concentration in sample 83U-3, taken 4.5 ft below the sediment surface. Tidal action may reverse the hydraulic gradient in the area proximate to the creek. This would produce a reciprocating flow of oxygenated creek water into the sediments and mix oxygen into the contaminated ground water. Benzene may have been degraded aerobically. In any case, benzene and the other BTEX compounds did not discharge to the stream at detectable concentrations (see sample 83U-1).

Kinetics of Bioattenuation in Ground Water at Eglin AFB

First-order rate constants were calculated by correcting the downgradient concentration for dilution. The rate constants were calculated as:

$$\text{Rate} = \frac{\ln(\text{corrected conc. downgradient}/\text{conc. upgradient})}{\text{residence time}}$$

Based on this relationship, rates were calculated for flow path segments from samples 80H-3 to 83Z-2 and 83Z-2 to 83U-3. The residence time in each segment was assumed to be 5 wk.

The rates of anaerobic bioattenuation (Table 2) were some of the fastest that have ever been encountered by staff of the Robert S. Kerr Environmental Research Laboratory, probably due to the high water temperatures. There seemed to be preferential removal of toluene and o-xylene in the segment close to the spill. Rates of removal of ethylbenzene and m+p-xylene increased after toluene and o-xylene were depleted.

Table 2. First-Order Rate Constants for Bioattenuation of BTEX Compounds in a Plume of Ground Water Contaminated by JP-4

Compound	80H-3 to 83Z-2	83Z-2 to 83U-3
	(per week)	
Benzene	None	None
Toluene	-0.94	-0.38
Ethylbenzene	-0.21	-0.38
p-Xylene	-0.14	-0.57
m-Xylene	-0.14	-0.73
o-Xylene	-1.5	Cannot calculate

Stoichiometry of Bioattenuation at Eglin AFB

There was very little oxygen, nitrate, or sulfate available for respiration of the BTEX compounds in the plume of contaminated ground water (see Table 1). There was an increase in the concentration of methane and iron and a corresponding decrease in aromatic fuel hydrocarbons along the flow path, however. Assuming the following stoichiometry for methanogenesis from BTEX compounds,

$$2\ CH + 3/2\ H_2O \rightarrow 5/4\ CH_4 + 3/4\ CO_2,$$

approximately 1.0 mg of methane is produced for each 1.3 mg of BTEX destroyed. If 80H-3 and 83Z-2 are compared, the concentration of methane at 83Z-2, corrected for dilution, would be 43.5 mg/L. The increase in methane from 80H-3 to 83Z-2 would be 39.8 mg/L. Corrected for dilution, the concentration of BTEX plus TMB in 83Z-2 is 7.69 mg/L, a decrease of 16.4 mg/L compared with 80H-3. This decrease in aromatic petroleum-derived hydrocarbons would be expected to produce 12.6 mg/L of methane. Some of the methane sampled at 83Z-2 may have come from the natural degradation of the peat. In any case, the accumulation of methane is sufficient to rationalize the destruction of the aromatic fuel hydrocarbons along the flow path.

Intrinsic Bioremediation of Ground Water at Hill AFB, Utah

Hill AFB is situated on a bird's foot delta formed by the Weber River in Pleistocene Lake Bonneville. Leaking distribution pipes from an underground storage tank released JP-4 jet fuel to the water table aquifer under the POL. An area with oily phase JP-4 extends approximately 1,000 ft downgradient of the spill (Figure 3). The oily phase hydrocarbons and the plume of contaminated ground water are confined to the channel sands of the delta deposits (Figure 4). The elevation of the water table drops 56 ft across the length of the spill. Slug testing of monitoring wells indicates a hydraulic conductivity near 8.5 ft per day, corresponding to an interstitial seepage velocity of 1.6 ft per day.

Continuous cores were taken near the source of the spill (82I in Table 3), near the midpoint (82D), at the lower edge of the spill (82C), and just beyond the edge of the spill (82B). The continuous cores started in clean material above the spill and extended through the spill into clean material underneath the interval containing hydrocarbon. The continuous cores were subdivided into core samples representing 0.3 vertical ft of the subsurface. Near the spill, JP-4 appeared in the capillary fringe (Table 3). The concentration maximum of 14,800 mg/kg was located 0.5 ft above the water table. A second interval that contained JP-4 extended from 3.8 to 5.2 ft below the water table, with TPH concentrations that ranged from 1,290 to 3,830 mg/L. At the midpoint of the spill (82D), only one core sample contained significant concentrations of hydrocarbons. That core sample came from 1.0 ft below the water table. At the lower edge, two core samples representing 0.6 vertical ft had significant concentrations of hydrocarbons. Again these core samples were at or just below the water table. At the midpoint and lower edge of the spill, hydrocarbons were not detected in core material collected above or below the samples reported in Table 3 (detection limit 10 mg/kg). Concentrations of hydrocarbons in the midpoint and lower edge of the spill were less than 700 mg/kg.

Monitoring wells were installed in the boreholes used to acquire the core samples. Additional monitoring wells were installed downgradient of the lower edge of the spill.

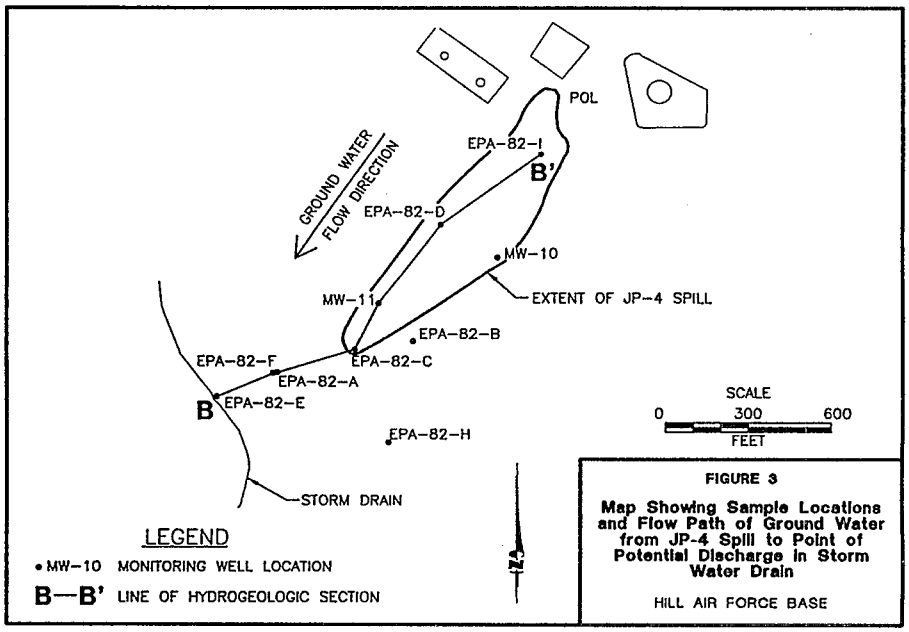


Figure 3. Flow path of ground water through a JP-4 spill at Hill AFB to the point of discharge in a storm drain: plan view.

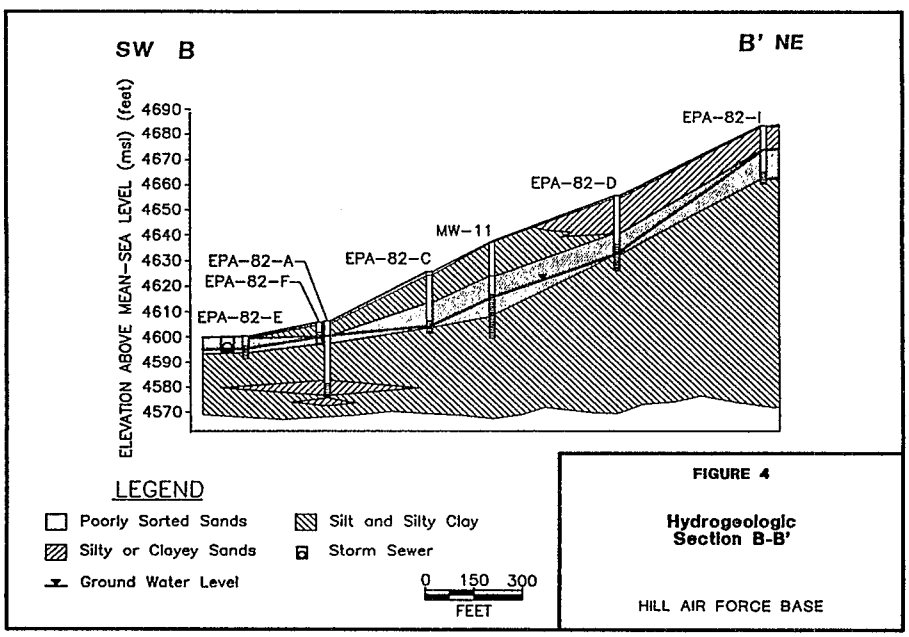


Figure 4. Flow path of ground water from a JP-4 spill at Eglin AFB to the point of discharge in a storm drain: cross section.

Table 3. Vertical Distribution of Oily Phase Hydrocarbons at Hill AFB

Core	Elevation	TPH	Benzene	Toluene	Ethyl-benzene	1,2,4-TMB
	(ft)	(mg/kg)				
82I, near the spill area, water table elevation 4,664.53 ft						
82I-5	4,665.7	4,330	0.0326	0.0266	14.5	49.9
82I-4	4,665.4	3,770	0.517	0.235	4.8	42.7
82I-3	4,665.0	14,800	4.55	2.73	47.7	167
82I-2	4,664.6	5,870	0.401	12.6	17.5	69.8
82I-1	4,664.3	398	<0.01	0.142	0.556	4.43
82I-27 to 82I-19	4,663.9 to 4,661.0	<300				
82I-17	4,660.7	1,290	0.653	0.591	3.39	2.34
82I-37	4,659.3	1,370	0.712	0.182	2.72	5.38
82I-32	4,659.0	3,830	0.0136	0.032	1.24	8.37
82D, downgradient of spill, water table elevation 4,631.7 ft						
82D-24	4,631.0	77.1				
82D-23	4,630.7	572.0	0.271	<0.01	1.48	3.11
82C, lower end of spill, water table elevation 4,603.4 ft						
82C-20	4,603.5	593.0	<0.01	0.0176	0.00618	1.03
82C-19	4,603.2	638.0	0.0062	<0.01	0.0180	1.16
82B, below the oil spill, water table elevation 4,608.3 ft						
82B-20	4,608.0	0.7	<0.01	<0.01	<0.01	<0.01
82B-19	4,607.7	1.0	<0.01	<0.01	<0.01	<0.01

Correcting for Dilution at Hill AFB

The TMBs were remarkably persistent in ground water from the area containing oily phase hydrocarbons (Table 4). Concentrations of the TMBs in water from the lower edge of the spill varied from 50 percent to 147 percent of the concentration at the source, while the concentrations of benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene were reduced to 0.02, 0.9, 5.6, 5.5, 3.4, and 0.23 percent of the initial concentration. The saturated thickness of the channel sands was at most a few feet, and, therefore, there was little opportunity

for dispersive dilution of the contaminated ground water into clean ground water underneath the plume. Once the ground water moved past the spill, it was remediated rapidly. Concentrations of all the aromatic hydrocarbons are low in well 82B just past the lower edge of the spill.

Table 4. Changes in Ground-Water Chemistry Along a Flow Path Through a JP-4 Spill Undergoing Sulfate Reduction

	Location Along Flow Path to Surface Water				
Compound	82I	MW-11	82D	82C	82B
	(μg/L)				
Benzene	2,740	336	96	4.9	<1
Toluene	327	90	10	3.1	4.3
Ethylbenzene	486	139	147	27	<1
p-Xylene	784	230	149	43	<1
m-Xylene	1,370	635	383	47	<1
o-Xylene	1,140	204	103	2.6	<1
1,3,5-TMB	162	71	129	238	1.1
1,2,4-TMB	495	165	183	324	1.4
1,2,3-TMB	240	69	89	120	<1
	(mg/L)				
BTEX and TMB	7.7	2.1	1.3	2.1	0.001
Oxygen		0.1	1.3	0.5	1.2
Nitrate + Nitrite - N		0.4	0.5	0.1	0.4
Sulfate		98	193	50	64
Methane	0.68	0.022	<0.001	0.002	<0.001
Iron II		0.05	1.7	0.84	0.11

Stoichiometry of Bioattenuation at Hill AFB

Similar to the plume at Eglin AFB, neither oxygen nor nitrate is available for respiration of the BTEX compounds within the spill area (Table 4). Oxygen concentrations as high as 8.0 mg/L occur outside the spill. Unlike the case at Eglin, there was little accumulation of iron II and

practically no methane production in the spill. Sulfate concentrations were high throughout the spill. Assuming the following stoichiometry,

$$8\ CH + 5\ SO_{4-2} \rightarrow 5\ S^{-2} + 8\ CO_2 + 4\ H_2O,$$

4.6 mg of sulfate would be required to degrade 1.0 mg of BTEX and TMB. The 7.7 mg/L of BTEX and TMB present at the source would have a total theoretical demand of 35 mg/L of sulfate. Concentrations in excess of the theoretical demand remain in the water after it has moved away from the spill. There is an adequate supply of sulfate to remediate the plume through sulfate reduction alone.

Concentrations of sulfate were higher in ground water near the source. It is possible that the lower concentrations of sulfate near the lower edge of the spill represent the sulfate demand exerted. It is just as possible that they represent natural variations in sulfate concentrations.

Hydrogen sulfide did not accumulate in ground water undergoing intrinsic remediation at Hill AFB. Unimpacted sediments at the site are tan or brown colored, while contaminated samples are black. Iron minerals in the aquifer matrix must act to precipitate sulfide. Sulfide very likely precipitated as iron II sulfide.

The concentrations of electron acceptors were compared in ground water at various distances from the lower edge of the spill. Well 82B is just outside the lower edge; wells 82F, 82H, and 82E are 300, 400, and 500 ft downgradient of the spill. These wells are screened in the water-table aquifer (Figure 4); well 82A is adjacent to 82F but is screened in the first confined aquifer underneath the water table aquifer.

None of the wells outside the spill had significant concentrations of aromatic hydrocarbons (Table 5). Water adjacent to the spill (82B) was depleted in oxygen and nitrate.

Intrinsic Bioremediation of Oily Phase JP-4 Jet Fuel at Hill AFB

Two samples of floating oil from monitoring well MW-10, near the midpoint of the spill, were analyzed by gas chromatography/mass spectrometry (GC/MS) to determine the number-average mean molecular weight of the weathered fuel. Values of 156 and 160 daltons were determined on duplicate samples.

The concentration of individual hydrocarbons in ground water in contact with oily phase JP-4 was estimated using Raoult's Law. With data from Table 3, the concentration of an individual petroleum hydrocarbon (mg/kg) was divided by its molecular weight to express its concentration in moles/kg core material. The concentration of total petroleum hydrocarbons (TPHs) was divided by 160 to express TPH in moles/kg core material. The mole fraction of the individual hydrocarbon was calculated by dividing moles of individual hydrocarbon per kilogram by moles of TPH per kilogram. Then the mole fraction was multiplied by the water solubility of the individual petroleum hydrocarbons to estimate the equilibrium concentration in ground water.

Table 5. Changes in Ground-Water Chemistry Along a Flow Path Downgradient of a JP-4 Spill

	Location Along Flow Path to Surface Water				
Compound	82B	82F	82E	82H	82A
	(μg/L)				
BTEX	<1	<1	<1	<1	<1
TMB	<1	<1	<1	0.9	2.0
	(mg/L)				
Oxygen	1.2	1.1	2.7	5.4	0.3
Nitrate + Nitrite - N	0.4	5.1	5.6	2.0	0.1
Sulfate	72.2	55.5	65.8	55.7	60.5
Methane	<0.001	0.006	<0.001	<0.001	0.001
Iron II	0.11	0.04	0.02	0.19	0.1

Concentrations of individual petroleum hydrocarbons in water from monitoring well 82I, near the source of the spill, were in reasonable agreement with the concentrations predicted from the cores that had the highest TPH values (see cores 82I-3, 82I-17, and 82I-37 in Table 6 and Table 3). The JP-4 in the capillary fringe appeared to be aerobically weathered. There was extensive removal of benzene and toluene in the more shallow cores 82I-5 and 82I-4, while ethylbenzene and 1,2,4-TMB were not removed.

Concentrations in water from the well at the midpoint of the spill (82D) were considerably lower than concentrations predicted from the core material. Oily-phase material at this location could not remove individual hydrocarbons from ground water through partitioning processes.

Core material at the lower edge of the oil spill (82C) was very highly weathered with respect to benzene, toluene, and ethylbenzene, while weathering of 1,2,4-TMB was less extensive. When core 82I-37 near the source and 82C-19 at the lower edge were compared, the mole fraction of benzene was reduced by a factor of 53, while the mole fraction of 1,2,4-TMB was reduced by a factor of 2.2. When concentrations in monitoring well 82I near the source and 82C near the lower edge were compared, the concentration of benzene was reduced by a factor of 560 while the concentration of 1,2,4-TMB was reduced by a factor of 1.5.

Within an order of magnitude, the concentrations in ground water were in equilibrium with the mole fraction in the oily phase. Concentrations predicted for ground water were higher than measured concentrations, indicating that sorption or partitioning could not be responsible for removal of the individual hydrocarbons from ground water.

Table 6. Comparison of the Concentration of Benzene, Toluene, and Ethylbenzene Measured in Ground Water to the Concentration Predicted Using Partitioning Theory From the Mole Fraction of Those Compounds in Extracts of Core Material

Core	Elevation	Benzene	Toluene	Ethyl-benzene	1,2,4-TMB
	(ft)	Measured Concentration (μg/L)* Predicted Concentration (μg/L)			
82I, near the spill area, water table elevation 4,664.53 ft					
11/93		**2,740***	**372***	**486***	**495***
82I-5	4,665.7	22.8	5.5	769	900
82I-4	4,665.4	513	55.6	289	884
82I-3	4,665.0	1,150	165	740	881
82I-2	4,664.6	254	1,923	684	929
82I-1	4,664.3	103	320	321	869
82I-27 to 82I-19	4,663.9 to 4,661.0	<300			
82I-17	4,660.7	1,870	410	603	135
82I-37	4,659.3	1,940	119	456	307
82I-32	4,659.0	13.2	7.5	74.3	171
82D, downgradient of spill, water table elevation 4,631.7 ft					
7/93	4,631.7	**96***	**10***	**147***	**183***
11/93	4,631.7	**174***	**4.6***	**30.8**	**119***
82D-23	4,630.7	1,769	15.6	594	460
82C, lower end of spill, water table elevation 4,603.4 ft					
7/93	4,603.4	**4.9***	**3.2***	**27***	**324***
11/93	4,603.0	**<1***	**8.4***	**6.8***	**68.9***
82C-20	4,603.5	<63	26.6	2.4	135
82C-19	4,603.2	36.3	13.9	6.5	142

Kinetics of Bioattenuation at Hill AFB

There is no straightforward approach to calculate the kinetics of bioattenuation in ground water in contact with oily-phase material. For the ground-water plume at Eglin AFB, the distance between wells along a flow path and the estimated interstitial seepage velocity of ground water was used to estimate residence time of the contaminants. At Hill AFB, the contaminated ground water is in contact with oily-phase material. The major fraction of individual contaminant hydrocarbons in the aquifer is partitioned to the oily phase, which is moving slowly if it is moving at all. Travel time of ground water is not related to residence time of contaminants, making it impossible to determine the kinetics of attenuation from data at different locations collected at the same time. Kinetics must be inferred from long-term monitoring data, which are not available at the present time.

If we assume that the spill started 30 years ago, that the JP-4 at the lower edge was the first oil spilled, and that the mole fraction of benzene in JP-4 used at Hill AFB has not changed appreciably over time, a comparison of the mole fraction of benzene in 83I-3 near the source and 83C-19 near the lower edge of the spill indicates a reduction in the mole fraction of benzene to 3 percent of the original concentration. If kinetics are first order on time, the rate would be -0.11/year.

References

1. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground-water environment. Environ. Geol. Water Sci. 16(2):135-141.

2. Wilson, J.T., D.H. Kampbell, and J. Armstrong. 1994. Natural bioreclamation of alkylbenzenes (BTEX) from a gasoline spill in methanogenic ground water. In: R.E. Hinchee, B.C. Alleman, R.E. Hoeppel, and R.N. Miller, eds. Hydrocarbon bioremediation. Ann Arbor, MI: Lewis Publishers.

A Natural Gradient Tracer Experiment in a Heterogeneous Aquifer With Measured In Situ Biodegradation Rates: A Case for Natural Attenuation

Thomas B. Stauffer and Christopher P. Antworth
Armstrong Laboratory, Tyndall AFB, FL

J. Mark Boggs
Engineering Laboratory, Tennessee Valley Laboratory, Norris, TN

William G. MacIntyre
School of Marine Science, College of William and Mary, Gloucester Point, VA

Biodegradation rates of organic compounds have been measured in a heterogeneous unconfined aquifer at Columbus Air Force Base (AFB), Columbus, Mississippi, during a pulse release experiment. Reaction rate calculations were based on a kinetic model that includes the hydrologic characteristics of the aquifer. Degradation kinetics were approximately first order with the following rate constants: benzene, 0.0066 d^{-1}; p-xylene, 0.0141 d^{-1}; naphthalene, 0.0063 d^{-1}; o-dichlorobenzene, 0.0059 d^{-1}.

Introduction

Biodegradation rates of organic contaminants in aquifers are needed for use in fate and transport models. Field experiments for determination of *in situ* biodegradation rates are desirable because laboratory measurements may not relate to conditions in an aquifer. Madsen (1) notes in a recent review "that determination of microbial activity in disturbed, displaced environmental samples incubated in the laboratory is likely to be quantitatively, even qualitatively different from the same determination *in situ*." Reliable estimation of an *in situ* biodegradation rate requires introduction of a known mass of contaminant at a defined time zero, and observation of contaminant concentration variation in space and time. Confirmation of biodegradation requires maintenance of mass balances and determination of organic compound degradation products. To our knowledge, no experiments to accurately measure biodegradation rates and confirm biodegradation in an aquifer are found in the literature.

The objective of this research was to measure *in situ* biodegradation rates of organic compounds. Accordingly, an experimental pulse injection of tritiated water and organic solutes has been conducted at Columbus AFB at the macrodispersion experiment (MADE) site. The injection was into the saturated zone of the heterogeneous unconfined aquifer formed by fluvial sedimentation. Kinetics of *in situ* biodegradation of benzene, p-xylene, naphthalene, and o-dichlorobenzene in the Columbus aquifer are reported here and related to the structural and hydrologic properties of the aquifer. The Columbus aquifer material has a wide range of particle sizes and large spatial variation in horizontal hydraulic conductivity (K_h), from $<10^{-4}$ to 1 cm/s. The heterogeneity is in contrast to the generally lower (10^{-4} to 10^{-3} cm/s) values and less variable K_h field at the Borden Canadian Forces Base, Ontario (2).

A summary of hydrogeologic properties of the Columbus aquifer and a description of the MADE site are given by Boggs et al. (3). Rehfeldt et al. (4) measured the spatial distribution of hydraulic

conductivity at the MADE site using borehole flow meters and other techniques. Figure 1 shows the K_h distribution over a vertical section directed along the test plume axis, and indicates large-scale heterogeneity and structures that Rehfeldt et al. (4) refer to as channels. Close to the injection wells K_h is relatively low, with values near 10^{-3} cm/s from the phreatic surface to the lower confining layer and extending about 40 m downgradient from the injection location. Immediately beyond this region, K_h increases to values near 10^{-1} cm/s in the upper 3 m of the aquifer, which are maintained out to 200 m, while K_h in the lower portion of the aquifer remains low. Thus, a near surface channel crosses the intermediate and far field at the site. These observations suggest that solute transport and distribution might be analogous to the behavior of a hypothetical leaking reactor located at the injection wells, with the near field region of the aquifer representing the reactor vessel and the upper portion of the far field serving as the leak. A leaky reactor kinetic model including radioactive decay and biodegradation was developed for use with field data to obtain *in situ* biodegradation rates for organic compounds in the Columbus aquifer. Radiocarbon measurements using ^{14}C-labeled p-xylene were done to confirm biodegradation of p-xylene to its degradation products.

Experimental Methods

The experiment (MADE2) is generally similar in design to the Borden site test described by Mackay et al. (5). A 2-day pulse injection of water containing ^3H_2O and organic solutes was begun on June 26, 1990. Injection wells were closely spaced on a line normal to the flow direction at locations given in Boggs et al. (3). The intersection line formed by the well plane and a vertical plane along the flow path is shown in Figure 1. Locations of injection and sampling wells are shown in plan view in Figure 2.

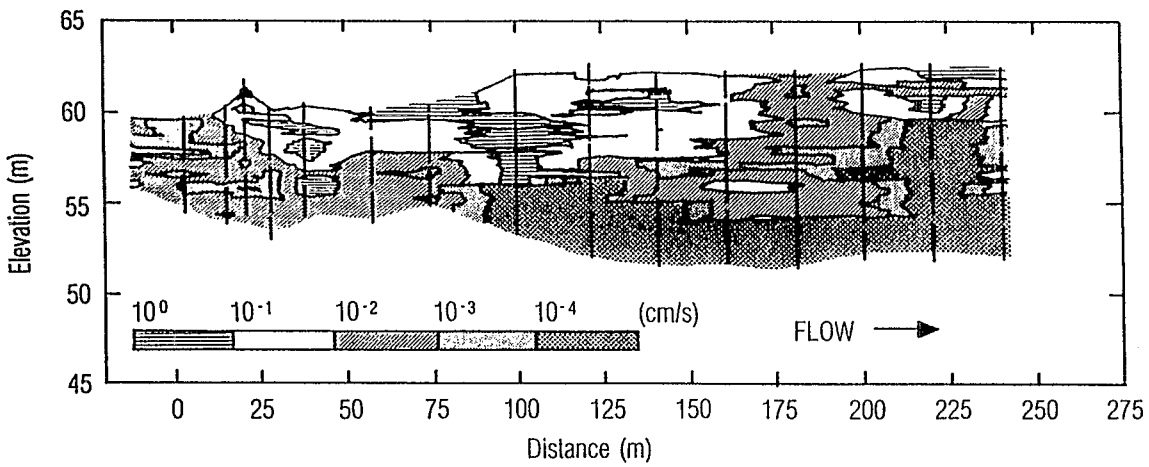


Figure 1. Distribution of hydraulic conductivity over a vertical section containing the center line of the plume.

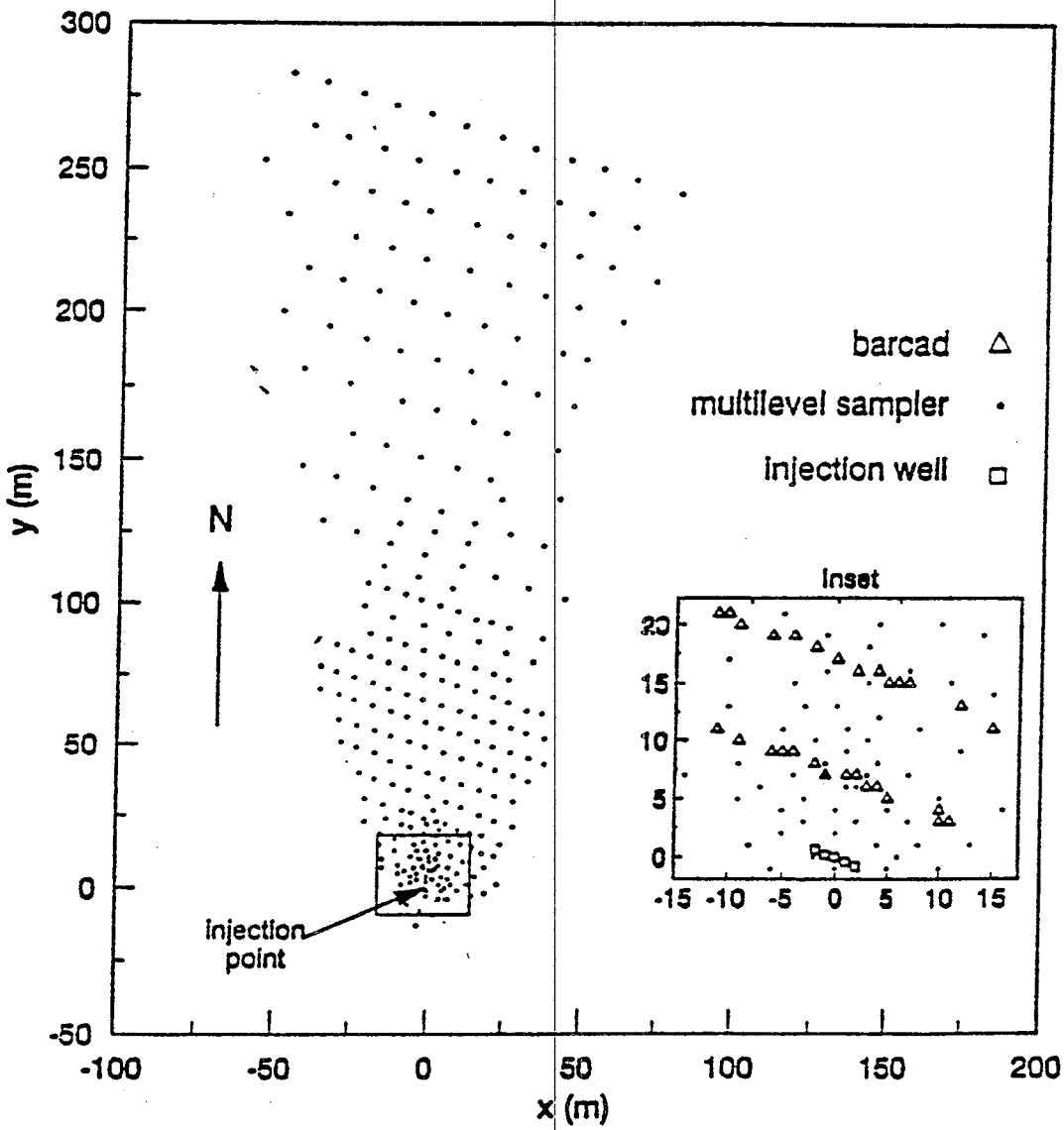


Figure 2. Plan view of the injection and sampling wells at the MADE2 site.

Experimental parameters for the MADE2 test were: injection volume, 9,600 L; injection time, 47.5 hr; injection wells screened over a 0.6-m interval at 4 m below the phreatic surface in the saturated zone of the aquifer; and five injection wells in a line normal to the hydraulic gradient and spaced at 1-m intervals with equal flow to each well. Injection concentrations were: tritium, 55.6 nCi/mL; benzene, 68.1 mg/L; naphthalene, 7.23 mg/L; p-xylene, 51.5 mg/L containing ring-labeled ^{14}C p-xylene, 2.77 nCi/mL; o-dichlorobenzene, 32.8 mg/L. Tritium and ^{14}C were analyzed by liquid scintillation counting of water samples. Concentrations of the organic compounds in water were determined by solvent extraction into pentane containing toluene as an internal standard, and analysis of the extract was made by gas chromatography (GC) with flame ionization detection. Most sampling wells contained multilevel samplers, but BARCAD water samplers were used in a few wells. Water was collected from the sampling wells and analyzed to provide three-dimensional snapshots of solute concentrations at 27, 132, 224, 328, and 440 d after injection. Statistical moments for each snapshot were calculated by establishing a triangular grid followed by vertical integration of concentrations at each well, and spatial integration was calculated over the grid by the method of Garabedian (6), which was previously applied at the MADE site by Adams and Gelhar (7). The agreement between the calculated zeroth moments and the mass of ^3H_2O injected confirmed mass balance for ^3H_2O. Selected wells from high and low solute concentration regions of the plume were analyzed for p-xylene degradation by ^{14}C counting methods 421 d after injection. Each water sample was subsampled in the field. A 2-mL subsample was mixed with cocktail and counted to obtain total ^{14}C in the water as either p-xylene or its degradation products. A 20-mL subsample was extracted with 2 mL of unlabeled p-xylene, and 1 mL of the xylene layer was transferred to scintillation cocktail and counted for ^{14}C p-xylene, which remained in the organic layer. Finally, a 10-mL subsample was made basic by adding 1 mL 3N NaOH and 1 mL 3N $Ca(NO_3)_2$, and centrifuged to isolate a precipitate containing $Ca^{14}CO_3$. The washed precipitate and 2 mL of supernatant water were placed in separate scintillation vials and counted. These analyses determined the amount of ^{14}C carbonate produced by complete degradation of ^{14}C p-xylene and the amount of ^{14}C in water-soluble organic intermediate products, respectively.

Leaky Reactor Model

Organic solutes remaining in the low K_h region near the injection wells may be regarded as semiconfined in a reactor zone that is stirred by advection and dispersion. This reactor is considered to leak by advection through a near surface channel with relatively high K_h, with replacement water supplied by ground-water flow across the upstream boundary of the reactor zone. The conceptual model of this situation is shown in Figure 3. This model compares well with the K_h distribution shown in Figure 1. Reactions occurring in the reactor zone are tritiated water (Tr) decay, with a rate constant (k_d) of 1.548×10^{-3} d^{-1}, and biodegradation of organic compounds, assumed to be first order with rate constants k_b, k_x, k_n, and k_c for benzene (B), xylene (X), naphthalene (N), and o-dichlorobenzene (C), respectively. The leak rate for each solute from a well-mixed reactor should be first order, with the same constant, k_l, for all solutes. Sorption-desorption processes at aquifer material surfaces are assumed to be very fast relative to the other processes considered here, and to be rate-limited by physical transport of organic solute molecules to and from the solid-solution interface. Biodegradation and leakage occur simultaneously in the reactor zone by the scheme given in Figure 3. The overall kinetics can be expressed by the following set of linear differential equations with initial conditions: at $t = t_0 = 0$, $[Tr]_0 = 0.539$ Ci, $[B]_0 = 660$ g, $[X]_0 = 402$ g, $[N]_0 = 70$ g, $[C]_0 = 318$ g, where square brackets represent solute mass and t is time following injection.

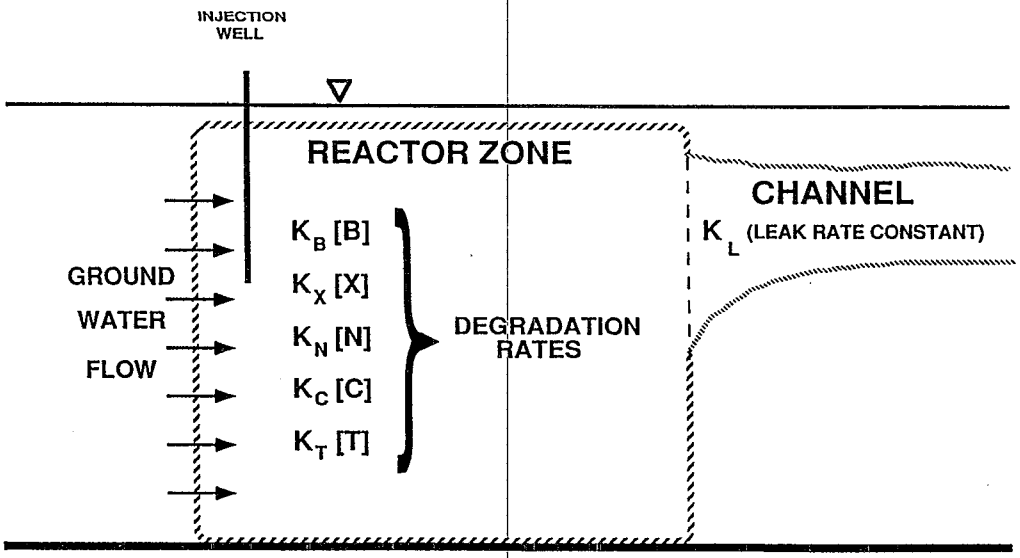


Figure 3. Diagram of the leaky reactor model.

Analytic solutions of equations 1 to 5 with these conditions are the integrated rate laws (equations 6 to 10) describing solute concentrations as functions of time. The leak rate constant k_l is calculated by solving equation 6, using the known k_d of tritium. Constants k_b, k_x, k_n, and k_c are then determined by substitution of k_l and solving equations 7 through 10.

$$-\frac{d[Tr]}{dt} = k_d[Tr] + k_l[Tr] \qquad (1)$$

$$-\frac{d[B]}{dt} = k_b[B] + k_l[B] \qquad (2)$$

$$-\frac{d[X]}{dt} = k_x[X] + k_l[X] \qquad (3)$$

$$-\frac{d[N]}{dt} = k_n[N] + k_l[N] \qquad (4)$$

$$-\frac{d[C]}{dt} = k_c[C] + k_l[C] \qquad (5)$$

$$k_l = \frac{\ln\left(\frac{[Tr]_0}{[Tr]}\right)}{t} - k_d \qquad (6)$$

$$k_b = \frac{\ln\left(\frac{[B]_o}{[Tr]_o}\right)}{t} + \frac{\ln\left(\frac{[Tr]}{[B]}\right)}{t} + k_d \qquad (7)$$

$$k_x = \frac{\ln\left(\frac{[X]_o}{[Tr]_o}\right)}{t} + \frac{\ln\left(\frac{[Tr]}{[X]}\right)}{t} + k_d \qquad (8)$$

$$k_n = \frac{\ln\left(\frac{[N]_o}{[Tr]_o}\right)}{t} + \frac{\ln\left(\frac{[Tr]}{[N]}\right)}{t} + k_d \qquad (9)$$

$$k_c = \frac{\ln\left(\frac{[C]_o}{[Tr]_o}\right)}{t} + \frac{\ln\left(\frac{[Tr]}{[C]}\right)}{t} + k_d \qquad (10)$$

Organic solutes were retarded slightly relative to ^3H_2O by weak sorption on the aquifer material (8), but this effect was negligible when compared with concentration changes due to biodegradation. Laboratory batch sorption coefficients on a composite sample of Columbus aquifer material for naphthalene, o-dichlorobenzene, p-xylene, and benzene were 0.085, 0.065, 0.048, and 0.059 L/kg, respectively. Accordingly, this model does not incorporate terms for sorption of solutes in the reactor zone.

Results

The distribution of ^3H_2O in sampling wells on the plume axis 224 d after injection is presented in Figure 4a. It is apparent that a large fraction of the ^3H_2O mass remained near the injection wells after 224 d. Biodegradation of organic solutes occurred primarily in a reactor zone approximately delineated by the p-xylene distribution at 224 d after injection. Figure 4b shows that p-xylene was approximately confined within 20 m of the injection wells. The same distribution pattern also held for the other organic solutes. Confinement of organic solutes to the reactor zone occurred because their biodegradation was rapid relative to the leak rate from the reactor zone.

The spatial distributions of K_h in Figure 1 and of ^3H_2O in Figure 4a are similar, which is expected because hydraulic conductivity is the controlling parameter for transport of an unretained solute. High ^3H_2O concentrations remained in the neighborhood of the injection wells 224 d after injection, with lower concentrations in the upper portion of the aquifer from about 30 m to 250 m downgradient. There was little ^3H_2O downgradient in the lower portion of the aquifer between 30 m and 175 m depth. This distribution indicates that solutes were transported downgradient from the low K_h near the injection wells through an upper channel whose size, location, and K_h govern the solute loss rate from the source region. Very little transport occurred

in the lower portion of the aquifer. The observed transport of ^3H_2O during this experiment was consistent with the leaky reactor model.

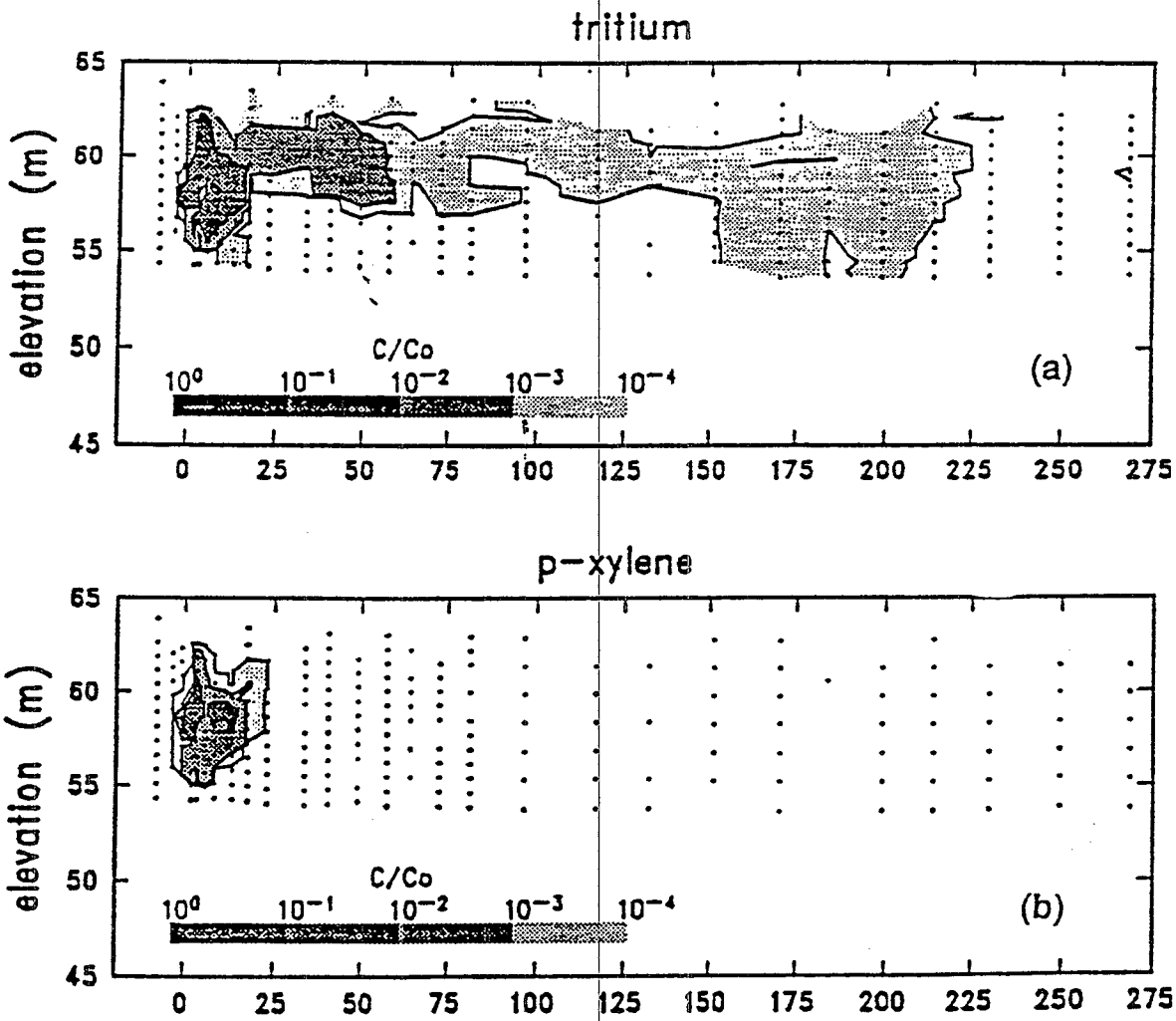


Figure 4. Distribution of (a) normalized tritium and (b) normalized p-xylene concentration zone over a vertical section containing the center line of plume motion.

Leakage of solutes was determined by the loss of tritium from the reactor zone, defined as the portion of the plume volume within 10 m downstream from the injection wells. The amount of tritium in the reactor zone at a given time was calculated by spatial integration. Total tritium in this zone decreased exponentially with time, as shown in Figure 5. The tritium values have been corrected for radioactive decay. This plot indicates that solute leakage from the reactor is first order, with leakage rate constant, $k_l = 5.45 \times 10^{-3}\ d^{-1}$. A mass balance for tritium calculated using spatial integration over the entire plume showed that the injected tritium mass was accounted for at the times given in Figure 5. This implies that the tritium decrease in the reactor zone was indeed due to a process analogous to leakage.

Biodegradation rates within the reactor zone are approximately first order, as shown in Figure 6. Departure of the curves from linearity is attributed to microbial processes. There is an apparent lag period for microbial activity soon after the injection, during which degradation rates are low. This lag period is followed by degradation at a maximum rate, which is characteristic of the microbial metabolism. Finally, the rate decreases late in the reaction, as the solutes (substrates) are depleted.

Biodegradation rate constants for the organic solutes in the reactor zone (k_{max}(reactor)), determined from the maximum slopes in Figure 6, are presented in Table 1. The maximum rate constants ($k_{max(corr)}$(reactor)) in the second column have been corrected for organic solute leakage from the reactor zone. Maximum biodegradation rate constants for each organic solute were also calculated by spatial integration over the entire well field, and are included in Table 1 as k_{max}(whole field). These values are independent of the leaky reactor model.

Degradation rate calculations for p-xylene are based on analyses of p-xylene by GC. Ring-labeled ^{14}C p-xylene was included in the injection solution to demonstrate that reductions in p-xylene concentration were a result of biodegradation. Microorganisms mineralize ^{14}C p-xylene to water-soluble labeled intermediates and $^{14}CO_2$ (predominantly as $H^{14}CO_3^-$ at ground-water pH). ^{14}C counting of whole water samples does not distinguish between degraded and intact p-xylene, and thus does not measure degradation of ^{14}C-labeled organic compounds. Detection of these products provides a strong indication that p-xylene has biodegraded in the aquifer.

Results of measurement of ^{14}C p-xylene degradation are given in Table 2. Total ^{14}C in the water sample and the amount of ^{14}C in the water after extraction were used to calculate the fraction of p-xylene converted to all products. Total ^{14}C in the water sample and the ^{14}C in the carbonate precipitate were used to calculate the fraction of p-xylene converted to CO_2.

These p-xylene conversion figures compare well with mass-balance-based conversions calculated from the total p-xylene remaining in the plume at day 421, which were interpolated from snapshot data. Mass-balance-based conversions are based on GC analysis and on the known mass of p-xylene injected. They are included in the last column of Table 2.

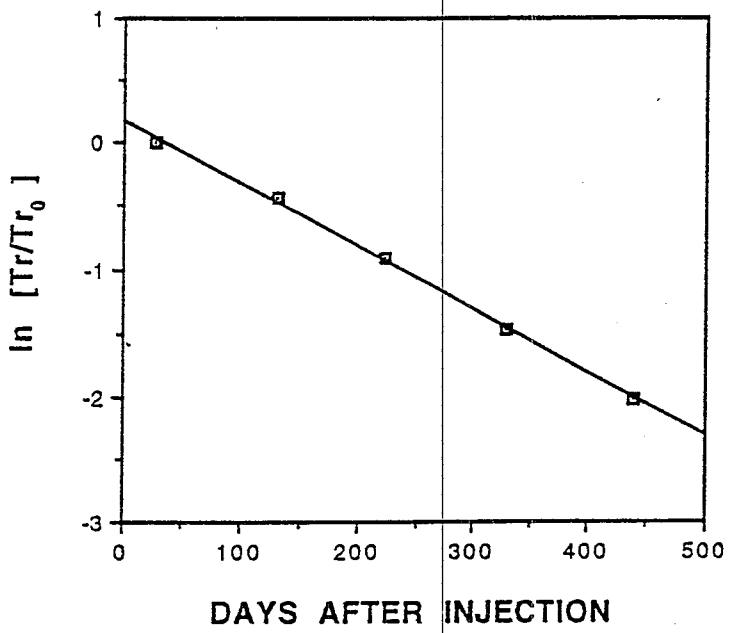


Figure 5. Tritiated water content in the reactor organic as a function of time.

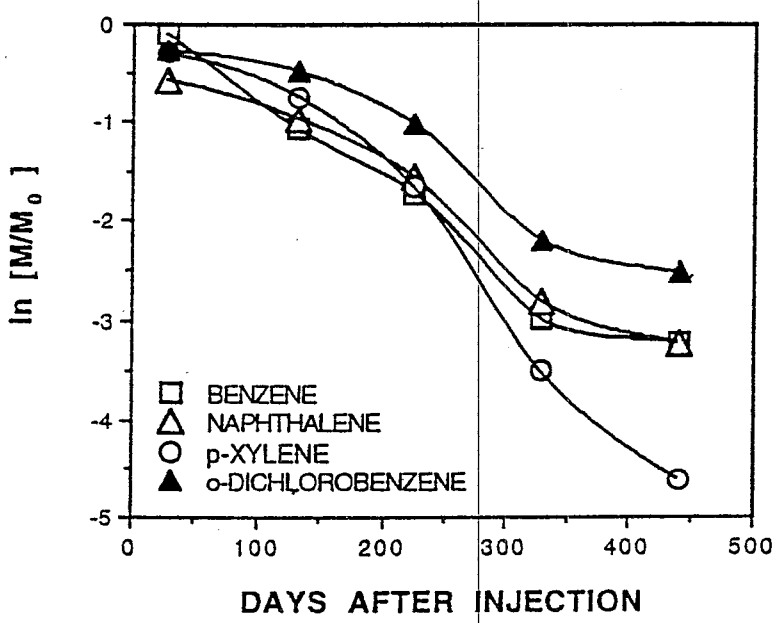


Figure 6. Degradation curves for the compounds in the reactor zone.

Table 1. Maximum Biodegradation Rate Constants From the MADE2 Site

	k_{max}(reactor) (d^{-1})	$k_{max(corr)}$(reactor) (d^{-1})	k_{max}(whole field) (d^{-1})
Benzene	0.0120	0.0066	0.0104
p-Xylene	0.0196	0.0141	0.0187
Naphthalene	0.0118	0.0063	0.0104
o-Dichlorobenzene	0.0114	0.0059	0.0100

Table 2. Degradation of p-Xylene in Water Samples Taken After 421 Days, Expressed as Weight Percent Converted

	% 14C p-Xylene Converted to All Products	% 14C p-Xylene Converted to CO_2	Mass Balance Based % p-Xylene Converted
[xylene]>1 ppm (n=8)	85.1 (± 6.3)	73.3 (± 11.1)	98
[xylene]>1 ppm (n=10)	82.6 (± 6.1)	74.2 (± 6.2)	98

The values in the second column are on the high, but normal, side for $^{14}CO_2$ release. This implies that most of the p-xylene went to energy production and was not converted to biomass. The difference between degradation in the high and low concentration regions of the aquifer is not significant. The difference of the means for p-xylene converted to all products and p-xylene converted to CO_2 may imply that some intermediate products are present, but this difference may also be attributable to analytical anomalies (i.e., loss of $Ca^{14}CO_3$ during precipitate transfer prior to counting). Agreement between the first and third columns of Table 2 indicates the consistency of p-xylene degradation measurements by GC and ^{14}C counting methods. The small difference between these numbers is due to incorporation of ^{14}C into biomass and insoluble carbonates. Most p-xylene degradation products apparently remained in the local ground water.

Discussion

Biodegradation rates given in Table 1 are based on field observations of solute behavior and are an essential input in modeling organic contaminant fate and transport in this aquifer material. The relative rates are as expected, with p-xylene most rapidly biodegraded. Figure 6 indicates that biodegradation in the Columbus aquifer is a first-order process. Simkins and Alexander (9) have indicated that biodegradation can be expected to follow Monod kinetics for a microbial population not limited by nutrients and with a sufficient substrate concentration, but first-order kinetics are observed at low substrate concentrations. Organic solute concentrations

in the MADE2 test were quite low, so this conclusion is consistent with experimental results. Larson (10) notes that the rate of decrease in concentration as a function of substrate concentration can often be expressed as a first-order equation, and that first-order kinetics are generally expected for biodegradation at low organic substrate concentrations. Applicability of the leaking reactor model is site specific, and its success with the MADE2 test data is a fortuitous circumstance dependent on the arbitrarily selected positions of the injection wells in the Columbus aquifer. It is encouraging that the two methods of calculating biodegradation rates gave similar results, thus providing confidence that these rates are useful for predictive purposes.

Organic solutes in MADE2 biodegraded under aerobic conditions in the aquifer. The organic solute concentrations injected were chosen to be too low to significantly deplete dissolved oxygen in the reactor zone of the aquifer. Maintenance of oxic conditions was confirmed by monitoring dissolved oxygen and redox potential of water samples during the experiment. Thus the biodegradation rates reported here were not affected by oxygen limitation. For very large releases of similar organic compounds, the conditions near the source might rapidly become reducing due to the biological oxygen demand. Kinetic models to determine biodegradation rates in this situation would be complex due to the need to include oxygen transport terms and the potential for degradation by anaerobic bacteria. It is therefore wise to use small injection amounts in field experiments to determine biodegradation rates.

In MADE2, the organic solutes degraded quickly. These results suggest that, for similar solutes, aquifer remediation activities should be restricted to the source region, which might include pumping to remove nonaqueous-phase liquids or excavation of contaminated aquifer material. The source would be reduced but not eliminated by this treatment. In an aquifer with approximately steady flow, the plume of organic solutes from the reduced source would reach a steady state, with the boundary determined by the hydrology of the site, sorption, *in situ* biodegradation, and oxygen and nutrient supply.

Conclusions

Controlled-release experiments similar to the MADE2 test are needed to determine accurate biodegradation rates for use in ground-water contaminant fate and transport models of aquifer situations. The MADE2 study has demonstrated the practicality of these experiments and obtained *in situ* degradation rates for four organic contaminants in the Columbus aquifer. These rates will be used in the design and modeling stages of a new field test at the MADE site, which is now in preparation.

References

1. Madsen, E.L. 1991. Determining *in situ* biodegradation: Facts and challenges. Environ. Sci. Technol. 25(10):1,663-1,673.

2. Robin, M.J.L., E.A. Sudicky, R.W. Gillham, and R.G. Kachanoski. 1991. Spatial variability of strontium distribution coefficients and their correlation with hydraulic conductivity in the Canadian Forces Base Borden aquifer. Water Resour. Res. 27(10):2,619-2,632.

3. Boggs, J.M., S.C. Young, and L.M. Beard. 1992. Field study of dispersion in a heterogeneous aquifer, 1. Overview and site description. Water Resour. Res. In press.

4. Rehfeldt, K.R., J.M. Boggs, and L.W. Gelhar. 1992. Field study of dispersion in a heterogeneous aquifer, 3. Geostatistical analysis of hydraulic conductivity. Water Resour. Res. In press.

5. Mackay, D.M., D.L. Freyberg, and P.V. Roberts. 1986. A natural gradient experiment on solute transport in a sand aquifer, 1. Approach and overview of plume movement. Water Resour. Res. 22(13):2,017-2,029.

6. Garabedian, S.P., D. LeBlanc, L.W. Gelhar, and M.A. Celia. 1991. Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 2. Analysis of spatial moments for a nonreactive tracer. Water Resour. Res. 27(5):911-924.

7. Adams, E.E., and L.W. Gelhar. 1992. Field study of dispersion in a heterogeneous aquifer, 2. Spatial moments analysis. Water Resour. Res. In press.

8. MacIntyre, W.G., T.B. Stauffer, and C.P. Antworth. 1991. A comparison of sorption coefficients determined by batch, column, and box methods on a low carbon aquifer material. Ground Water 29(6):908-913.

9. Simkins, S., and M. Alexander. 1984. Models for mineralization kinetics with the variables of substrate concentration and population density. Appl. Environ. Microbiol. 47(6):1,299-1,306.

10. Larson, R.J. 1979. Role of biodegradation kinetics in predicting environmental fate. In: Maki, A.W., et al., eds. Biotransformation and fate of chemicals in the aquatic environment. Washington DC: American Society for Microbiology.

Traverse City: Distribution of the Avgas Spill

David W. Ostendorf
Civil and Environmental Engineering Department, University of Massachusetts, Amherst, MA

Abstract

The capillary tension/liquid saturation equations of Parker and Lenhard (1) and Lenhard and Parker (2) provide a reasonably accurate description of the vertical distribution of the separate phase aviation gasoline (avgas) in solid core samples taken from the U.S. Coast Guard Air Station in Traverse City, Michigan.

Introduction

The depth of a continuous liquid below the ground surface is directly related to its capillary tension in the absence of vertical velocity, since the sum of the potential and pressure heads forms a vertically uniform hydraulic head under static conditions. Thus, the theory (1) describing capillary tension/saturation relations for immiscible, continuous fluids also finds expression as vertical profiles of water and avgas in the absence of infiltration. Lenhard and Parker (2) recognize this equivalence and propose profiles for total liquid and avgas saturation that are reasonably borne out by Ostendorf et al. (3) in their analysis of solid core data from five stations in the avgas plume at Traverse City (Figure 1). We summarize the theory here and discuss some implications of the distribution.

Vertical Distribution of Free Avgas

The vertical distribution of water and free avgas in the contaminated soil is idealized in Figure 2. The water is more strongly attracted to the solid grains than the avgas and fills the smaller pores in the soil, forming an interface with free avgas. The free avgas in turn faces the soil gas in the large pores, which control the overall saturation of the soil as a consequence. Residual avgas may be trapped as discontinuous bubbles within the water phase due to hysteresis and a fluctuating water table.

The volumetric water θ_W, residual avgas θ_{LR}, and irreducible water θ_{WR} contents combine to define an effective apparent water saturation S_W and comprise the total saturation S when they are added to the free avgas content θ_{LF} (1).

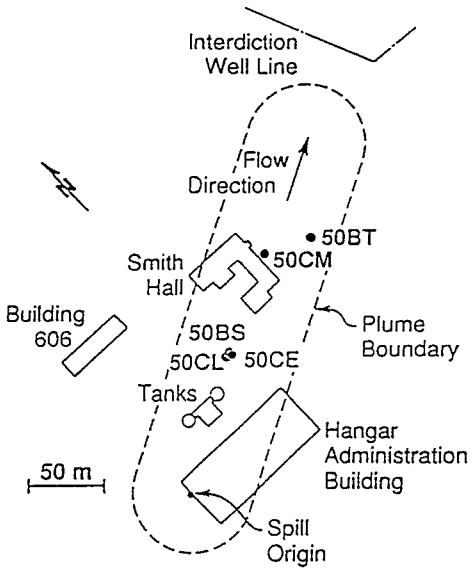


Figure 1. Site plan, U.S. Coast Guard Air Station.

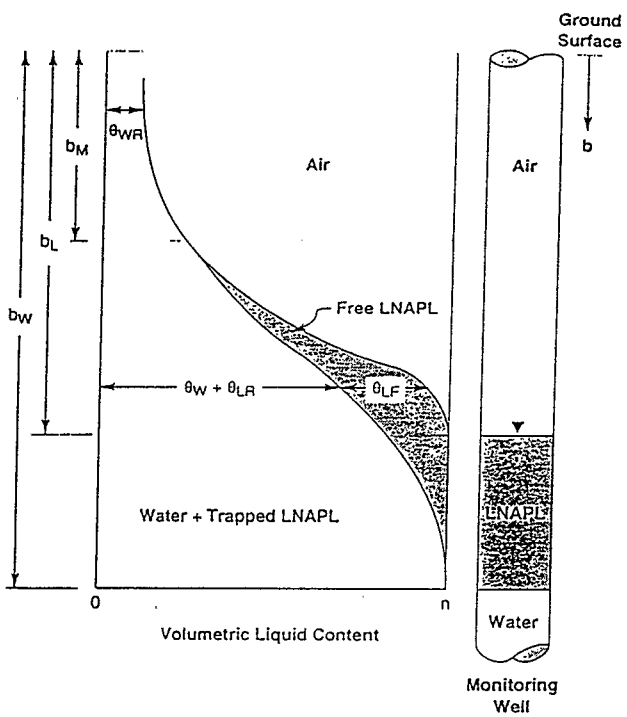


Figure 2. Vertical distribution of liquids in soil and a monitoring well.

$$S_W = \frac{\theta_W + \theta_{LR} - \theta_{WR}}{n - \theta_{WR}} \qquad (1a)$$

$$S = \frac{\theta_W + \theta_{LR} + \theta_{LR} - \theta_{WR}}{n - \theta_{WR}} \qquad (1b)$$

with porosity n. The total saturation is controlled by the tension across the avgas/air interface and varies with depth b below the ground surface in the absence of dynamic effects associated with infiltration

$$S = S_W \qquad (b_M > b) \qquad (2a)$$

$$S = \{1 + [\beta_L(b_L - b)]^{\alpha}\}^{(1/\alpha)-1} \qquad (b_L > b > b_M) \qquad (2b)$$

$$S = 1 \qquad (b > b_L) \qquad (2c)$$

Lenhard and Parker (2) derive equation 2 as an application of van Genuchten's (4) pore size distribution to separate phase contamination in soil. Figure 2 displays the minimum depth b_M of free avgas occurrence, along with the avgas table b_L and water table b_W existing in a hypothetical monitoring well. Note that the avgas does not occupy all the pores at a given elevation and extends above the avgas table in the soil due to capillary tension. Thus, the monitoring well levels, though necessary to determine liquid tensions, do not explicitly determine the vertical distribution of avgas in the soil. The pore size distribution of the soil is also needed to specify the profile.

These latter data are characterized by the pore size uniformity exponent α and the scaling factor β_L appearing in equation 2b. The latter parameter may be expressed in terms of the mean pore radius $\bar{r}$ by noting that the avgas/air surface tension σ_{LA} relates fluid tension to interfacial radius

$$\beta_L = \frac{\rho_L g \bar{r}}{2\sigma_{LA}} \qquad (3)$$

with gravitational acceleration g, avgas density ρ_L, and an assumed zero contact angle. Table 1 lists parameter values calibrating the data from five stations at Traverse City (3). Observations (circles) and theory (curve) for a typical total saturation profile are sketched in Figure 3. A mean pore radius of 5.4×10^{-5} m is implied by equation 3. A simple extension of a classical grain size based model of $\bar{r}$ checks this estimate. We note that $\bar{r}/2$ is the hydraulic radius of the mean pore size flowing full, and equate this to a modified Fair and Hatch (5) estimate of the quantity

$$\frac{\bar{r}}{2} = \frac{V_{VOIDS}}{A_{SOLIDS}} \qquad (4a)$$

$$\bar{r} = \frac{\bar{d}(n - \theta_{WR})}{3(1 - n + \theta_{WR})} \qquad (4b)$$

Table 1. Total and Avgas Saturation Profile Parameters at Traverse City

Symbol	Parameter	Value
n	Porosity	0.367
θ_{WR}	Irreducible moisture content	0.059
ρ_L	Avgas density	7.07 kg/m^3
α	Pore size uniformity	3.00
β_L	Avgas scaling factor	8.20 m^{-1}
β_W	Water scaling factor	1.53 m^{-1}
Δ	Water table amplitude	0.35 m
Υ	Trapping factor	40

The observed mean grain size of 3.8 x 10^{-4} m at Traverse City leads to a mean pore size value of 5.7 x 10^{-5} m, in excellent agreement with the equation 3 value.

The water/avgas interface controls the water saturation in the presence of the free avgas

$$S_W = \{1 + [\beta_W(b_W - b)]^{\alpha}\}^{(1/\alpha)-1} \qquad (b_W > b > b_M) \qquad (5a)$$

$$S_W = 1 \qquad (b > b_W) \qquad (5b)$$

$$\beta_W = \beta_L \frac{[(\rho/\rho_L) - 1]\sigma_{LA}}{\sigma_{WL}} \qquad (5c)$$

with water density ρ and scaling factor β_W predicated on the water/avgas surface tension σ_{WL}. The upper extent b_M of free avgas may be estimated by equating the total saturation (equation 2b) and the water saturation (equation 5a) at this elevation. A water/air interface with a surface tension σ_{WA} governs the water saturation above this depth

$$b_M = \frac{\beta_L b_L - \beta_W b_W}{\beta_L - \beta_W} \tag{6a}$$

$$S_W = (1 + \{\frac{\beta_L \sigma_{LA}}{\sigma_{WA}} [b_L - b_W + \frac{\rho}{\rho_L} (b_W - b]\}^{\alpha})^{(1/\alpha)-1} (b_M > b) \tag{6b}$$

The free avgas saturation S_{LF}, in view of equation 1, is simply given by

$$S_{LF} + S - S_W \tag{7}$$

Figure 4 shows a typical free avgas profile at the site, based upon the scaling factors of Table 1.

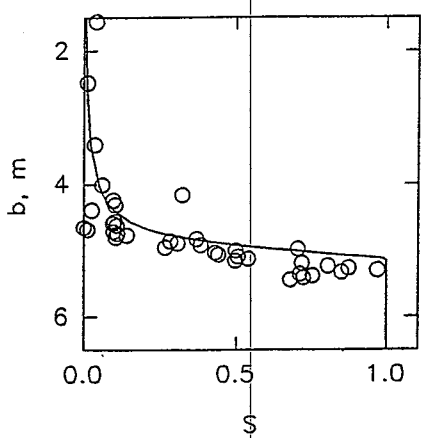


Figure 3. Total saturation, Core 50BT.

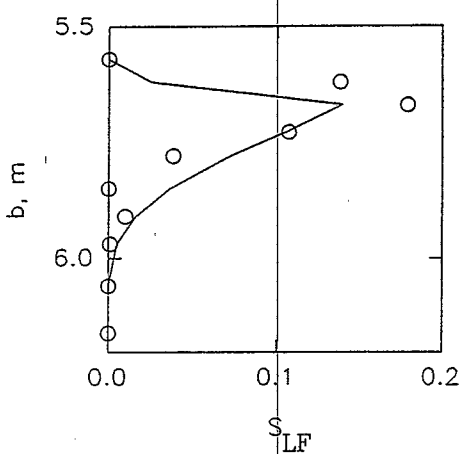


Figure 4. Free avgas, Core 50CE.

Vertical Distribution of Residual Avgas

Residual avgas may be attributed to hysteretical trapping of product as it rises and falls through the water wet soil over a fluctuating water table. Free liquids at a given depth b experience progressively stronger capillary tensions as the water table falls due to their higher position above this reference level. After the table attains a maximum depth and begins to rise, the water/avgas interface becomes steadily larger due to a decreasing capillary tension. The encroaching water occludes some of the avgas, giving rise to a discontinuous residual fraction within the water phase.

Historical maximum and minimum effective water saturations S_{WMAX}, S_{WMIN} are established by corresponding minimum (b_{WMIN}) and maximum (b_{WMAX}) water table depths, respectively

$$S_{WMIN} + \{1+[\beta_W(b_{WMAX}-b)]^{\alpha}\}^{(1/\alpha)-1} \tag{8a}$$

$$S_{WMAX} + \{1+[\beta_W(b_{WMIN}-b)]^{\alpha}\}^{(1/\alpha)-1} \tag{8b}$$

$$b_{WMIN} = b_{WMAX} - \Delta \tag{8c}$$

Ostendorf et al. (3) infer the historical water table excursion amplitude Δ cited in Table 1 from water level variations in nearby Lake Michigan. Parker and Lenhard (1) suggest that the extreme saturations induced by extreme water positions trap residual avgas saturation S_{LR} that is given by

$$S_{LR} = \frac{1-S_{WMIN}}{1+Y(1-S_{WMIN})} \qquad (b_{WMAX} > b > b_{WMIN}) \tag{9}$$

with empirical trapping factor Y. Ostendorf et al. (3) calibrate residual saturation profiles from their five stations with the trapping factor cited in Table 1, with the typical results sketched in Figure 5.

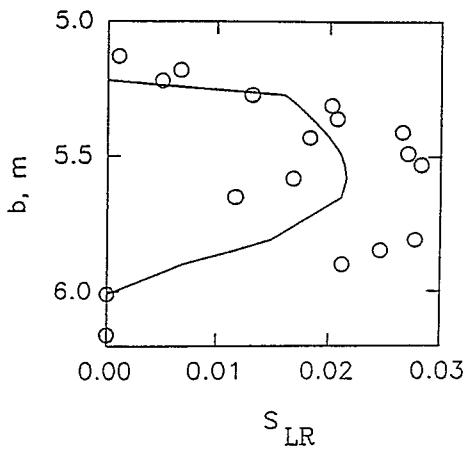


Figure 5. Residual avgas, Core 50CL.

Discussion

The vertical distribution of free and residual avgas has important implications for the estimation of separate phase contamination from monitoring well observations. The depth integrated mass M_{LF} of free avgas may be estimated formally by integrating equations 2b, 5a, 6a, and 7 from the water table to the upper limit of free avgas occurrence, with the result

$$M_{LF} = \rho_L \int_{b_M}^{b_W} S_{LF} db \tag{10a}$$

$$M_{LF} = \frac{\rho_L}{\beta_W} \{\beta_W (b_W - b_L) - (1 - (\frac{\beta_W}{\beta_L}) I[\frac{\beta_W (b_W - b_L)}{1 - \frac{\beta_W}{\beta_L}}]\} \tag{10b}$$

$$I(y) = \int_0^y (1 + y'^{\alpha})^{(1/\alpha)-1} dy' \tag{10c}$$

The integral function I(y) varies with the uniformity exponent of the pore sizes, while its argument is determined by the scaling factors and the product thickness in the monitoring well. Figure 6 displays the equilibrium variation of the depth integrated mass predicted at Traverse City as a function of the monitoring well avgas thickness. We note the exclusion of the residual mass from this estimate, since the trapped avgas is not continuously connected to product in the monitoring well. For a point of reference, Figure 5 implies a depth integrated residual avgas mass of about 5.3 kg/m^2; if this mass were free avgas, we would observe a 0.3-m product thickness in a monitoring well.

The methylene chloride extract chromatograms are composed primarily of known compounds (6), so that the composition of the avgas can be examined at a given depth. We note distillation of avgas as a function of depth in the solid core samples, as suggested by a profile from station 50BS (Figure 7). The open circles correspond to relatively volatile avgas compounds, with pure phase vapor densities of 0.27 to 1.00 kg/m^3 (at 12°C). This fraction becomes more important in the lower elevations due presumedly to decreased volatilization losses in the wetter region of the soil. The mid-range volatiles (closed circles), with vapor densities of 0.14 to 0.27 kg/m^3, are quite uniformly distributed, while the heavy compounds (triangles), with vapor densities less than 0.14 kg/m^3 in magnitude, tend to dominate the blend of hydrocarbons in higher, drier soil due to stripping away of the lighter fraction.

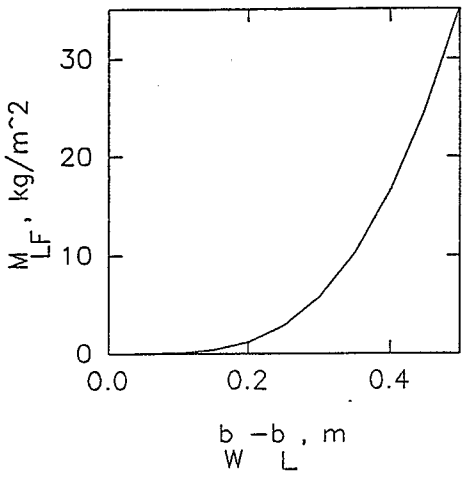


Figure 6. Depth integrated free avgas mass.

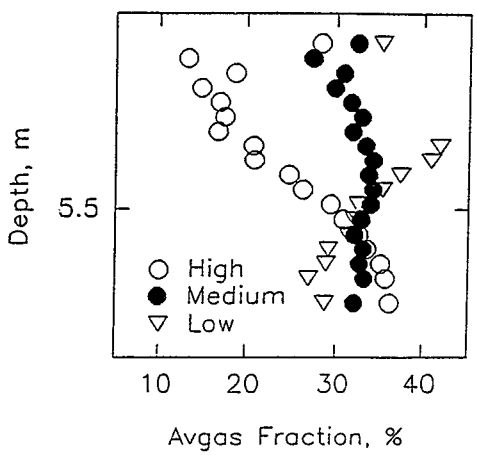


Figure 7. Avgas composition, 50BS.

The partitioning of avgas into free and residual fractions has important implications on its downgradient fate and transport as well. Figure 2 suggests that the free avgas occupies a relatively high-permeability, saturated soil region below the avgas table and a lower-permeability, unsaturated zone above the table. Since both these regions share a common horizontal gradient due to the slope of the avgas table, we anticipate slower and faster zones of horizontal separate phase transport. This vertical profile of horizontal specific avgas discharge is very nonuniform for sands with high values like that at the site. The phenomenon can be approximated as a pseudosorptive process, with a linear balance between a mobile fraction and a reversible, immobile fraction "sorbed" by capillary tension (7). Pursuing this analogy further, the residual avgas can be thought of as an irreversibly sorbed partition, lost from the mobile fraction by hysteretical trapping. The net effect of these mechanisms is that the avgas travels with the underlying ground water, but at a retarded velocity.

The free avgas is relatively easy to strip out of the soil due to its direct interface with air. The residual avgas is much more difficult to remediate, since it is surrounded by essentially immiscible water. We accordingly expect an initial period of relatively rapid remediation in response to soil venting or air sparging, followed by an asymptotically lower removal rate exacerbated by avgas distillation.

References

1. Parker, J.C., and R.J. Lenhard. 1987. A model for hysteretic constitutive relations governing multiphase flow, 1. Saturation pressure relations. Water Resour. Res. 23:2,187-2,196.

2. Lenhard, R.J., and J.C. Parker. 1990. Estimation of free hydrocarbon volume from fluid levels in monitoring wells. Ground Water 28:57-67.

3. Ostendorf, D.W., R.J. Richards, and F.P. Beck. 1993. LNAPL retention in sandy soil. Ground Water 31:285-292.

4. van Genuchten, M.T. 1980. A closed form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. Am. J. 44:892-898.

5. Fair, G.M., and L.P. Hatch. 1933. Fundamental factors governing the streamline flow of water through sand. J. Am. Waterworks Assoc. 25:1,551-1,565.

6. Ostendorf, D.W., L.E. Leach, E.S. Hinlein, and Y.F. Xie. 1991. Field sampling of residual aviation gasoline in sandy soil. Ground Water Monitor. Rev. 11:107-120.

7. Ostendorf, D.W. 1990. Long-term fate and transport of immiscible aviation gasoline in the subsurface environment. Water Sci. Tech. 22:37-44.

Traverse City: Geochemistry and Intrinsic Bioremediation of BTX Compounds

Barbara H. Wilson, John T. Wilson, Don H. Kampbell, and Bert E. Bledsoe
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK

John M. Armstrong
The Traverse Group, Inc., Ann Arbor, MI

Introduction

Loss of petroleum products from underground storage tanks, pipelines, and accidental spills is a major source of contamination of unsaturated soils, aquifer solids, and ground water. Volatile aromatics such as benzene, toluene, ethylbenzene, and the xylenes (BTEX) are more soluble in water than the aliphatic and higher molecular-weight aromatic constituents of petroleum products (1). Once released to the subsurface, petroleum compounds are subject to aerobic microbial processes. The low-molecular-weight alkanes and aromatics are readily biodegraded in oxygenated ground water, depleting the ground water of available oxygen (2,3). Reoxygenation of the ground water may occur through reaeration from soil gases, ground-water recharge, and usually inefficient mixing with surrounding oxygenated ground waters (4,5). Although ground waters near the perimeter of the contaminant plume may be reoxygenated, the interior of the plume will remain anoxic for a distance downgradient. Anaerobic biological processes can account for most of the removal of BTEX from the plume (6,7). The biogeochemical mechanisms that contribute to anaerobic processes in the subsurface, however, are not well understood.

The impact of anaerobic microbial processes on the fate of monoaromatics, substituted aromatics, and chlorinated hydrocarbons in anoxic subsurface environments has been studied in laboratory and field situations (8-12). Field evidence of biotransformation of *o*-, *m*-, and *p*-xylene was observed in methanogenic landfill leachate with their preferential removals compared with other alkylbenzenes present (13). Methanogenesis has been observed at two sites with ground water contaminated with creosote (14,15). Denitrifying, iron-reducing, sulfate-reducing, and methanogenic activities found in ground water at the first site were highly correlated with the biodegradation of creosote; methane was only detected in the ground water that had been contaminated with creosote. Intermediate products of methane fermentation, formate and acetate, were found in the ground water at the second site.

In 1969 the unsaturated soil and ground water underlying the U.S. Coast Guard Air Station at Traverse City, Michigan, were contaminated with an estimated 25,000 gal of aviation gasoline when a flange in an underground storage tank failed. Dissolution of the aromatics in the ground water resulted in concentrations of 36 mg to 40 mg of total alkylbenzenes per liter near the center of the plume. The subsurface contamination existed as residual-phase hydrocarbon, dissolved-phase aromatics, and gaseous hydrocarbons resulting from volatilization (16-18). The plume of dissolved-phase aromatics extended from the air station into the East Arm of Grand Traverse Bay and affected numerous drinking water wells. The area near the leaking underground storage tank was used to store degreasing solvents and to conduct degreasing

operations during aircraft maintenance. A small plume of chlorinated solvents lies adjacent to the gasoline plume.

Geochemical Characterization

Geochemical analyses of the water samples collected at Traverse City revealed waters of four distinct geochemistries: 1) the heart of the plume, 2) an anaerobic zone of treatment, 3) an aerobic zone of treatment, and 4) a pristine or renovated zone. The water from the heart of the plume contained high concentrations of methane and BTEX, with no detectable oxygen. These waters were surrounded by an anaerobic zone of treatment with greatly reduced concentrations of dissolved aromatics, no oxygen, and substantial concentrations of methane. Surrounding the anaerobic zone of treatment was an aerobic zone of treatment with measurable oxygen, small quantities of methane, and very low concentrations of the alkylbenzenes. The perimeter of the plume was surrounded by a renovated or pristine zone with high concentrations of oxygen, no detectable alkylbenzenes, and no methane.

Gas chromatography/mass spectrometry (GC/MS) analyses of the waters confirm the presence of BTEX at Traverse City. Also found were the chlorinated compounds 1,2-dichloroethane (1,2-DCA), tetrachloroethylene (PCE), and 1,1,1-trichloroethane (TCA). The GC/MS analyses of waters from wells R, S, and Q (Figure 1a) identified phenols and aromatic acids indicative of anaerobic microbial action on the soluble aromatic constituents of petroleum products (7,19,20). These compounds are found in portions of the plume with substantial concentrations of methane and no detectable oxygen, and are probably precursors of the methane. Complete information on the geochemical characterization of the ground waters at Traverse City, collection of aquifer material, analytical methods used, and microcosm construction may be found in Wilson et al. (21).

Laboratory Studies

To confirm field evidence of intrinsic bioremediation, laboratory microcosm studies were conducted on aquifer material from the U.S. Coast Guard Air Station. Material for aerobic and anaerobic fate studies was collected from three locations in the plume (Figure 1a). Aquifer material from site A (11.7 m to 12.3 m below land surface), the zone of anaerobic treatment, was used to construct the microcosms for the anaerobic fate study. Aquifer material from site B (9.6 m to 10.2 m below land surface), the aerobic zone of active biological treatment, and from site C (6.6 m to 7.2 m below land surface), the pristine or renovated zone, was used to prepare the aerobic fate studies. Autoclaved controls were prepared from the site C material. The compounds added to the microcosms were benzene, toluene, *p*-xylene, o-xylene, TCA, TCE, and chlorobenzene.

The initial compound concentrations and results of the fate studies at various incubation times are shown in Table 1. Benzene, toluene, *p*-xylene, and o-xylene were biodegraded in both aerobic and anaerobic aquifer material. The removals were quite rapid for all compounds in each of the three geochemical zones studied, whether in the anaerobic zone of treatment, the aerobic zone of treatment, or the renovated (pristine) material. By the end of 8 wk of incubation of the compounds in the anaerobic aquifer material, the concentrations of benzene, toluene, *p*-xylene, and o-xylene had been reduced one order of magnitude. The biotransformation of the

four compounds in the aerobic zone of biological treatment occurred even more rapidly. By the end of 2 wk of incubation, the concentrations for all four compounds were decreased by two orders of magnitude. Similar losses were seen in material from the renovated/pristine zone.

Table 1. Behavior of Benzene, Alkylbenzenes, TCA[a], TCE[b], and Chlorobenzene in Aquifer Material From an Aviation Gasoline Plume

Subsurface Material	Compound (μg/L Pore Water)							
	Week	Benzene	Toluene	*m* + *p*-Xylene	o-Xylene	TCA	TCE	Chloro-benzene
A, anaerobic treatment, 11.7 m to 12.3 m below land surface	0	450	420	440	410	570	540	500
	4	12	56	78	41	420	260	66
	8	6	40	17	6	580	340	34
	95[c]	nd[d]	nd	nd	nd	73	54	3
B, active aerobic treatment, 9.6 m to 10.2 m below land surface	0	450	420	390	390	600	650	500
	2	2	2	1	2	440	440	53
	4	5	5	2	1	540	480	50
	14	2	2	1	nd	430	260	30
C, aerobic renovated, 6.6 m to 7.2 m below land surface	0	420	380	370	370	600	540	500
	2	4	3	3	3	580	540	100
	4	1	3	1	1	620	600	106
	14	—	—	—	—	650	500	67
C, autoclaved, 6.6 m to 7.2 m below land surface	0	420	380	370	370	600	650	500
	2	380	290	200	190	590	540	300
	4	240	230	170	180	560	430	210

[a]1,1,1-Trichloroethane
[b]Trichloroethylene
[c]Concentrations at this time interval were determined by GC/MS; concentrations at other time intervals were determined by GC. All values are means of triplicate analyses.
[d]Not detected, detection limit of 0.1 μg/L

At the end of 4 wk of incubation, the respective concentrations for benzene, toluene, *p*-xylene, and o-xylene in the autoclaved samples were 57 percent, 61 percent, 46 percent, and 49 percent of the original concentrations. Due to the removals of BTX in the controls, a second set of autoclaved samples was prepared. The concentrations after 16 wk of incubation in the duplicated controls were benzene, 83 percent; toluene, 66 percent; *m*- + *p*-xylene, 51 percent; o-xylene, 50 percent; TCA, 86 percent; TCE, 73 percent; and chlorobenzene, 58 percent. The

cause for the removal of organics in the controls has not been determined; however, sorption to aquifer solids probably occurred. Chlorobenzene was also biodegraded in each of the three geochemical zones studied. Decreases of one order of magnitude were observed for chlorobenzene in both the aerobic and anaerobic zones of biological treatment after 4 wk of incubation. Similar removal was seen in the renovated/pristine material after 14 wk of incubation. In the autoclaved samples, 44 percent of the chlorobenzene remained after 4 wk of incubation.

No significant biotransformation of TCA or TCE, compared with the controls, was observed at the end of 8 wk of incubation. Evidence of reductive dechlorination of both compounds, however, was indicated by GC/MS analyses of anaerobic microcosms at 95 wk of incubation by the identification of 1,1-dichloroethylene (1,1-DCE) and 1,1-dichloroethane (1,1-DCA) (22,23).

Headspace concentrations of methane were measured immediately before sampling to determine the maintenance of methanogenic conditions in the microcosms. Methane was found in all the anaerobic samples, with concentrations ranging from 50 ppm to 100 ppm; no methane was found in the headspace of the aerobic or autoclaved samples.

Correspondence Between Laboratory and Field Data

As part of a settlement with the State of Michigan, the U.S. Coast Guard monitors alkylbenzene concentrations in selected monitoring wells quarterly. Three of the monitoring wells (M30 near site S, M31 near site Q, and M2 near site A in Figure 1) lie along a flow path. The time required for water to move from one well to the next can be estimated by dividing the distance between the wells by the flow velocity (approximately 1.5 m per day). This value was determined directly from tracer tests, and is confirmed by calculations based on the hydraulic conductivity of the aquifer and its hydraulic gradient (24). Water takes 10 wk to flow from S to Q, and 24 wk to flow from S to A. The first-order rate of biodegradation along a segment of aquifer between the monitoring wells can be estimated by dividing the concentration in the well distal to the spill by the concentration in the proximate well, taking the natural logarithm, then dividing by the time required for water to flow between the wells.

Table 2 portrays the depletion of total BTX between S and Q and between S and A for the years 1984 through 1987. The rate constants are surprisingly consistent. A purge field was installed and put on line in mid-1985 to prevent further migration of the plume from Coast Guard property. As soon as the purge field was put into operation, the water behind the field near site A (Figure 1a) became stagnant, and concentrations of BTX began to drop. Solution concentrations of BTX dropped to low values by late 1985 (data not shown). Because the water was not moving, the decline in concentration over time could be used to estimate the first-order rate constant for anaerobic BTX biotransformation in the part of the aquifer near site A (Table 3).

Figure 1a

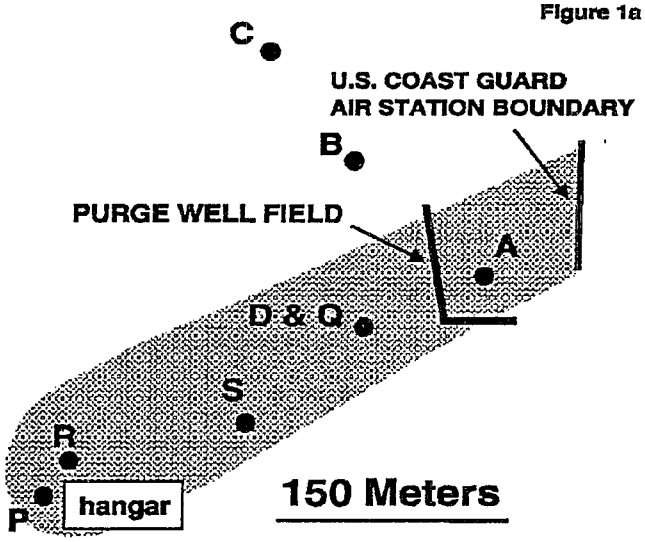


Figure 1a. Locations of wells in an aviation gasoline plume at the U.S. Coast Guard Air Station at Traverse City. Well A is located in the plume below the purge field; well B is located in the aerobic zone of treatment; well C is located in the pristine region surrounding the plume; and wells D, P, Q, R, and S are located in the plume above the purge field.

Figure 1b

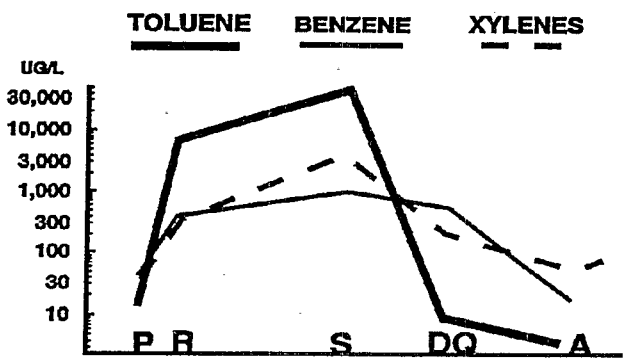


Figure 1b. Concentration of BTX in monitoring wells along a flow path down the central axis of the plume in the first quarter of 1986.

Table 2. First-Order Rates of Anaerobic Biotransformation (per Week) of Total BTX Along Segments in the Aquifer

Year	S to Q, Quarter of Year		S to A, Quarter of Year	
	First	Third	First	Third
1984	0.11	0.17	0.10	0.09
1985	0.02	0.27	0.07	cnc[a]
1986	0.43	0.14	0.20	cnc
1987	0.34	0.10	0.33	cnc

[a]Cannot calculate: the plume was intercepted by a purge well field and did not reach site A.

Table 3. Comparison of the First-Order Rates (per Week) of Anaerobic Biotransformation of BTX

Compound	Microcosms[b]	Aquifer Segment[b] S to Q	Change Over Time at A[c], 6/85 to 10/85
Benzene	0.5	0.05	0.17
Toluene	0.3	1.3	0.47
m + *p*-Xylene	0.4		
o-Xylene	0.5		
All xylenes		0.03	0.10

[a]Laboratory microcosm studies
[b]Along flow path segments in the aquifer
[c]At a site with stagnant ground water behind a purge well field

Sediment samples for the microcosm study were acquired from site A in late 1985, and this study was conducted in the first quarter of 1986. Figure 1b depicts the concentration of BTX in monitoring wells along a flow path down the central axis of the plume at that time. Table 3 compares the depletion of BTX along the aquifer segment S to Q during the first quarter of 1986 and the depletion in the static water at site A in the last half of 1985 with the rates of anaerobic BTX biotransformation in the microcosm study.

The rate of disappearance of BTX compounds as measured in aerobic microcosms does not compare well with actual rates of aerobic BTX degradation in the field. The rate of degradation in the field is controlled by mass-transport limitations for oxygen (4,5), while laboratory studies are limited by reaction rates. The anaerobic fate study compared quite favorably with those rates

measured by field data. Methanogenesis and other anaerobic processes are not limited by the availability of oxygen in either microcosms or subsurface materials. Mass-transport considerations are therefore not as critical to the comparison of microcosm and field data. Anaerobic microcosms might prove to be a valuable tool to evaluate intrinsic biorestoration of aquifers contaminated with petroleum products.

Conclusions

The results of the laboratory study confirm field evidence of both aerobic and anaerobic transformation of alkylbenzenes and suggest that intrinsic aerobic and anaerobic *in situ* biorestoration of ground water contaminated with petroleum products can occur. The anaerobic transformations seen at this site and confirmed by the laboratory study provide an attractive alternative to aerobic restoration. The removals of the alkylbenzenes in the anaerobic material were quite rapid and compared favorably with removals seen in the aerobic zone of treatment. Comparison of first-order rates of disappearance in anaerobic microcosms with those calculated from field data show acceptable agreement. Anaerobic processes in the subsurface are probably limited by *in situ* reaction rates rather than by mass-transport limitations for nutrients. Potentially, anaerobic microcosm studies could be useful in the evaluation of intrinsic bioremediation of petroleum-contaminated subsurface materials.

The aerobic degradation of alkylbenzenes in subsurface environments has been well documented (25,26) and is currently the state-of-the-art for restoration of petroleum contamination. Anaerobic biotransformation, however, can enhance *in situ* biorestoration in oxygen-depleted regions of a plume where heavily contaminated ground water has excessive oxygen demand. Naturally occurring anaerobic biological processes can potentially remediate ground water contaminated with petroleum products and significantly increase the reliability of existing remediation technologies.

References

1. Coleman, W.E., J.W. Munch, R.P. Streicher, H.P. Ringhand, and F.C. Kopfler. 1984. The identification and measurement of components in gasoline, kerosene, and no. 2 fuel oil that partition into the aqueous phase after mixing. Arch. Environ. Contam. Toxicol. 13:171-178.

2. Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. Microbiol. Rev. 45(1):180-209.

3. Gibson, D.T., and V. Subramanian. 1984. Microbial degradation of aromatic hydrocarbons. In: D.T. Gibson, ed. Microbial degradation of organic compounds. New York: Marcel Dekker. pp. 181-252.

4. Borden, R.C., and P.B. Bedient. 1986. Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation, 1. Theoretical development. Water Resour. Res. 22(13):1,973-1,982.

5. Borden, R.C., P.B. Bedient, M.D. Lee, C.H. Ward, and J.T. Wilson. 1986. Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation, 2. Field application. Water Resour. Res. 22(13):1,983-1,990.

6. Baedecker, M.J., D.I. Siegel, P. Bennett, and I.M. Cozzarelli. 1988. The fate and effects of crude oil in a shallow aquifer, 1. The distribution of chemical species and geochemical facies. In: Mallard, G.E., and S.E. Ragone, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30). Water Res. Invest. Rep. 88-4220. pp. 13-20.

7. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1988. The fate and effects of crude oil in a shallow aquifer, II. Evidence of anaerobic degradation of monoaromatic hydrocarbons. In: Mallard, G.E., and S.E. Ragone, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30, 1988). Water Res. Invest. Rep. 88-4220. pp. 21-33.

8. Kuhn, E.P., P.J. Colberg, J.L. Schnoor, O. Wanner, A.J.B. Zehnder, and R.P. Schwarzenbach. 1985. Microbial transformations of substituted benzenes during infiltration of river water to ground water: Laboratory column studies. Environ. Sci. Technol. 19(10):961-968.

9. Lovley, D.R., M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.J.P. Phillips, and D.I. Siegel. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. Nature 339:297-300.

10. Lovley, D.R. and D.J. Lonergan. 1990. Anaerobic oxidation of toluene, phenol, and *p*-cresol by the dissimilatory iron-reducing organism, GS-15. Appl. Environ. Microbiol. 56(6):1,858-1,864.

11. Suflita, J.M., S.A. Gibson, and R.E. Beeman. 1988. Anaerobic biotransformations of pollutant chemicals in aquifers. J. Ind. Microbiol. 3:179-194.

12. Wilson, B.H., G.B. Smith, and J.F. Rees. 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. Environ. Sci. Technol. 20(10):997-1,002.

13. Reinhard, M., N.L. Goodman, and J.F. Barker. 1984. Occurrence and distribution of organic chemicals in two landfill leachate plumes. Environ. Sci. Technol. 18(12):953-961.

14. Ehrlich, G.G., D.F. Goerlitz, E.M. Godsy, and M.F. Hult. 1982. Degradation of phenolic contaminants in ground water by anaerobic bacteria: St. Louis Park, Minnesota. Ground Water 20(6):703-710.

15. Goerlitz, D.F., D.E. Troutman, E.M. Godsy, and B.J. Franks. 1985. Migration of wood-preserving chemicals in contaminated ground water from a sand aquifer in Pensacola, Florida. Environ. Sci. Technol. 19(10):955-961.

16. Kampbell, D.H., J.T. Wilson, and D.W. Ostendorf. 1990. Simplified soil gas sensing techniques for plume mapping and remediation monitoring. In: Kostecki, P.T., and E.J. Calabrese, eds. Petroleum Contaminated Soils. Chelsea, MI: Lewis Publishers. pp. 125-139.

17. Ostendorf, D.W. 1990. Long-term fate and transport of immiscible aviation gasoline in the subsurface environment. Water Sci. Technol. 22:37-44.

18. Rifai, H.S., P.B. Bedient, J.T. Wilson, K.M. Miller, and J.M. Armstrong. 1988. Biodegradation modeling at aviation fuel spill site. J. Environ. Eng. 114(5):1,007-1,029.

19. Grbić-Galić, D. 1989. Microbial degradation of homocyclic and heterocyclic aromatic hydrocarbons under anaerobic conditions. Develop. Ind. Microbiol. 30:237-253.

20. Grbić-Galić, D., and T.M. Vogel. 1987. Transformation of toluene and benzene by mixed methanogenic cultures. Appl. Environ. Microbiol. 53(2):254-260.

21. Wilson, B.H., J.T. Wilson, D.H. Kampbell, B.E. Bledsoe, and J.M. Armstrong. 1990. Biotransformation of monoaromatic and chlorinated hydrocarbons at an aviation gasoline spill site. Geomicrobiol. J. 8:225-240.

22. Barrio-Lage, G., F.Z. Parsons, R.S. Nassar, and P.A. Lorenzo. 1986. Sequential dehalogenation of chlorinated ethenes. Environ. Sci. Technol. 20(1):96-99.

23. Klečka, G.M., S.J. Gonsior, and D.A. Markham. 1990. Biological transformations of 1,1,1-trichloroethane in subsurface soils and ground water. Environ. Toxicol. Chem. 9:1,437-1,451.

24. Sammons, J. 1994. Personal communication between John Sammons, The Traverse Group, Inc., and the authors.

25. Lee, M.D., J.M. Thomas, R.C. Borden, P.B. Bedient, C.H. Ward, and J.T. Wilson. 1988. Biorestoration of aquifers contaminated with organic compounds. CRC Crit. Rev. Environ. Control 18:29-89.

26. Raymond, R.L. 1974. Reclamation of hydrocarbon contaminated waters. U.S. Patent Office 3,846,290.

Mathematical Modeling of Intrinsic Bioremediation at Field Sites

Hanadi S. Rifai
Energy and Environmental Systems Institute, Rice University, Houston, TX

Introduction

Intrinsic bioremediation is an important attenuation mechanism at contaminated field sites because it limits pollutant migration and reduces contaminant mass in the subsurface. Quantifying the impact of intrinsic bioremediation at a field site involves conducting a comprehensive field sampling program in conjunction with extensive modeling of contaminant transport and fate. This paper reviews the basic data requirements for modeling intrinsic bioremediation at field sites and discusses some of the available models that can be used for that purpose. The limitations of existing models for simulating biodegradation are presented, as well as the difficulties in validating and verifying these models. Finally, a few case studies of modeling intrinsic bioremediation are reviewed.

Intrinsic Bioremediation Processes

Intrinsic bioremediation refers to the reduction of contaminant mass at a field site due to biodegradation. This reduction can occur under aerobic or anaerobic conditions. When oxygen is utilized as the electron acceptor, the process is referred to as *aerobic respiration*. When oxygen is not present *(anoxic* conditions), microorganisms can use organic chemicals or inorganic anions as alternate electron acceptors. Anaerobic biodegradation refers to *fermentative, denitrifying, iron-reducing, sulfate-reducing,* or *methanogenic* processes. To quantify the impact of intrinsic bioremediation on contaminant concentrations at a field site, one needs to develop an accurate picture of the distribution of electron acceptors both in pristine and contaminated areas. The concentrations of the electron acceptor in pristine areas provide an indication of the biodegradation potential at the site. The disappearance or decline of electron acceptor concentrations in contaminated areas provides an indication that biodegradation may be occurring.

Existing Biodegradation Models

The biodegradation of contaminants in ground water is mainly controlled by the rate of the reaction and the availability of the electron acceptor. A mathematical expression that represents the chemical reaction can be written to account for the effect that the rate of the reaction has on biodegradation. This mathematical expression can then be combined with the transport equation to account for the electron acceptor limitation effect on the biodegradation process in the subsurface.

Many biodegradation models have been developed in recent years, most of which utilize some kinetic expression for biodegradation (see Table 1). The models listed in Table 1 simulate a number of aerobic and anaerobic biodegradation processes subject to specified conditions and

assumptions. The difficulties involved in applying these models include 1) the data required as input to the model is lacking, such as the kinetic rate parameters or estimates of the hydraulic conductivity; 2) the majority of these models are proprietary and very few are public domain models; and 3) modeling in general is complicated and time-consuming, and requires a certain level of expertise.

Table 1. Biodegradation Models

Name	Description	Author(s)
-	1-D, aerobic, microcolony, Monod	Molz et al. (1)
BIOPLUME	1-D, Monod	Borden et al. (2)
-	1-D, analytical first-order	Domenico (3)
BIO1D	1-D, aerobic and anaerobic, Monod	Srinivasan and Mercer (4)
-	1-D, co-metabolic, Monod	Semprini and McCarty (5)
-	1-D, aerobic, anaerobic, nutrient limitations, microcolony, Monod	Widdowson et al. (6)
-	1-D, aerobic, co-metabolic, multiple substrates, fermentative, Monod	Celia et al. (7)
BIOPLUME II	2-D, aerobic, instantaneous	Rifai et al. (8)
-	2-D, Monod	MacQuarrie et al. (9)
BIOPLUS	2-D, aerobic, Monod	Wheeler et al. (10)
ULTRA	2-D, first-order	Tucker et al. (11)
-	2-D, denitrification	Kinzelbach et al. (12)
-	2-D, Monod, Biofilm	Odencrantz et al. (13)

Modeling of Intrinsic Bioremediation at Field Sites

Many case studies of simulating biodegradation at field sites exist in the general literature. In this paper, four case studies are reviewed that combine field and laboratory investigation programs with modeling studies.

Conroe Superfund Site, Texas

Borden et al. (2) applied the first version of the BIOPLUME model to simulate biodegradation at the Conroe Superfund site in Texas. The United Creosoting Company (UCC) site was operated as a wood-preserving facility from 1946 to 1972. Wastes disposed in two unlined ponds were composed of predominantly polycyclic aromatic hydrocarbons and pentachlorophenol (PCP). Monitoring of the site has shown elevated levels of organic contaminants in the soil and ground water, as well as elevated levels of chloride in the ground water. The ground-water velocity at the UCC site is approximately 5 m/yr.

Oxygen exchange with the unsaturated zone was simulated by Borden et al. (2) as a first-order decay in hydrocarbon concentration. The loss of hydrocarbon due to horizontal mixing with oxygenated ground water and resulting biodegradation was simulated by generating oxygen and hydrocarbon distributions independently and then combining them by superposition. Simulated oxygen and hydrocarbon concentrations closely matched the observed values. The Conroe Superfund site was one of the first sites to be modeled using a biodegradation expression in a transport model.

Traverse City Site, Michigan

The Traverse City field site is a U.S. Coast Guard Air Station located in Grand Traverse County in the northwestern portion of the lower peninsula of Michigan. The ground water at the site is contaminated with organic chemicals from a leaking underground storage tank. The main contaminants at the site are benzene, toluene, and xylenes (BTX). The contaminant plume ranges from 150 ft to 400 ft wide and is about 4,000 ft long. A pumping wellfield system was installed at the downgradient end of the dissolved plume to control offsite migration.

A modeling effort of natural attenuation at the site was completed by Rifai et al. (8) with the BIOPLUME II model. Modeling was performed for the period before the pumping wells were installed and also for the period after the wells were turned on. The data in Figure 1 show the results of the model simulation along the center line of the plume for the period before the wellfield was turned on. The model predictions by Rifai et al. (8) matched the observed concentrations at the monitoring wells reasonably well except in the vicinity of well M31. Rifai et al. (8) indicated that this was because the simulation did not account for anaerobic biodegradation, which was occurring in the interior of the plume.

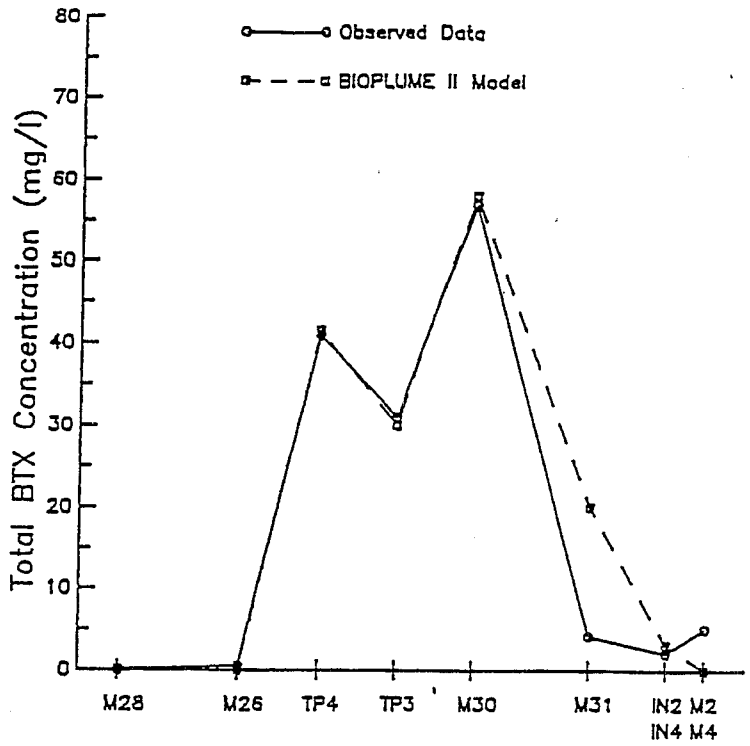


Figure 1. BIOPLUME II model predictions for the Traverse City field site (8).

Gas Plant Facility in Michigan

Soluble hydrocarbon and dissolved oxygen (DO) were characterized in a shallow aquifer beneath a gas plant facility in Michigan by Chiang et al. (14). The distributions of BTX in the aquifer had been monitored in 42 wells for a period of 3 years. The site geology is characterized as a medium to coarse sand with interbeds of small gravel and cobbles. The general direction of ground-water flow is northwesterly. The depth to water table ranges from 10 ft to 25 ft below land surface, and the slope of the water table was estimated as 0.006. Based on ground-water and soil sampling data, Chiang et al. (14) concluded that the flare pit was the major source of the hydrocarbons found in the aquifer, while the slope oil tank was a secondary source.

Chiang et al. (14) evaluated a first-order decay biodegradation approach and the BIOPLUME II model for simulating biodegradation at the gas plant facility. Using the model and assuming first-order decay, several simulations were made to match the observed benzene concentration distribution of 1/22/85 by setting the observed concentration distribution of 11/1/84 as the initial condition. The variables involved included the distribution of the leakage/spill rates between the flare pit and the slope oil tanks and macrodispersivities of the aquifer.

The BIOPLUME II model was used to simulate the July 1987 data by setting the observed concentration distribution of February 1987 as an initial condition. The data in Figure 2 show the comparison between the measured and the simulated soluble BTX concentrations of July 1987. As can be seen from Figure 2, the model predictions for BTX were reasonable. The model predictions for oxygen concentrations, however, were not as similar. The authors attributed the

differences to the fact that the BIOPLUME II model assumes a requirement of 3 ppm of oxygen for 1 ppm of benzene, whereas the actual requirement is in the range of 1 ppm to 3 ppm.

Cliffs-Dow Superfund Site

Ground water at the Cliffs-Dow site is contaminated with low levels of phenolic and polycyclic compounds. The aquifer sediments at the site consist of mostly coarse sands and gravels. The hydraulic conductivity ranges between 3.5×10^{-3} to 4.6×10^{-2} cm/sec. The principal contaminants found at the site near the source area include phenol, several methyl-substituted phenols, and naphthalene at concentrations ranging from 220 μg/L to 860 μg/L. Based on the analysis of samples obtained from monitoring wells, Klecka et al. (4) found that the levels of organic contaminants are reduced to near or below the detection limit within a distance of 100 m downgradient from the source. Further analyses of the ground-water chemistry were used to verify that biodegradation was occurring at the site and causing the disappearance of the contaminants.

The migration of organic constituents in the aquifer was simulated using the BIO1D model and assuming a first-order decay expression. Half-lives for the contaminants at the site were estimated from the results of soil microcosm experiments based on the time required for 50-percent disappearances of the parent compound. The velocity was varied over a range from 0.2 to 0.46 m/d, which is representative of the range of ground-water flow rates at the site.

Figure 3 illustrates the impact of biodegradation on contaminant concentrations at the site. Model simulations performed using a half-life of 2 d indicated that levels of the phenolic components were reduced by greater than 99 percent within a distance of 30 m downgradient of the source. When the half-life was increased by a factor of 10, the concentrations were reduced to a similar extent within 75 m. Because of the dominance of biodegradation, increases in ground-water velocity from 0.2 to 0.46 m/d had minor effects on the level of attenuation predicted with the model.

Conclusions

A number of biodegradation models have been developed over the last 10 years. These models are generally similar in that they simulate the transport and biodegradation of a number of components in the ground water. The models differ in the mathematical biodegradation expressions that they use and in the numerical procedures used to solve the complicated system of equations. Application of these models to field sites has proven to be complicated due to the lack of biodegradation parameters that can be measured in the field for model input. As a result, most modeling applications at the field scale have resorted to first-order decay or instantaneous representation of the biodegradation process.

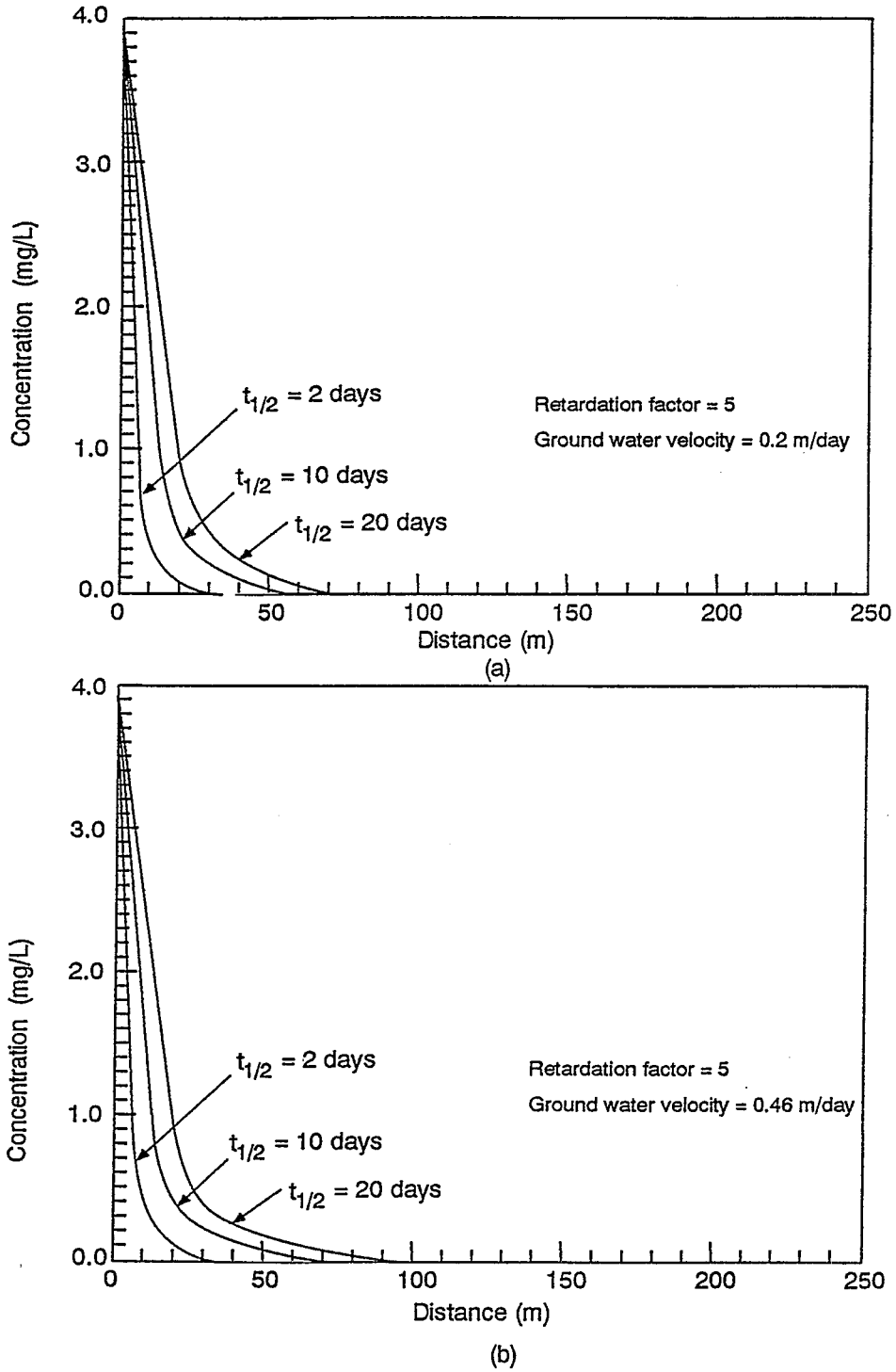


Figure 2. BIO1D model predictions for the Cliffs-Dow Superfund site (15).

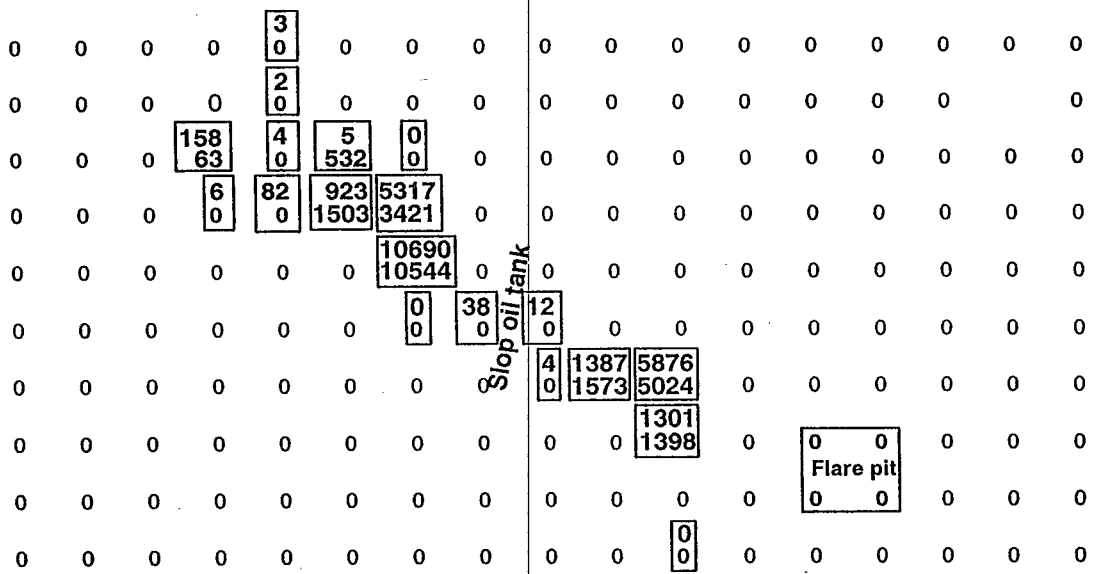


Figure 3. BIOPLUME II model predictions for the gas plant facility in Michigan (14)—top number: observed data; bottom number: simulated data.

References

1. Molz, F.J., M.A. Widdowson, and L.D. Benefield. 1986. Simulation of microbial growth dynamics coupled to nutrient and oxygen transport in porous media. Water Resour. Res. 22(8):1,207-1,216.

2. Borden, R.C., P.B. Bedient, M.D. Lee, C.H. Ward, and J.T. Wilson. 1986. Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation, 2. Field application. Water Resour. Res. 13:1,983-1,990.

3. Domenico, P.A. 1987. An analytical model for multidimensional transport of a decaying contaminant species. J. Hydrol. 91:49-58.

4. Srinivasan, P., and J.W. Mercer. 1988. Simulation of biodegradation and sorption processes in ground water. Ground Water 26(4):475-487.

5. Semprini, L., and P.L. McCarty. 1991. Comparison between model simulations and field results for *in situ* biorestoration of chlorinated aliphatics, 1. Biostimulation of methanotrophic bacteria. Ground Water 29(3):365-374.

6. Widdowson, M.A., F.J. Molz, and L.D. Benefield. 1988. A numerical transport model for oxygen- and nitrate-based respiration linked to substrate and nutrient availability in porous media. Water Resour. Res. 24(9):1,553-1,565.

7. Celia, M.A., J.S. Kindred, and I. Herrera. 1989. Contaminant transport and biodegradation, 1. A numerical model for reactive transport in porous media. Water Resour. Res. 25(6):1,141-1,148.

8. Rifai, H.S., P.B. Bedient, J.T. Wilson, K.M. Miller, and J.M. Armstrong. 1988. Biodegradation modeling at aviation fuel spill site. J. Environ. Eng. 114(5):1,007-1,029.

9. MacQuarrie, K.T.B., E.A. Sudicky, and E.O. Frind. 1990. Simulation of biodegradable organic contaminants in ground water, 1. Numerical formulation in principal directions. Water Resour. Res. 26(2):207-222.

10. Wheeler, M.F., C.N. Dawson, P.B. Bedient, C.Y. Chiang, R.C. Borden, and H.S. Rifai. 1987. Numerical simulation of microbial biodegradation of hydrocarbons in ground water. Proceedings of the Solving Ground Water Problems With Models Conference, Denver, CO (February 10-12). Dublin, OH: National Water Well Association (NWWA).

11. Tucker, W.A., C.T. Huang, J.M. Bral, and R.E. Dickinson. 1986. Development and validation of the underground leak transport assessment model (ULTRA). Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston, TX (October-November). Dublin, OH: National Water Well Association (NWWA). pp. 53-75.

12. Kinzelbach, W., W. Schäfer, and J. Herzer. 1991. Numerical modeling of natural and enhanced denitrification processes in aquifers. Water Resour. Res. 27(6):1,123-1,135.

13. Odencrantz, J.E., A.J. Valocchi, and B.E. Rittman. 1990. Modeling two-dimensional solute transport with different biodegradation kinetics. Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Houston, TX (October-November). Dublin, OH: National Water Well Association (NWWA).

14. Chiang, C.Y., J.P. Salanitro, E.Y. Chai, J.D. Colthart, and C.L. Klein. 1989. Aerobic biodegradation of benzene, toluene, and xylene in a sandy aquifer: Data analysis and computer modeling. Ground Water 6:823-834.

15. Klecka, G.M., J.W. Davis, D.R. Gray, and S.S. Madsen. 1990. Natural bioremediation of organic contaminants in ground water: Cliffs-Dow Superfund site. Ground Water 4:534-543.

Biogeochemical Processes in an Aquifer Contaminated by Crude Oil: An Overview of Studies at the Bemidji, Minnesota, Research Site

Robert P. Eganhouse, Mary Jo Baedecker, and Isabelle M. Cozzarelli
U.S. Geological Survey, Reston, VA

Abstract

Crude oil inadvertently released from a pipeline in a remote area of north-central Minnesota has altered the geochemistry of a shallow aquifer. Part of the oil was sprayed over a large area to the west of the pipeline, and another portion accumulated in an oil body that now floats on the water table to the east of the point of discharge. Dissolution of oil components into the ground water and microbial degradation of the oil have resulted in the formation of distinct geochemical zones in which a variety of natural biogeochemical reactions can be observed. Upgradient from the oil body in the "spray zone," concentrations of total dissolved organic carbon (TDOC), Ca, Mg, and HCO_3^- are greater and pH is lower than measurements observed in native ground water. These differences reflect the transport of oil constituents to the water table by recharge, oxidation under aerobic conditions, and dissolution of carbonates. Beneath and just downgradient from the oil body, oxygen is depleted, and anaerobic degradation reactions (Fe and Mn reduction, methanogenesis) dominate. This is evidenced by increased concentrations of Fe^{2+}, Mn^{2+}, CH_4, and TDOC in ground water. Volatile hydrocarbons, mainly benzene and its alkylated derivatives, represent 26 percent of the TDOC in this zone. Microbially mediated removal of these compounds within the anoxic zone is indicated by the presence of structurally related oxygenated intermediates (for example, alkylated benzenecarboxylic acids) and differences in the removal rates of isomeric alkylbenzenes. Downgradient from the anoxic zone, mixing of oxygenated water with plume constituents leads to removal of iron (via precipitation) and virtually all of the oil-derived organic constituents. Within a distance of 200 m downgradient from the oil body, the geochemistry of the ground water is virtually indistinguishable from that of native ground water. Data collected over an 8-yr period demonstrate that while the contaminant plume has become increasingly reducing in character, its size has not changed significantly. This attests to the efficiency of natural processes in removing/attenuating the oil-derived contaminants of primary concern at this site.

Introduction

Contamination of ground water by intentional or inadvertent releases of crude oil or refined petroleum products is a widespread problem, and a great deal of effort (and money) is presently being devoted to remediation efforts. The efficacy of current engineering approaches is subject to considerable debate. One thing is clear, however. For future remediation efforts to be effective and useful, we must improve our understanding of how nature responds to such impacts. In principle, this should permit the manipulation of natural processes for purposes of contaminant removal. Investigations that have been carried out at the Bemidji, Minnesota, crude oil spill site by the U.S. Geological Survey since 1984 are aimed at developing such an understanding. The present paper discusses some of the major findings of those studies.

Methods

Sampling and Analysis

Wells were installed at the study site using a hollow stem auger without lubricants or grease on the equipment (1). Augers for the drill rig and stainless steel well screens were steam cleaned prior to use. The polyvinyl chloride casings were 5 cm in diameter. Two types of wells were installed. Water table wells were emplaced so that stainless steel screens (1.5 m long) intersected the water table at the approximate midpoint of the screen; locations are shown in Figure 1. Deeper wells were installed below the water table with screen lengths of 0.15 m or 0.61 m (Figure 2).

Samples of water, sediment, and oil were collected and subjected to a variety of chemical analyses. Water samples to be used for determination of inorganic constituents and dissolved organic carbon were collected with submersible pumps, whereas a Teflon bailer was used to collect water for determination of organic constituents. The analyses included 1) **water**—dissolved oxygen (DO), volatile dissolved organic carbon (VDOC), nonvolatile dissolved organic carbon (NVDOC), methane, pH, Eh, major cations (Ca, Mg, Na, K), alkalinity, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, sulfide, iron (total δ Fe^{2+}), Mn^{2+}, Si, Ba, Al, Sr, $\delta^{13}C_{methane}$, $\delta^{13}C_{TIC}$ (TIC=total dissolved inorganic carbon), volatile hydrocarbons (VHCs), extractable hydrocarbons, XAD resin isolates, and low-molecular-weight organic acids; 2) **oil**—$\delta^{13}C$, elemental analysis (C,H,N,S), hydrocarbons, ^{13}C-NMR, and heavy metals; and 3) **sediment**—$\delta^{13}C$, hydrocarbons, and elemental analysis (C,H,N,S). Details of the methods of sample collection and analysis are given by Eganhouse et al. (2, 3) for hydrocarbons; by Leenheer and Huffman (4), Huffman and Stuber (5), and Thorn and Aiken (6) for XAD resin isolates; by Baedecker and Cozzarelli (7), Baedecker et al. (8), and Bennett et al. (9) for inorganic constituents, methane, and elemental analyses; and by Cozzarelli et al. (10, 11) for low-molecular-weight organic acids.

Site Description

The study site is in north central Minnesota near the town of Bemidji (Figure 1). The aquifer is a pitted and dissected glacial outwash underlain by a poorly permeable till at about 24 m below land surface. The outwash sediments are heterogeneous and composed of moderately calcareous (6 percent carbonates), moderately to poorly sorted sands consisting primarily of quartz and feldspar of fine-to-medium grain size (1, 12). Coring studies have revealed that the sands are variably interbedded with gravel deposits and clay lenses. The water table is 6 m to 10 m below land surface, and ground-water flow is to the east-northeast (Figure 1), discharging into an unnamed lake approximately 300 m downgradient of the spill site. Estimates of the flow velocities near the water table range from 0.05 meters/day (m/d) to 0.5 m/d (9) for fine-grained and coarse-grained sediment, respectively.

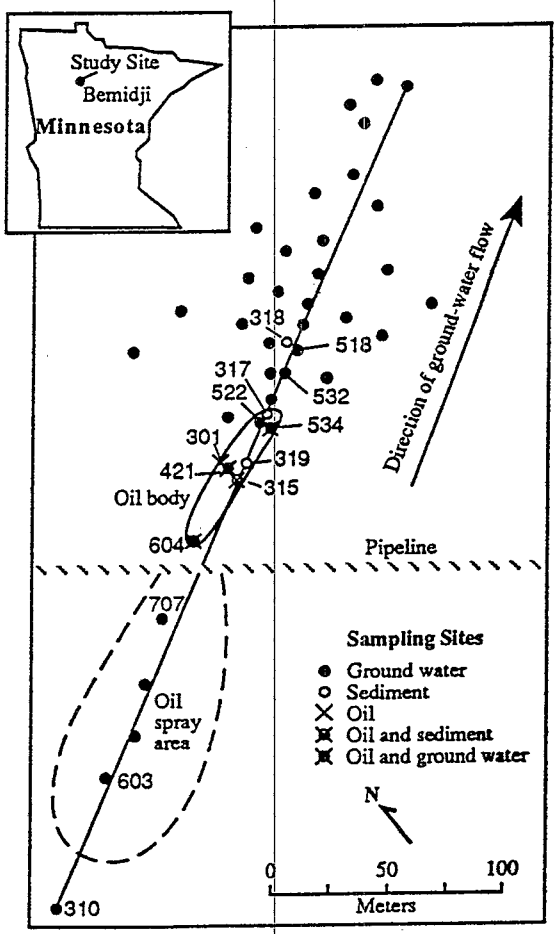


Figure 1. Map of the field site near Bemidji showing location of the ruptured pipeline, approximate location of the oil body, area over which oil was sprayed, and sampling locations (2).

A pipeline rupture occurred in August 1979, spilling 1,670 m^3 of crude oil. A portion of the 410 m^3 of crude oil unaccounted for after the cleanup effort is present in a body of oil floating on the water table. The oil body described here is irregularly distributed over a 7-m to 8-m vertical interval of unconsolidated sediment above the water table; by 1990, it had spread to a length of 70 m to 80 m in the direction of ground-water flow (13). An area upgradient of this oil body received oil spray during the pipeline rupture, and crude oil coated only the surface sediment. This area, extending 140 m to 180 m to the west-southwest of the pipeline and encompassing approximately 6,500 m^2, is hereafter referred to as the "spray area" (see Figure 1).

Results and Discussion

Effects of the Crude Oil on Ground-Water Geochemistry

Formation of Geochemical Zones. The inadvertent introduction of crude oil to this aquifer has resulted in marked alteration of geochemical conditions in the ground water. The driving force for these changes has been the microbial degradation of metabolizable organic matter, in this case represented by soluble constituents of the oil. After several years of research during the mid to late 1980s, it became evident that the saturated zone of this aquifer could be characterized by geochemically distinct zones. These zones, depicted in a cross section centered on the main contaminant plume in the direction of ground-water flow (Figure 2), correspond to: I—uncontaminated native ground water, II—ground water upgradient of the oil body but within the "spray area," III—anoxic ground water immediately beneath and downgradient of the oil body, IV—suboxic transitional zone where anoxic ground water from zone III mixes with more oxygenated ground water further downgradient, and V—oxygenated ground water that increasingly approaches conditions of the native ground water. The geochemistry of the ground water in each zone reflects that of the water upgradient from it and processes (e.g., sorption, dilution, degradation, dissolution, gas exchange) occurring within that zone.

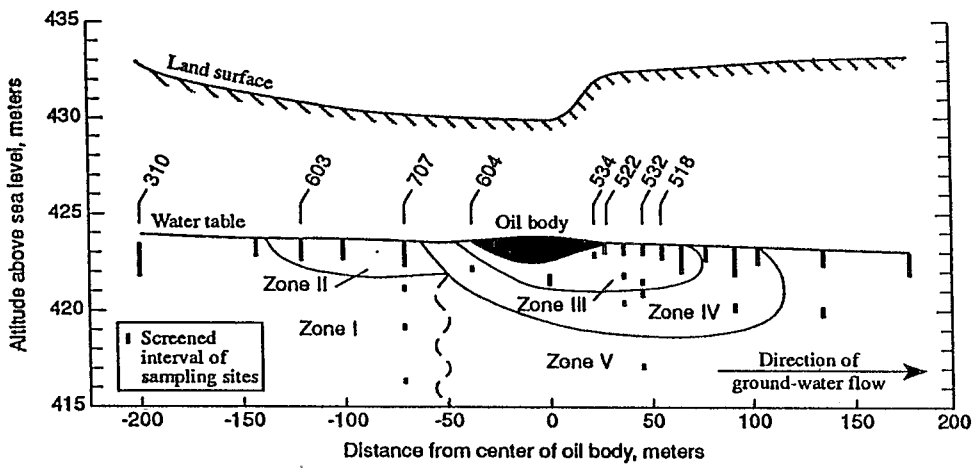


Figure 2. Cross section of the aquifer near Bemidji along main sampling transect. Locations of water table and deep wells indicated as filled bars (2). For a detailed description of zonation, see Baedecker et al. (8).

The native ground water (**zone I**) is a dilute Ca-Mg-HCO_3^- water with total dissolved solutes <400 mg/L, a Ca:Mg ratio of 2.2:1, a median DO concentration of 7.68 mg/L, and a pH of 7.6 to 7.8. TDOC concentrations are approximately 2 mg/L to 3 mg/L. The chemical composition is controlled by carbonate equilibria and, to a lesser extent, by dissolution of quartz, feldspar, and clay minerals and by the degradation of naturally occurring organic material (8).

Ground water within **zone II** is influenced by the aerobic degradation of soluble oil constituents originally deposited at land surface by the spraying of oil from the ruptured high pressure pipeline. In this area, oil is known to have penetrated the upper 4 cm to 6 cm of the soil. The quantities were insufficient, however, for formation of a discrete oil phase. Ground water in zone II exhibits elevated concentrations of TDOC, Ca, Mg and HCO_3^-; lower pH (about 0.5 to 1 pH unit); and a slightly reduced DO concentration. Carbon dioxide partial pressures (P_{CO2}) calculated by Bennett et al. (9) are as high as $10^{-1.5}$ atm (as compared with ambient atmospheric values of $10^{-3.5}$ atm). The TDOC concentrations are nearly an order of magnitude greater than those found in the native ground water. While the additional TDOC in zone II is undoubtedly derived from the oil, virtually all of it represents partially oxidized transformation products, not hydrocarbons (2). No VHCs were detected. The few petroleum hydrocarbons that are present have compositions that indicate extensive biodegradation. Presumably, some of the degradation/oxidation occurred in the unsaturated zone followed by transport of soluble transformation products to the water table during recharge. The slight depression of oxygen concentration in ground water in this zone indicates that some degradation is likely to be occurring within the ground water as well. If removal of the NVDOC is occurring via aerobic respiration, however, the rate of supply of NVDOC must exceed its rate of removal because NVDOC concentrations tend to increase with approach to zone III. Bennett and others (9) have suggested that the large increases in Ca, Mg, and HCO_3^- with increasing P_{CO2}, as well as the similarity of the [Ca +Mg]/[HCO_3-] mole ratio of ground water in this zone to that of the native ground water, indicate that the principal reaction responsible for generating the plumes of alkali-earth solutes is dissolution of carbonates by reaction with carbonic acid. Because these processes are occurring under oxic (as opposed to anoxic) conditions, the primary chemical signatures of the contaminant plumes reflect the products of organic remineralization (HCO_3^-) and transformation (TDOC) and those resulting from acidification (pH, Ca, Mg), not redox reactions.

Zone III encompasses ground water near, downgradient from (about 75 m), and in immediate contact with the oil to a depth of about 3 m below the water table. Dramatic changes in ground-water geochemistry result from the dissolution of soluble oil constituents and their metabolism, leading to complete consumption of oxygen and the dominance of anoxic degradation reactions, including iron and manganese reduction and methanogenesis. Sulfate reduction and denitrification are not important in this system because of the very low concentrations of SO_4^{2-} and NO_3^- found in the native ground water. In this zone, TDOC concentrations rise to a maximum of 48 mg/L, and a significant fraction of this is VDOC (42 percent). The volatile compounds are dominated (approximately 63 percent) by a mixture of saturated, aromatic, and alicyclic hydrocarbons derived from the oil, the most important constituents of which are benzene and a complex assemblage of alkylbenzenes. Methane is found in the ground water, and field measurements of Eh indicate a strongly reducing environment. In 1987 the average stable carbon isotope ratios for TDOC ($\delta^{13}C_{TIC}$) and methane ($\delta^{13}C_{methane}$) were -8.23 and -55.45 per mil, respectively. The average $\delta^{13}C$ value for TIC in native ground water is -12.55 per mil. The heavier ratio for TIC in zone III, thus, reflects fractionation resulting from methanogenesis. The most dramatic changes in inorganic chemistry are seen as large increases in the concentrations of dissolved iron and manganese that result from mobilization of these redox species in response to the microbially mediated oxidation of hydrocarbons. Silica concentrations also increase due to enhanced dissolution of silicate minerals. Other compounds present in the ground water of zone III, but not found in the oil or (except in trace amounts) ground water in zones I and II, are a complex mixture of oxygenated products of hydrocarbon degradation, including low-molecular-weight organic acids (10, 11). The acids are structurally related to coexisting monoaromatic hydrocarbons from the oil. Those

organic acids that have been identified correspond to aromatic hydrocarbons whose concentrations decrease most rapidly within the anoxic zone, whereas no potential acid intermediates were found for aromatics which appear to be more stable within zone III. These results signal the partial oxidation of hydrocarbons to more soluble metabolites.

Zone IV is a transition zone characterized by small but detectable quantities of oxygen. Dissolved iron and silica decrease to below detection limits at the boundary of this zone due to precipitation reactions. Low-molecular-weight organic acids are at or below detection limits, and the concentrations of all oil-derived hydrocarbons are much lower than in the ground water of zone III. Ca, Mg, and Sr also decrease but rather gradually. Bennett and others (9) have hypothesized that this is the result of dispersive mixing and that transport of these constituents is conservative.

Evolution of the Contaminant Plume. Figure 3 depicts the concentrations of dissolved Fe^{2+}, Mn^{2+}, methane, and $\delta^{13}C_{TIC}$ from ground water taken from zone III near the downgradient edge of the oil body for the years 1984 to 1992 (8, 14). At this site, concentrations of methane and Fe^{2+} increased by factors of 100 and 25, respectively, during the first 5 years. Thereafter, the concentrations of methane and Fe^{2+} have virtually leveled off. Over the same period, manganese concentrations first increased and then declined, whereas $\delta^{13}C_{TIC}$ has increased continuously. These variations in the contaminant plume chemistry reflect evolutionary changes in the biology and geochemistry of this perturbed system with continued supply of hydrocarbons and depletion of terminal electron acceptors.

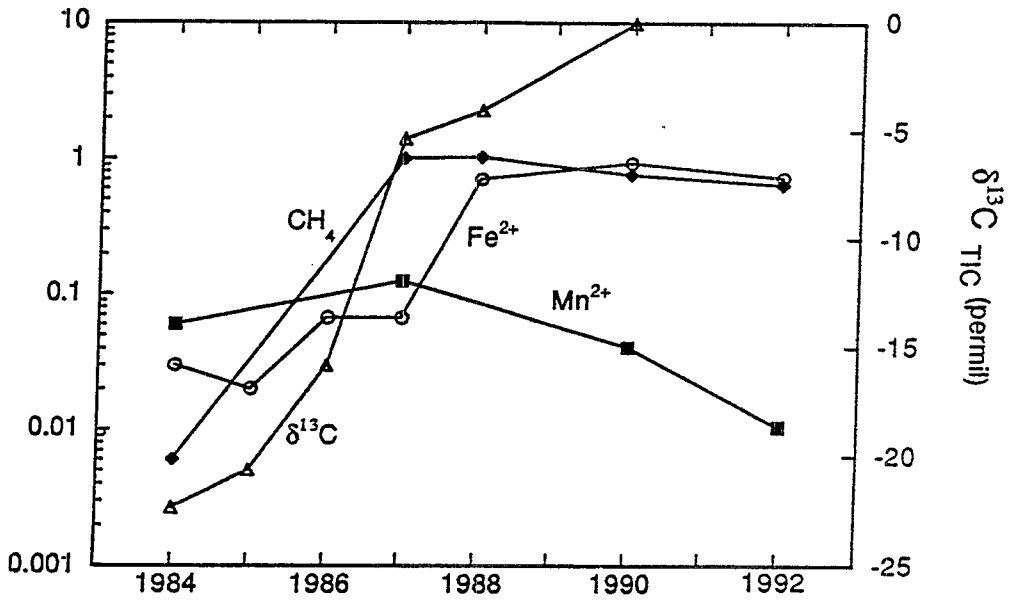


Figure 3. Concentrations of dissolved ferrous iron, manganese, methane (in millimoles), and $\delta^{13}C$ in per mil of TDOC for the years 1984 to 1992 (14).

In particular, it would appear that manganese reduction was an important degradative process at the earliest stages of plume evolution, but as time has progressed iron reduction and methanogenesis have become dominant, presumably due to depletion of the supply of reducible manganese. As of 1992, the dominant process at this location appears to be methanogenesis. This is supported by the steady increase in $\delta^{13}C_{TIC}$. During this same period, the distribution and size of the contaminant plume, as measured by the concentrations of monoaromatic hydrocarbons (2), have not changed appreciably. While our understanding of the factors controlling plume evolution remains limited and the size and shape of the contaminant plume itself has not changed, it is clear that the biogeochemistry within the plume is dynamic.

Transport and Fate of Oil-Derived Contaminants

The following discussion considers the transport and fate of the monoaromatic hydrocarbons within zones III and IV. Benzene is the dominant individual VHC in anoxic ground water near the leading edge of the oil body (70 percent), reaching concentrations in excess of 9,300 μg/L. The C_{1-4} alkylated benzenes are second in abundance, representing approximately 14 percent of the total VHCs. Alkanes, consisting of a complex mixture of normal and branched hydrocarbons with four to seven carbon atoms, account for 12 percent of the VHCs. Cyclic hydrocarbons (cyclopentanes and cyclohexanes), cycloaromatics (e.g., alkylated indans), and heteroatomic species (e.g., tetrahydrothiophenes) are relatively minor constituents (total less than 4 percent). Thirty-one meters farther downgradient from this site (but still within zone III), the VHC composition is markedly different. The relative abundance of alkanes (and toluene; see Figure 4) is reduced, and benzene plus monoaromatic hydrocarbons with two to four alkyl carbon atom substituents dominate (96 percent). Benzene represents 90 percent of the total VHCs. These compositional differences are also found among individual C_{1-4} (alkylated) benzenes. There are four isomeric C_2-benzenes, eight isomeric C_3-benzenes, and 22 isomeric C_4-benzenes. All of these compounds, with the exception of t-butylbenzene, which was not detected in the crude oil, are present in the contaminated ground water within zone III. The composition of the monoaromatic hydrocarbons changes systematically with distance downgradient from the oil body and with increasing depth in the saturated zone (15, 16). Most importantly, isomeric alkylbenzenes show dramatically different apparent removal rates downgradient from the oil body. Because these isomers have similar physical properties, the attenuation of VHCs (and therefore VDOC) is attributable to biological, rather than physical, processes.

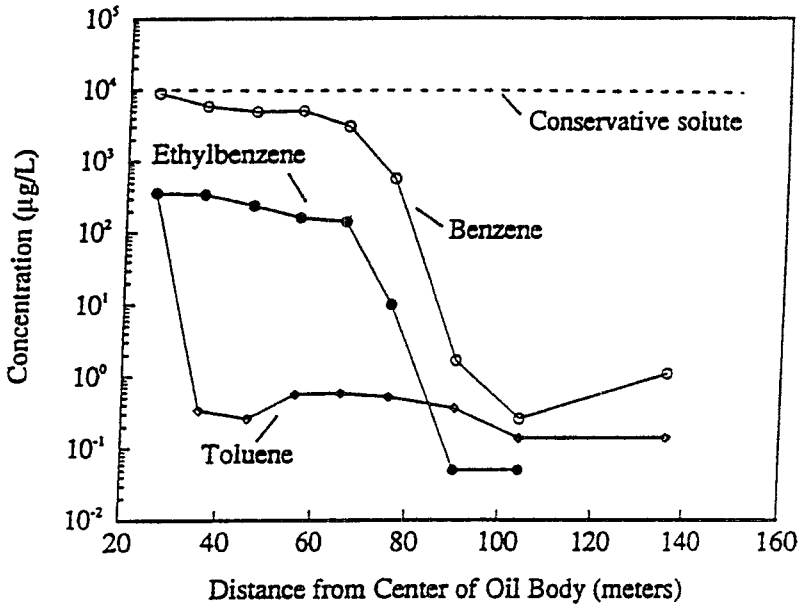


Figure 4. Concentrations of benzene, toluene, and ethylbenzene (μg/L) along the flowpath of the contaminant plume. Also shown is the concentration of a conservative solute with an assumed starting concentration of 10,000 μg/L. Model assumptions discussed in Baedecker et al. (8); figure from Mallard and Baedecker (17).

This hypothesis is reinforced by data illustrated in Figure 4. Here concentrations of benzene, toluene, ethylbenzene, and a conservative tracer (see Baedecker et al. [8] for discussion) are shown as a function of distance downgradient from the center of the oil body. Two features of these data are readily apparent. First, the concentration changes observed for these aromatic hydrocarbons greatly exceed what would be predicted on the basis of conservative transport. Second, because benzene, toluene, and ethylbenzene form an homologous series with increasing K_{OW}s (octanol-water partition coefficients), one would expect that a systematic pattern of removal rates would be found if sorption was the dominant process. This obviously is not the case, as toluene is very rapidly removed by comparison with either benzene or ethylbenzene. Clearly, biodegradation is the most important process limiting the transport of these hydrocarbons.

Conclusions

At the Bemidji field site, the introduction of crude oil to the subsurface has resulted in dramatic changes in the geochemistry of the ground water. Even so, natural processes, with biodegradation being most important, have effectively limited the transport of oil-derived contaminants to a distance of 200 m from the source. Continued monitoring of the contaminant plume has revealed the dynamic nature of the coupled biological and geochemical processes operative at this site. An understanding of these processes and the factors that affect plume evolution will be essential if we are to develop environmentally responsible remediation methods in the future.

References

1. Hult, M.F. 1984. Ground-water contamination by crude oil at the Bemidji, Minnesota, research site: An introduction. In: Proceedings of the U.S. Geological Survey toxic-waste technical meeting, Tucson, AZ (March 20-22). Water Res. Invest. Rep. 94-4188. pp. 1-15.

2. Eganhouse, R.P., M.J. Baedecker, I.M. Cozzarelli, G.R. Aiken, K.A. Thorn, and T.F. Dorsey. 1993. Crude oil in a shallow sand and gravel aquifer, II. Organic geochemistry. Appl. Geochem. 8:551-567.

3. Eganhouse, R.P., T. Dorsey, C. Phinney, and S. Westcott. 1993. Determination of C_6-C_{10} aromatic hydrocarbons in water by purge-and-trap capillary gas chromatography. J. Chromatog. 628:81-92.

4. Leenheer, J., and E.W.D. Huffman. 1979. Analytical method for dissolved organic carbon fractionation. Water Res. Invest. Rep. No. 79-4.

5. Huffman, E.W.D., and H.A. Stuber. 1985. Analytical methodology for elemental analysis of humic substances. In: Aiken, G.R., D.M. McKnight, R.L. Wershaw, and P. MacCarthy, eds. Humic substances in soil, sediment and water. New York, NY: John Wiley and Sons. pp. 433-456.

6. Thorn, K.A., and G.R. Aiken. 1989. Characterization of nonvolatile organic acids resulting from the biodegradation of crude oil by nuclear magnetic resonance spectrometry. In: Mallard, G.E., and S.E. Ragone, eds. Proceedings of the technical meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30, 1988). pp. 41-52.

7. Baedecker, M.J., and I.M. Cozzarelli. 1992. The determination and fate of unstable constituents in contaminated ground water. In: Lesage, S., and R.E. Jackson, eds. Ground-water quality and analysis at hazardous waste sites. New York, NY: Marcel Dekker. pp. 425-461.

8. Baedecker, M.J., I.M. Cozzarelli, D.I. Siegel, P.C. Bennett, and R.P. Eganhouse. 1993. Crude oil in a shallow sand and gravel aquifer, III. Biogeochemical reactions and mass balance modeling in anoxic ground water. Appl. Geochem. 8:569-586.

9. Bennett, P.C. D.I. Siegel, M.J. Baedecker, I.M. Cozzarelli, and M.F. Hult. 1993. Crude oil in a shallow sand and gravel aquifer, I. Hydrogeology and inorganic geochemistry. Appl. Geochem. 8:529-549.

10. Cozzarelli, I.M., M.J. Baedecker, R.P. Eganhouse, and D.F. Goerlitz. 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in ground water. Geochim. Cosmochim. Acta 58:863-877.

11. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground-water environment. Environ. Geol. Water Sci. 16:135-141.

12. Franzi, D.A. 1985. The surficial and subsurface distribution of aquifer sediments at the Bemidji research site, Bemidji, Minnesota. Presented at the Second Toxic-Waste Technical Meeting, Cape Cod, MA (October 21-25).

13. Essaid, H.I., W.N. Herkelrath, and K.M. Hess. 1991. Air, oil, and water distributions at a crude-oil spill site, Bemidji, Minnesota. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the technical meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15). pp. 614-620.

14. Baedecker, M.J., and I.M. Cozzarelli. 1994. Biogeochemical processes and migration of aqueous constituents in ground water contaminated with crude oil. In: Dutton, A.R., ed. Toxic substances and the hydrologic sciences. Minneapolis, MN: American Institute of Hydrology. pp. 69-70.

15. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1989. The fate and effects of crude oil in a shallow aquifer, II. Evidence of anaerobic degradation of monoaromatic hydrocarbons. In: Mallard, G.E., and S.E. Ragone, eds. In: Proceedings of the technical meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30, 1988). Water Res. Invest. Rep. 88-4220. pp. 21-34.

16. Eganhouse, R.P., T.F. Dorsey, C.S. Phinney, M.J. Baedecker, and I.M. Cozzarelli. 1987. Fate of monoaromatic hydrocarbons in an oil-contaminated aquifer: Evidence for the importance of microbial activity. In: Proceeding of the Geological Society of America 1987 annual meeting, Phoenix, AZ. 19:652.

17. Mallard, G.E., and M.J. Baedecker. 1993. Hydrocarbon transport and degradation in ground water: U.S. Geological Survey investigations. In: Pare, K.M., ed. Proceedings of the Air Combat Command environmental quality 1993 symposium, Langley AFB, VA (March 1-5) pp. 102-108.

Simulation of Flow and Transport Processes at the Bemidji, Minnesota, Crude-Oil Spill Site

Hedeff I. Essaid
U.S. Geological Survey, Menlo Park, CA

Abstract

The Bemidji, Minnesota, field site has provided an opportunity to study in detail the natural processes that occur following a crude-oil spill. Detailed field studies have characterized the subsurface oil distribution and the characteristics of the contaminated ground-water plume. Numerical models that simulate flow and transport processes are useful tools for integrating information collected in the field, for testing hypotheses, and for studying the relative importance of simultaneously occurring processes in complex, real-world systems. Numerical modeling of multiphase flow at the Bemidji site has illustrated the importance of spatial variability on the movement and distribution of oil in the subsurface. Solute-transport modeling that includes aerobic and anaerobic degradation processes is being used as a tool to study the field-scale, naturally occurring solute-transport and degradation processes occurring at the site.

Introduction

On August 20, 1979, a buried oil pipeline near Bemidji broke, spilling about 1.7×10^6 L (11,000 barrels) of crude oil (Figure 1). The site is located in a pitted and dissected glacial outwash plain. Depth to the water table ranges from 0 m to 8 m below land surface, and the flow through the aquifer is generally horizontal and northeastward towards an unnamed lake 300 m downgradient from the point of pipeline rupture. An estimated 1.2×10^6 L (7,800 barrels) of the spilled oil was removed by pumping from surface pools, trenching, burning, and excavating soil (1). The petroleum in the pipeline was under pressure, causing oil to be sprayed over approximately 6,500 m^2 when the pipeline broke. The oil collected in topographic depressions and trenched areas where large volumes of oil infiltrated into the subsurface, forming two main bodies of oil floating on the water table. The subsurface oil bodies provide a long-term, continuous source of hydrocarbon components that dissolve in and are transported with the flowing ground water.

Numerical models that simulate flow and transport processes are useful tools for integrating information collected in the field, for testing hypotheses, and for studying the relative importance of simultaneously occurring processes in complex, real-world systems. Many researchers working at the Bemidji site have focused considerable effort on characterizing the subsurface distribution of the oil and the nature of the resulting contaminated ground-water plume. This paper reviews this work, then briefly summarizes the results of numerical simulations of multiphase flow and of ground-water transport and biodegradation at the site.

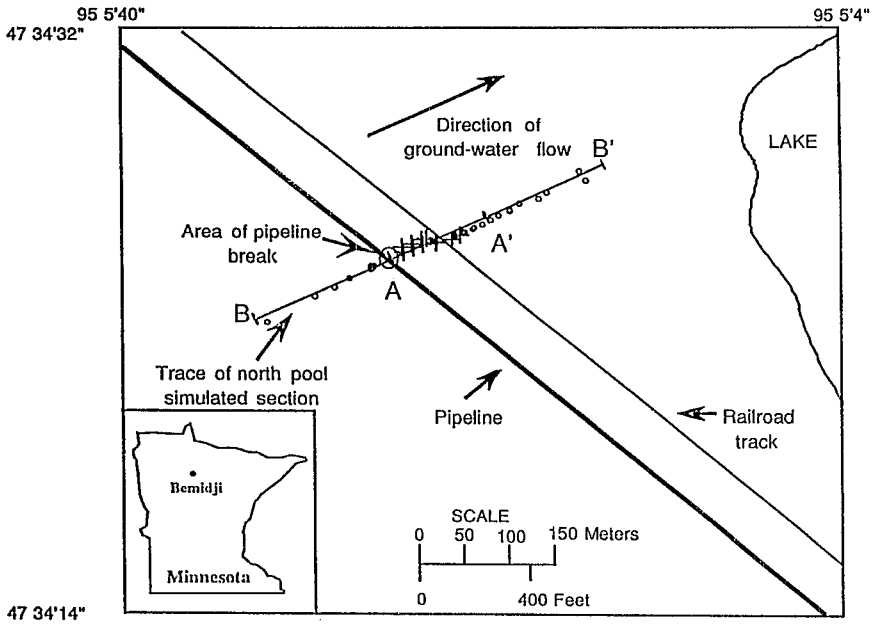


Figure 1. The north oil pool at the Bemidji crude-oil spill site. Plus symbols are locations of boreholes where samples were collected for saturation analyses, and circles are wells sampled for ground-water concentrations. The line A-A' is the trace of the multiphase flow simulation section, and B-B' is the trace of the transport simulation section.

The Observed Subsurface Oil Distribution

The Bemidji field site has provided an opportunity to study in detail the subsurface oil distribution following a spill. Field cores were collected for the purpose of determining the oil-saturation distribution (the fraction of the pore space that is occupied by oil) in the subsurface. Determination of the subsurface fluid-saturation distributions required the implementation of a sampling technique that could recover relatively undisturbed core samples from the unsaturated and saturated zones while maintaining the *in situ* pore-fluid distribution (2). To improve field sample collection, a freezing-tip core barrel was developed and used for sample collection (3). To allow visual inspection of the cores in the field, clear polycarbonate liners, 47 mm in diameter and 1.5 m long, were used within the core barrel.

Following retrieval, the cores were frozen and cut into 78-mm long subsamples using a circular saw fitted with a masonry blade. The oil saturation of each core was determined in the laboratory using a porous polyethylene (PPE) technique (2,4). In this process, strips of hydrophobic PPE are placed into a slurry created by adding water to a core sample. The PPE absorbs the oil from the sample but does not take up water. The amount of oil present in the core is calculated from the change in weight of the oily PPE strips. The sample is then dried in an oven, and water saturation is determined gravimetrically. Air saturation can then be calculated by subtracting the sum of oil and water saturation from unity. Following the saturation analysis, each sample was sieved to obtain the particle-size distribution.

To date, samples have been collected and analyzed from 10 boreholes (550 subsamples) at the site of the north oil pool (Figure 1). The three-dimensional distribution of oil saturation at the north pool obtained by kriging the observed data is shown in Figure 2 (5, 6). The oil distribution at this site is complex. A considerable amount of oil remains in the unsaturated zone at locations where oil infiltrated from a trench excavated following the spill. The maximum oil saturation measured at this site (0.74) was located downgradient from the zone of oil infiltration. The body of oil floating on the water table is not lens-shaped. The oil-saturation contours follow a sinuous path that is roughly parallel to the direction of ground-water flow. Thin silt lenses at the north pool site appear to have considerable influence on the observed oil-saturation distribution. These layers result in high residual oil saturations in the unsaturated zone and cause the shape of the oil body floating on the water table to be complex and irregular rather than lens-shaped.

Geostatistical and multiphase flow simulation have been used to assess the effect of spatial variability of hydraulic properties on the oil-saturation distribution at the site. Because of the difficulty of measuring sediment hydraulic properties for oil-contaminated samples, the particle-size distribution data were used to estimate the permeabilities (k) of the field samples and the retention curves (7). The mean and variance of the log(k) distribution (k in m^2) were -11.2 and 0.25, respectively, at the north pool. Figure 3 shows a cumulative probability plot of log(k) at the site. A linear relation indicates a lognormal distribution of k, and the slope of the line is related to the variance of k. The north pool plot of log k appears to consist of two linear segments, a distribution that suggests that the permeability distribution at this site consists of two lognormal populations: a coarse fraction (log(k)>-11.64) and a fine fraction (log(k)<-11.64).

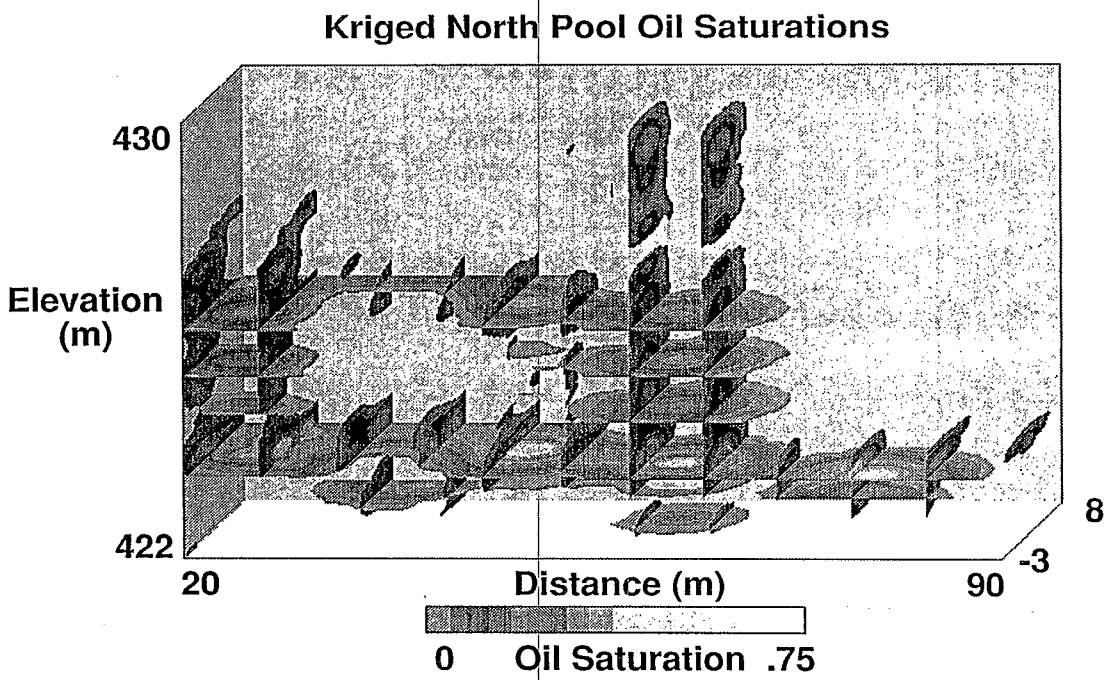


Figure 2. Three-dimensional oil saturation distribution at the north oil pool site. The water table is at an elevation of about 423.5 m above sea level.

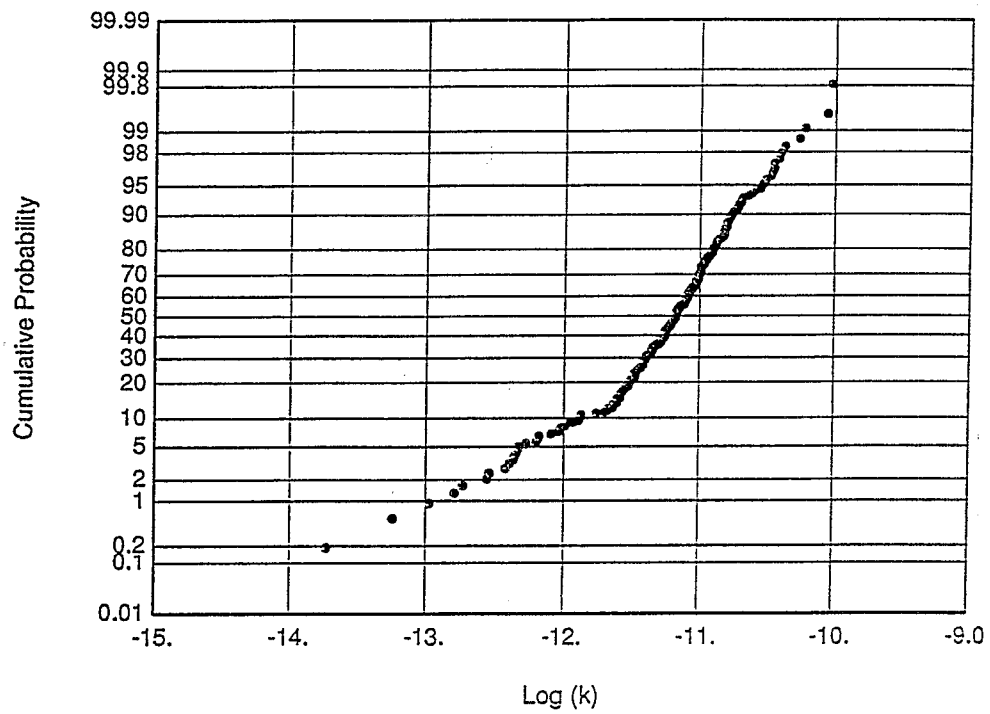


Figure 3. Cumulative probability plot of log (permeability) at the north pool site.

To obtain a regular grid of k values needed for the multiphase flow simulations, geostatistical simulation techniques (8) were used to generate k distributions for the north pool site that were conditioned on the values estimated from the core samples. A permeability realization was obtained that reproduced the geometry of the fine and coarse fractions and also reproduced the variability structure within these fractions. The details of this process are explained by Dillard (9) and Dillard et al. (10).

Multiphase Flow Modeling

A two-dimensional numerical model was developed and used to simulate multiphase flow along a longitudinal vertical transect parallel to the direction of flow at the north oil pool. The model solves a mass balance equation for the oil and water phases, assuming that the air phase is maintained at atmospheric pressure. An important feature of the model is that it incorporates hysteretic relations between capillary pressures and fluid saturations. The details of the model and the approaches used are given by Essaid et al. (7).

The model was used to simulate subsurface flow from the time of the spill in August 1979 until the samples were collected in June 1990. The simulated section was 120 m long and 10 m deep. The initial condition for the simulation was a hydrostatic water pressure distribution corresponding to the measured water-table elevation at the time of sampling. The lateral and bottom boundaries were assumed to be hydrostatic water-pressure boundaries. Oil was assumed to infiltrate through five constant oil pressure nodes at the top boundary representing the trench

that was excavated following the spill. Oil infiltration was stopped when the cumulative oil infiltration was equal to the estimated oil mass in the observed transect. More details of the north pool simulation are given by Dillard (9) and Dillard et al. (10).

Data from the first sample transect (Figure 4a) were compared with the two-dimensional simulated oil-saturation distribution. In the first simulation, a uniform mean k of 5×10^{-12} m^2 and uniform mean capillary pressure/saturation function parameters were used. A uniform k resulted in a symmetric, lens-shaped oil body (Figure 4b) that did not reflect the features of the observed oil distribution. In the second simulation, spatial variability of hydraulic properties was introduced, resulting in variability in oil saturations within the lens (Figure 4c). Very little oil was trapped in the unsaturated zone. The shape of the oil body floating on the water table became complex and irregular, with zones of low oil saturation corresponding to the low permeability silt layers. In the third simulation, hysteresis was introduced, causing more oil to become entrapped in the unsaturated zone (Figure 4d). The modeling results suggest that the silt layers and spatial variability exert a strong control on the oil distribution in the subsurface.

The Observed Ground-Water Plume

Numerous researchers working at the Bemidji crude-oil spill site have documented evidence for microbial activity and degradation of petroleum hydrocarbons in the field (11-18). As a result of these studies, five geochemical zones in ground water (Figure 5) have been identified at the site (11,12,19). Zone 1 consists of oxygenated, uncontaminated native ground water. Zone 2, which is below the area where the land surface was sprayed by oil following the pipeline rupture, is characterized by reduced oxygen concentrations and the presence of refractory high molecular-weight hydrocarbons. Zone 3, beneath and immediately downgradient from the separate-phase oil body, consists of an anoxic plume of ground water that contains high concentrations of hydrocarbons and methane. Zone 4 is the transition zone from anoxic conditions to fully oxygenated conditions, and concentrations of hydrocarbons decrease rapidly as a result of aerobic degradation processes. Zone 5 consists of oxygenated water downgradient of the contamination plume that contains slightly elevated concentrations of dissolved constituents. Long-term monitoring of the plume since 1984 has shown that, near the water table, the concentration of total dissolved organic carbon (TDOC) and dissolved oxygen (DO) downgradient from the oil body has remained relatively stable with time. In the anoxic zone (Zone 3), concentrations of reduced manganese (Mn) and iron (Fe) and of methane have increased with time, indicating a sequence of Mn reduction followed by Fe reduction and methanogenesis.

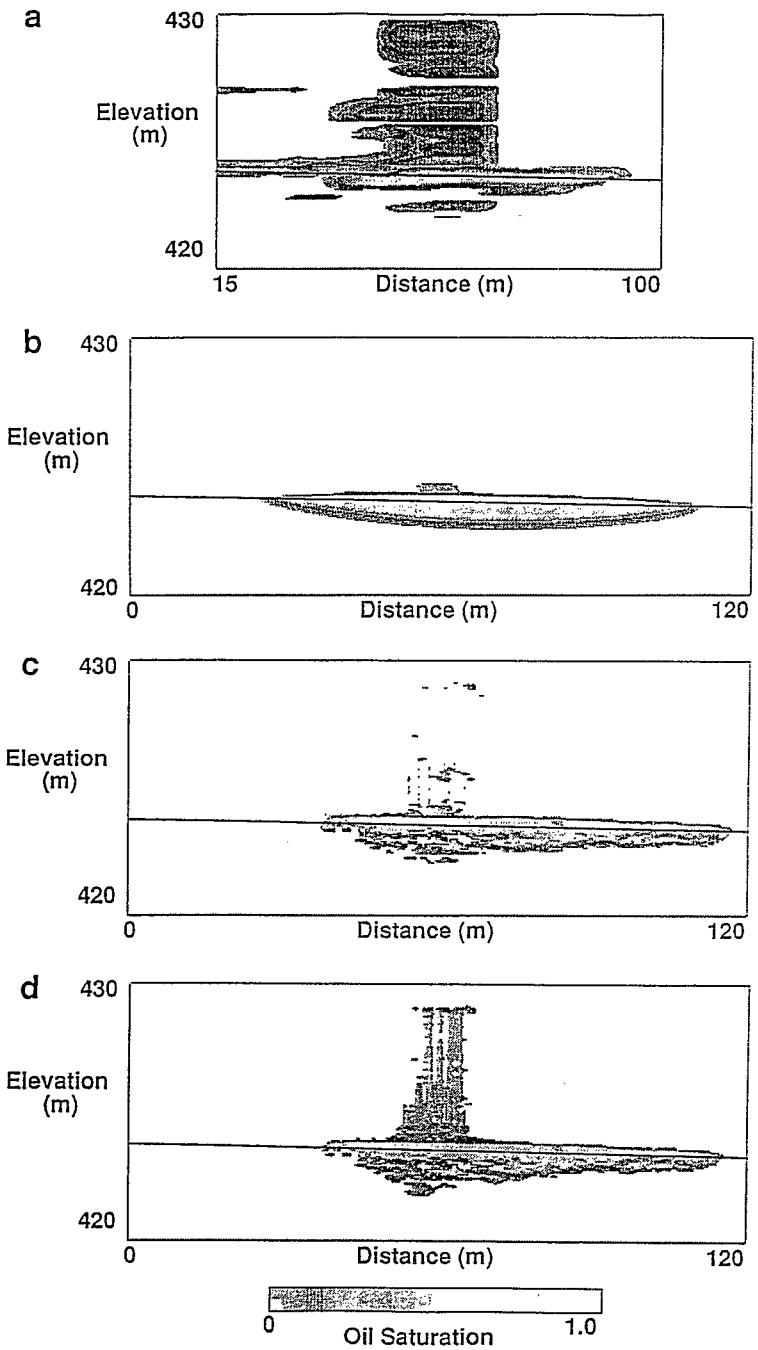


Figure 4. Oil saturation distributions along the sample transect: a) observed oil saturations, b) simulated oil saturations with uniform mean properties, c) simulated oil saturation with spatially variable properties, d) simulated oil saturation with spatially variable properties and hysteresis.

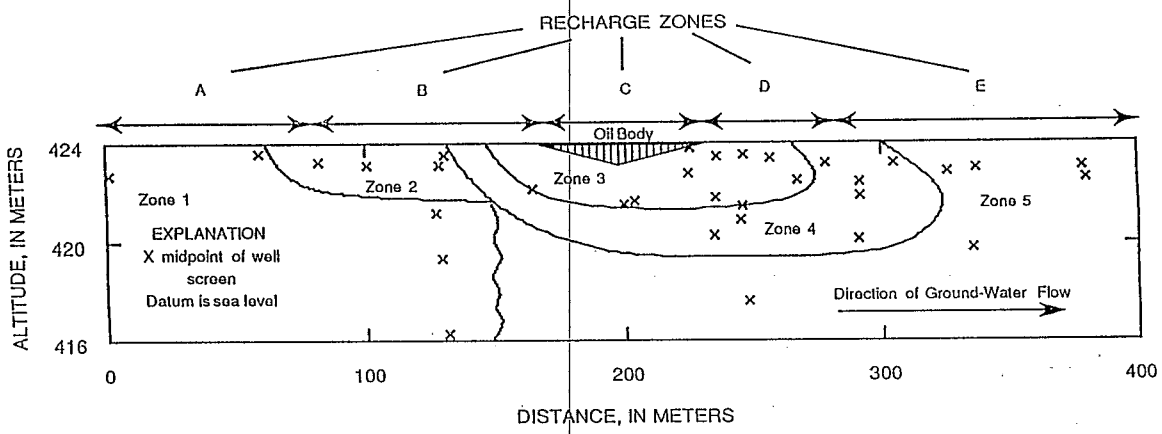


Figure 5. The simulated cross section showing the five geochemical zones in ground water.

Ground-Water Transport and Biodegradation Modeling

A two-dimensional, multispecies solute-transport model that incorporates biodegradation is being developed and applied to the ground-water system at the Bemidji site. The model is being used to quantify the field-scale degradation processes and to identify the important factors affecting the distribution of solute species in the field. The model simulates the aerobic and anaerobic degradation processes that have been observed in the contaminated ground-water plume at the spill site. The U.S. Geological Survey's Method of Characteristics transport model (20, 21) was expanded to handle multiple solutes and to include biodegradation terms. The approach of Kindred and Celia (22) was used to represent the biodegradation terms in the transport equation. Details of the model are given by Essaid et al. (23).

A vertical cross section of unit width that is approximately parallel to the direction of ground-water flow was simulated using the transport model for the period from the time of the spill in 1979 until September 1990 (Figure 5). Ground-water samples from numerous wells along this section have been analyzed over time (11,12,15). Steady-state flow, no sorption, and isothermal conditions were assumed. Four solutes and two microbial populations were modeled. TDOC was split into two fractions: degradable dissolved organic carbon (DDOC) and refractory dissolved organic carbon (RDOC). The remaining two solutes modeled were DO and methane. To represent the aerobic and anaerobic degradation processes, aerobic and methanogenic populations of bacteria were included in the simulations. Competitive inhibition was used to represent the suppression of methanogenesis by oxygen. In this manner, as oxygen in the ground water is consumed and an anoxic zone develops, the methanogens begin to flourish, resulting in increased methane production. Iron and manganese reductions were not included because of the complexity of incorporating the rock-water interactions of dissolution and precipitation into the transport model.

For simulation purposes, the system was represented by an initially clean aquifer with background dissolved organic carbon concentrations and fully oxygenated water. Following the oil spill, it was assumed that DDOC and RDOC dissolved and entered the aquifer with recharge water. The estimated values of initial concentrations and recharge water concentrations for each solute are given in Table 1. The oil present in the pore space within the oil body reduces water flow through this zone. The magnitude of reduction of water flow is a complex function of the oil distribution. As a first approximation of this effect, the hydraulic conductivity and recharge rate in the zone of the oil body were reduced to 25 percent of the aquifer values. No measurements or estimates are available for many of the transport and biodegradation parameters under natural field conditions. Therefore, reasonable estimates of these values were used in the simulations. The details of the simulation parameters and boundary conditions are given by Essaid et al. (23).

Table 1. Initial and Recharge Water Concentration (mg/L)*

Solute	Initial Concentration	Recharge Zone				
		A	B	C	D	E
DDOC	0.0	0.0	10.0	100.0	0.0	0.0
RDOC	2.0	2.0	20.0	30.0	2.0	2.0
TDOC	2.0	2.0	30.0	130.0	2.0	2.0
DO	9.0	9.0	3.0	0.0	0.0	9.0
Methane	0.0	0.0	0.0	0.0	0.0	0.0

*Recharge zones A through E are shown in Figure 5.

Transport Simulation Results

Observed and simulated profiles of TDOC, DO, and methane near the water table are plotted in Figure 6. The observed and simulated concentration profile of TDOC is shown in Figure 6a. The observed points show a concentration distribution at the water table that is relatively stable with time. The simulation has captured this feature, as can be seen by the similarity between the simulated 1986 and 1990 concentration profiles. There is an increase in TDOC concentration in the upgradient spray zone, followed by a rapid increase in TDOC concentration in the zone of the oil body. Downgradient from the oil body, the TDOC concentration decreases gradually to the background concentration. This decrease is a result of microbial and physical processes. There is anaerobic degradation of DDOC within the anoxic zone near the oil body and aerobic degradation of DDOC at the margins of the plume, where oxygenated recharge and ground water are encountered. Also, there is dilution of TDOC downgradient from the oil body as a result of the physical processes of displacement and mixing of flowing ground water with recharge water.

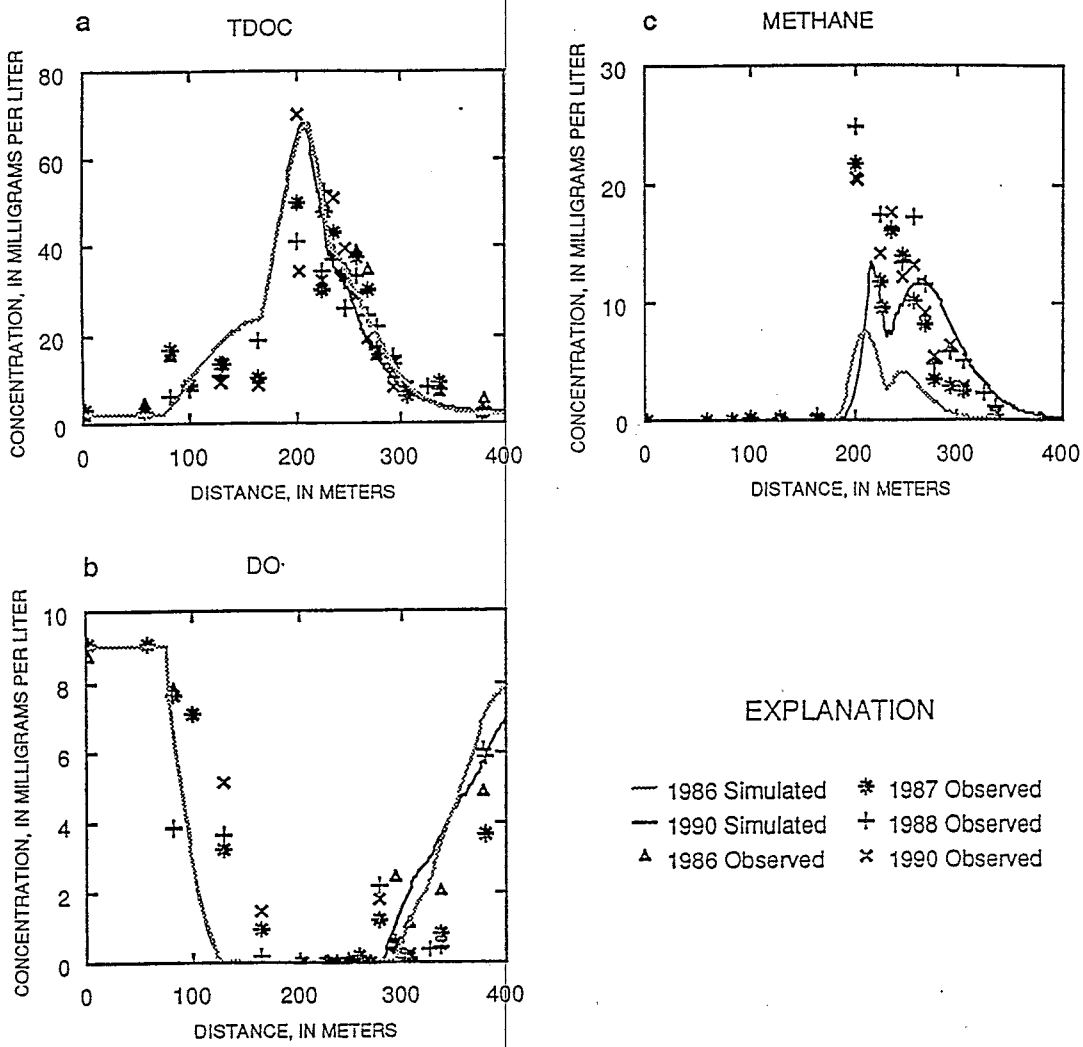


Figure 6. Graphs of simulated and observed concentrations at the water table: a) TDOC, b) DO, c) methane.

The simulated DO concentration (Figure 6b) decreases in the spray zone because of the assumed decrease in DO concentration in recharge water, caused by degradation of hydrocarbons in the unsaturated zone and by the consumption of oxygen by degradation in the ground water. Near the oil body and immediately downgradient from it, the DO of the recharge water is assumed to have been completely consumed in the unsaturated zone. An anoxic zone develops in this area. Farther downgradient, DO begins to increase as oxygenated recharge water enters the system.

Methane is produced in the anoxic zone that develops in the immediate vicinity and downgradient of the oil body. The methane peak is displaced downgradient from the center of the oil body because of the input of methane-free ground water from the upgradient area. The predicted decline in methane concentration at a distance of 230 m (Figure 6c) is a result of the upwelling of oxygenated water caused by the upward bending of flow lines around the oil body. The simulated profiles show a marked increase in methane production from 1986 to 1990 as the population of methanogens increases. This increase in methanogenesis results in a slight decrease in TDOC concentrations from 1986 to 1990 (Figure 6a). The rate of increase in methane production was quite sensitive to the biodegradation parameters used in the simulation.

To examine the effect of degradation on DDOC in the aquifer, two-dimensional distributions of DDOC for three different simulations are shown in Figure 7. In the first simulation, there is no degradation (Figure 7a); in the second simulation, degradation occurs (Figure 7b); and in the third simulation, degradation occurs and the hydraulic conductivity distribution is heterogeneous (Figure 7c). The distribution of DDOC for the case with no degradation (Figure 7a) reflects the physical processes of dispersion, diversion of flow around the oil body, and the depression of the plume beneath the water table because of the deflection of flow lines by incoming recharge water.

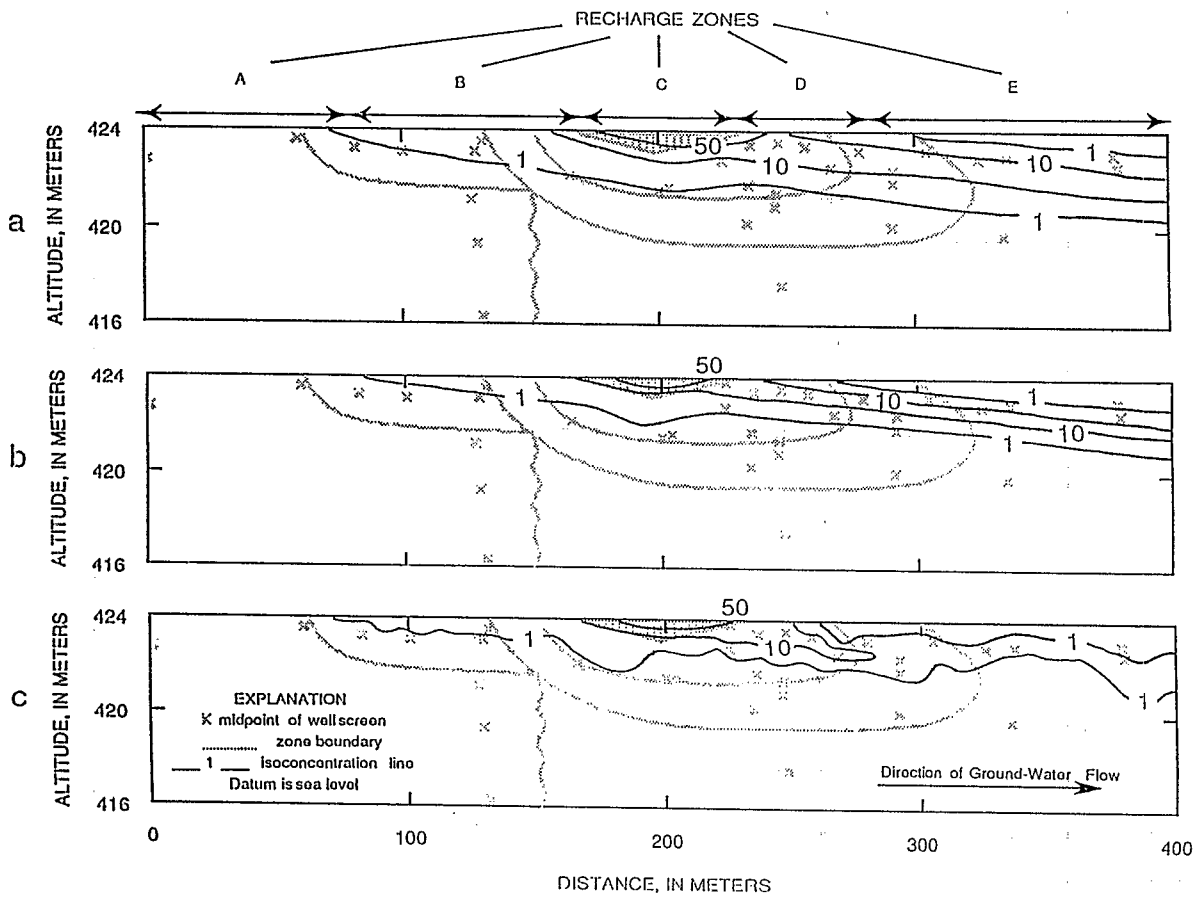


Figure 7. Simulated two-dimensional distributions of DDOC: a) with no degradation, b) with degradation, c) with degradation and spatial variability.

In the second simulation, the anaerobic and aerobic degradation processes result in a contaminant plume that is narrower than the plume in the first simulation and whose concentration gradients are comparatively sharp at the edges (Figure 7b). In this simulation, 46 percent of the total DDOC mass entering the aquifer is degraded: 14 percent by anaerobic degradation and 32 percent by aerobic degradation.

Previous work has shown that the hydraulic properties of the aquifer are spatially variable (7,9). To make the simulation more realistic, a heterogeneous hydraulic conductivity distribution was created using the methods of Dillard et al. (10) and was used in the transport model. Because of the complex flow field, an irregularly shaped plume develops (Figure 7c). The variability in flow paths and flow velocities results in increased mixing and dispersion of ground water. This, in turn, results in increased biodegradation. In this simulation, of the total DDOC mass entering the aquifer, 60 percent is degraded: 21 percent by anaerobic degradation and 39 percent by aerobic degradation.

The simulations represent a highly simplified representation of the true field conditions and neglect Fe and Mn reduction. Also, the parameters used in the simulations are highly uncertain. Nevertheless, the results do reproduce the general features of the observed contaminated ground-water plume. In addition to the kinetics of the biodegradation processes, important factors that affect the magnitude of degradation and the distribution of the solutes in the field are the recharge influx and the degree of dispersion and mixing in the ground-water system caused by heterogeneity of the hydraulic conductivity.

Summary

The Bemidji crude-oil spill site has provided an opportunity to study in detail the processes that occur following a spill of an organic immiscible fluid that is slightly soluble in water. Detailed field studies have characterized the subsurface oil distribution and the characteristics of the contaminated ground-water plume. Numerical modeling of multiphase flow has illustrated the importance of spatial variability on the movement and distribution of oil in the subsurface. Solute-transport modeling that includes aerobic and anaerobic degradation processes is being used as a tool to study the field-scale solute-transport and degradation processes. In addition to the kinetics of the biodegradation processes, important factors that affect the distribution of the solutes in the field are the recharge influx and the degree of dispersion and mixing in the ground-water system.

References

1. Hult, M.F. 1984. Ground-water contamination by crude oil at the Bemidji, Minnesota, research site: An introduction. In: Hult, M.F., ed. Ground-water contamination by crude oil at the Bemidji, Minnesota, research site. Water Res. Invest. Rep. 84-4188. pp. 1-15.

2. Hess, K.M., W.N. Herkelrath, and H.I. Essaid. 1992. Determination of subsurface fluid contents at a crude-oil spill site. J. Contam. Hydrol. 10:75-96.

3. Murphy, F., and W.N. Herkelrath. 1994. A sample-freezing drive shoe for a wireline-piston core sampler. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94:4014.

4. Cary, J.W., J.F. McBride, and C.S. Simmons. 1991. Assay of organic liquid contents in predominantly water-wet unconsolidated porous media. J. Contam. Hydrol. 8:135-142.

5. Essaid, H.I., W.N. Herkelrath, and L.A. Dillard. 1994. Field and modeling studies of multiphase fluid flow at the Bemidji, Minnesota, crude-oil spill site. In: Dutton, A.R., ed. Toxic Substances and the Hydrologic Sciences. Minneapolis, MN: American Institute of Hydrology. pp. 52-68.

6. Herkelrath, W.N., H.I. Essaid, and L.A. Dillard. 1994. Multiphase fluid distributions in a shallow water-table aquifer contaminated by crude oil. In: Dracos, T.H., and F. Stauffer, eds. Proceedings of the IAHR/AIRH Symposium on Transport and Reactive Processes in Aquifers, Zurich, Switzerland (April 11-15). Rotterdam, Netherlands: A.A. Balkema. pp. 537-542.

7. Essaid, H.I., W.N. Herkelrath, and K.M. Hess. 1993. Simulation of fluid distributions observed at a crude-oil spill site incorporating hysteresis, oil entrapment, and spatial variability of hydraulic properties. Water Resour. Res. 29(6):1,753-1,770.

8. Deutsch, C.V., and A.G. Journel. 1992. GSLIB: Geostatistical Software Library and user's guide. New York: Oxford University Press.

9. Dillard, L.A. 1993. Multiphase flow modeling of a crude-oil spill site using geostatistical simulation of soil hydraulic properties. M.S. thesis. Stanford, CA: Stanford University.

10. Dillard, L.A., H.I. Essaid, and W.N. Herkelrath. 1994. Multiphase flow modeling at the Bemidji, Minnesota, crude-oil spill site using geostatistical simulation of soil hydraulic properties. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

11. Baedecker, M.J., I.M. Cozzarelli, D.I. Siegel, P.C. Bennett, and R.P. Eganhouse. 1993. Crude oil in a shallow sand and gravel aquifer, 3. Biogeochemical reactions and mass balance modeling in anoxic ground water. Appl. Geochem. 8:569-586.

12. Bennett, P.C., D.I. Siegel, M.J. Baedecker, and M.F. Hult. 1993. Crude oil in a shallow sand and gravel aquifer, 1. Hydrogeology and inorganic geochemistry. Appl. Geochem. 8:529-549.

13. Chang, F.H., H. Wang, B. Denzin, and J. Buller. 1991. Kinetics of crude-oil biodegradation by bacteria indigenous to sediment and ground water. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15, 1991). Water Res. Invest. Rep. 91-4034. pp. 646-649.

14. Cozzarelli, I.M., R.P. Eganhouse, and M.J. Baedecker. 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground-water environment. Environ. Geol. Water Sci. 16:135-141.

15. Eganhouse, R.P., M.J. Baedecker, I.M. Cozzarelli, G.R. Aiken, K.A. Thorn, and T.F. Dorsey. 1993. Crude oil in a shallow sand and gravel aquifer, 2. Organic geochemistry. App. Geochem. 8:551-567.

16. Hiebert, F.K., and P.C. Bennett. 1992. Microbial control of silicate weathering in organic rich ground water. Science 258:278-281.

17. Hult, M.F., M.K. Landon, and H.O. Pfannkuch. 1991. Field validation of conceptual models of mobilization and transport of volatile petroleum derivatives in the unsaturated zone near Bemidji, Minnesota. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15, 1991). Water Res. Invest. Rep. 91-4034. pp. 621-626.

18. Lovley, D.R., M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.J.P. Phillips, and D.I. Siegel. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. Nature 339:297-299.

19. Baedecker, M.J., D.I. Siegel, P. Bennett, and I.M. Cozzarelli. 1989. The fate and effects of crude oil in a shallow aquifer, I. The distribution of chemical species and geochemical facies. In: Mallard, G.E., and S.E. Ragone, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30, 1988). Water Res. Invest. Rep. 88-4220. pp. 13-20.

20. Goode, D.J., and L.F. Konikow. 1989. Modification of a method-of-characteristics solute-transport model to incorporate decay and equilibrium-controlled sorption or ion exchange. Water Res. Invest. Rep. 89-4030. p. 65.

21. Konikow, L.F., and J.D. Bredehoeft. 1978. Computer model of two-dimensional solute transport and dispersion in ground water. U.S. Geological Survey Techniques of Water Resources Investigations. Book 7.

22. Kindred, J.S., and M.A. Celia. 1989. Contaminant transport and biodegradation, 2. Conceptual model and test simulations. Water Resour. Res. 26(6):1,149-1,160.

23. Essaid, H.I., M.J. Baedecker, and I.M. Cozzarelli. 1994. Use of simulation to study field-scale solute transport and biodegradation at the Bemidji, Minnesota, crude-oil spill site. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the Technical Meeting of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014 (in press).

An Overview of Anaerobic Transformation of Chlorinated Solvents

Perry L. McCarty
Department of Civil Engineering, Stanford University, Stanford, CA

Abstract

Intrinsic cometabolic transformation of chlorinated solvents commonly occurs at sites where co-contaminants are present as primary substrates to support the energy needs and metabolic activities of transforming bacteria. The extent of transformation that occurs depends upon the relative concentration of primary substrates and the microorganisms and environmental conditions present. Reduction of tetrachloroethene (PCE) and trichloroethene (TCE) to ethene has occurred at many sites, although transformations are often not complete. Evidence for intrinsic biotransformation of chlorinated aliphatic hydrocarbons (CAHs) is provided by the presence of CAH transformation products and indicators of anaerobic biogical activity, such as the disappearance of dissolved oxygen, nitrates, and sulfates, and the production of methane and soluble iron (II).

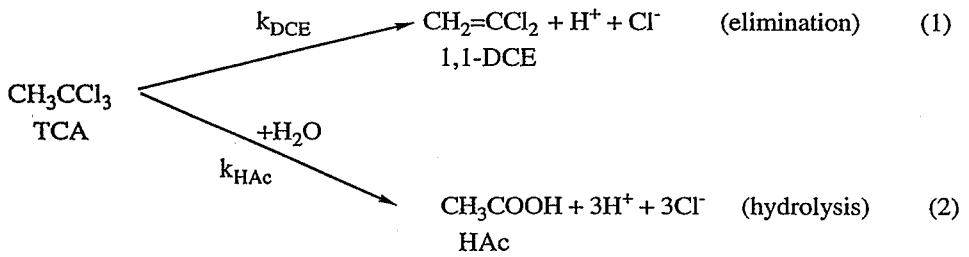
Introduction

Chlorinated solvents and their natural transformation products represent the most prevalent organic ground-water contaminants in the country. These solvents, consisting primarily of CAHs, have been used widely for degreasing of aircraft engines, automobile parts, electronic components, and clothing. Only during the past 15 years has it become recognized that CAHs can be transformed biologically (1). Such transformations sometimes occur under the environmental conditions present in an aquifer in the absence of planned human intervention, a process called intrinsic biotransformation (2). Conditions under which this is likely to occur with CAHs and the end products that can be expected are discussed in this paper.

The major chlorinated solvents are carbon tetrachloride (CT), PCE, TCE, and 1,1,1-trichloroethane (TCA). These compounds can be transformed by chemical and biological processes in soils to form a variety of other CAHs, including chloroform (CF), methylene chloride (MC), cis- and trans-1,2-dichloroethene (c-DCE, t-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1-dichloroethane (DCA), and chloroethane (CA). In CAH transformation, the microorganisms responsible cannot obtain energy for growth from the transformations. The transformations are brought about through co-metabolism or through interactions of the CAHs with enzymes or cofactors produced by the microorganisms for other purposes. In co-metabolism, other organic chemicals must be present to serve as primary substrates to satisfy the energy needs of the microorganisms. Chemical transformations of some CAHs can also occur within the timeframe of interest in ground water. Transformations that are likely, and the environmental conditions required, are discussed below.

Chemical Transformation

TCA is the only major chlorinated solvent that can be transformed chemically in ground water under all conditions likely to be found and within the one- to two-decade time span of general interest, although chemical transformation of CT through reductive processes is a possibility. TCA chemical transformation occurs by two different pathways, leading to the formation of 1,1-DCE and acetic acid (HAc):



The rate of each chemical transformation is given by the first-order reaction:

$$C = C_o e^{-kt} \quad (3)$$

where C is the concentration of TCA at any time t, C_o represents the initial concentration at t = 0, and k is a transformation rate constant. The overall rate constant for TCA transformation (kTCA) is equal to the sum of the individual rate constants ($k_{DCE} + k_{HAc}$). The transformation rate constants are functions of temperature:

$$k = Ae^{-E/0.008314K} \quad (4)$$

where A and E are constants and K is the temperature in degrees Kelvin. Table 1 provides a listing of values reported for A and E for TCA abiotic transformation by various investigators, and calculated values for the TCA transformation rate constant for 10°C, 15°C, and 20°C using equation 4. Also given is the average calculated TCA half-life based upon t1/2 = 0.69/k. The temperature effect on TCA half-life is quite significant.

Table 1. Reported First-Order TCA Abiotic Transformation Rates (k_{TCA})

		k_{TCA} (yr^{-1})			
A yr^{-1}	E kJ	10 °C	15 °C	20 °C	References
$3.47\ (10)^{20}$	118.0	0.058	0.137	0.32	Haag and Mill (3)
$6.31\ (10)^{20}$	119.3	0.060	0.145	0.34	Cline and Delfino (4)
$1.56\ (10)^{20}$	116.1	0.058	0.137	0.31	Jeffers et al. (5)
Average half-life (yr)		12	4.9	0.95	

Cline and Delfino (4) found that k_{DCE} equaled about 21 percent of K_{TCA}, and Haag and Mill (3) found it to be 22 percent. This means that almost 80 percent of the TCA is transformed into acetic acid. The 20-plus percent that is converted to 1,1-DCE, however, is of great significance because 1,1-DCE is considered more toxic than TCA, with a maximum contaminant level of 7 μg/L compared with 200 μg/L for TCA. Whenever TCA is present as a contaminant, 1,1-DCE can also be expected. In general, TCA is probably the main source of 1,1-DCE contamination found in aquifers.

Chloroethane, formed through biological transformation of TCA, can also be chemically transformed with a half-life on the order of months by hydrolysis to ethanol, which can then be biologically converted to acetic acid and nonharmful products (6).

Biological Transformations

CAHs can be oxidized or reduced, generally through co-metabolism, as noted in Table 2. In ground waters, intrinsic reductive transformations are most often noted, perhaps because the presence of intermediate products that are formed provide strong evidence that reductive transformations are taking place. Intrinsic aerobic transformation of TCE is also possible, although if it did occur, the intermediate products are unstable and more difficult, analytically, to measure. Thus, convincing evidence for the latter is difficult to obtain. Also, aerobic co-metabolism of TCE would only occur if sufficient dissolved oxygen and a suitable electron donor, such as methane, ammonia, or phenol, were present. Since circumstances under which the proper environmental conditions for significant aerobic co-metabolism are unlikely to occur often, intrinsic aerobic co-metabolism of TCE is probably of little significance. Evidence is ample, however, that anaerobic reductived transformations of CAHs occur frequently, and this process is important to the transformation of all chlorinated solvents and their transformation products. The major environmental requirement is the presence of sufficient concentrations of other organics that can serve as electron donors for energy metabolism, which often is the case in aquifers. Indeed, the extent to which reductive dehalogenation occurs may be limited by the amount of such co-contaminants present. Theoretically, only a 0.4-g chemical oxygen demand (COD) equivalent of primary substrate would be required to convert 1 g of PCE to ethene (7), but much more is actually required because of the co-metabolic nature of the transformation.

Figure 1 illustrates the potential chemical and biological transformation pathways for the four major chlorinated solvents under anaerobic environmental conditions (6). Freedman and Gossett (8) provided the first evidence for conversion of PCE and TCE to ethene, and de Bruin et al. (9) reported completed reduction to ethane. Table 3 indicates that while some transformations, such as CT to chloroform and carbon dioxide, may take place under mild reducing conditions such as those associated with denitrification, complete reductive transformation to inorganic end products and of PCE and TCE to ethene generally requires conditions suitable for methane fermentation. Extensive reduction, although perhaps not complete, can also occur under sulfate-reducing conditions. For methane fermentation to occur in an aquifer, the presence of sufficient organic co-contaminant is required to reduce the oxygen, nitrate, nitrite, and sulfate present. Some organics will be required to reduce the CAHs, and perhaps Fe(II) as well, if present in significant amounts. If the potential for intrinsic transformation of CAHs is to be evaluated, then the concentrations of nitrate, nitrite, sulfate, Fe(II), and methane, and of organics (as indicated by COD or total organic carbon [TOC]) should be determined. Unfortunately, such analyses are not considered essential in remedial investigations, but it is evident that they should be.

Table 2. Biodegradability of Chlorinated Solvents Under Aerobic or Anaerobic Conditions and Through Use as a Primary Substrate for Energy and Growth or Through Co-metabolism

	Carbon Tetrachloride (CT)	Tetrachloro-ethylene (PCE)	Trichloro-ethylene (TCE)	1,1,1-Tri-chloroethane (TCA)
Aerobic Biotransformation				
Primary substrate	No	No	No	No
Co-metabolism	No	No	Yes	Perhaps
Anaerobic Biotransformation				
Primary substrate	No	Perhaps	Perhaps	No
Co-metabolism	Yes	Yes	Yes	Yes
Hazardous intermediates	Yes	Yes	Yes	Yes
Chemical Transformation	Perhaps	No	No	Yes

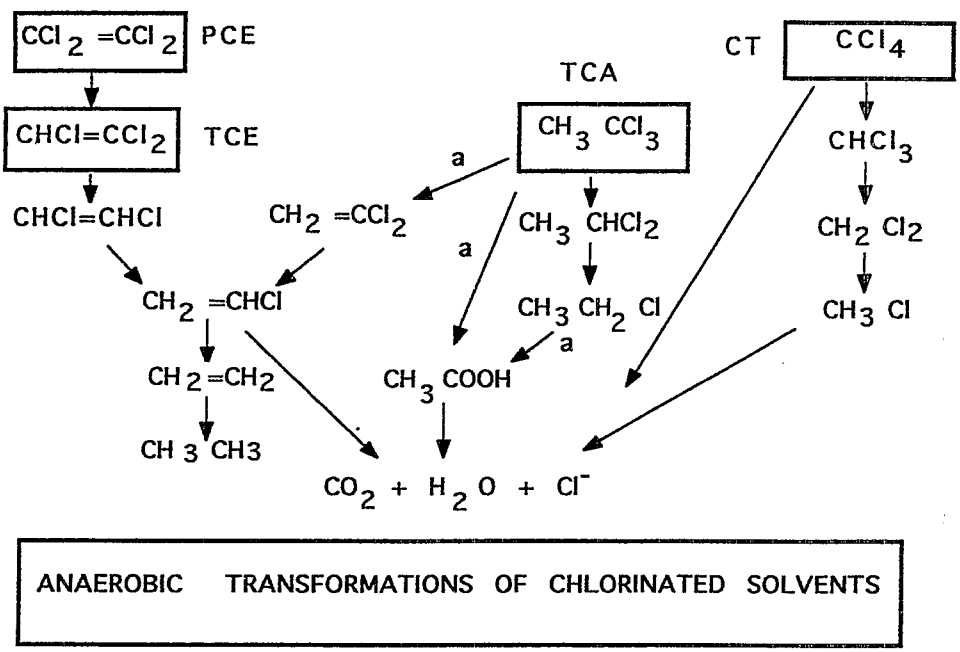


Figure 1. Anaerobic chemical and biological transformation pathways for chlorinated solvents.

Table 3. Environmental Conditions Generally Associated With Reductive Transformations of Chlorinated Solvents

	Redox Environment			
Chlorinated Solvent	All	Denitrification	Sulfate Reduction	Methanogenesis
Carbon tetrachloride		CT→CF	CT→CO_2+Cl^-	
1,1,1-Trichloroethane	TCA→1,1-DCE + CH_3COOH		TCA→1,1-DCA	TCA→CO_2+Cl^-
Tetrachloroethylene			PCE→1,2-DCE	PCE→ethene
Trichloroethylene			TCE→1,2-DCE	TCE→ethene

Case Studies

Major et al. (10) reported field evidence for intrinsic bioremediation of PCE to ethene and ethane at a chemical transfer facility in North Toronto. PCE was stored at the site 10 years prior to the study and contaminated the ground water below with both free and dissolved PCE. In addition to high concentrations of PCE (4.4 mg/L), high concentrations of methanol (810 mg/L) and acetate (430 mg/L) were found in the contaminated ground water; methanol and acetate are co-contaminants that served as the primary substrates for the transforming organisms. Where high PCE was found, TCE (1.7 mg/L), cis-DCE (5.8 mg/L), and VC (0.22 mg/L) were also found, but little ethene (0.01 mg/L) was found. At one downgradient well, however, no PCE or TCE was found, but cis-DCE (76 mg/L), VC (9.7 mg/L), and ethene (0.42 mg/L) were present, suggesting that significant dehalogenation had occurred. Other dichloroethylenes (1,1-DCE and trans-DCE) were not significant in concentration, indicating that cis-DCE was the major transformation intermediate. Microcosm studies also supported that biotransformation was occurring at the site, with complete disappearance of PCE, TCE, and cis-DCE and production of both VC and ethene. The conversions were accompanied by significant methane production, indicating that suitable redox conditions were present for the transformation.

Fiorenza et al. (11) reported on PCE, TCE, TCA, and dichloromethane (DCM) contamination of ground water at two separate locations at a carpet-backing manufacturing plant in Hawkesbury, Ontario. The waste lagoon was the major contaminated area, with ground water containing 492 mg/L of volatile fatty acids and 4.2 mg/L of methanol, organics that appeared to provide the co-contaminants that served as primary sources of energy for the dehalogenation reactions. Here, the sulfate concentration was nondetected, but the concentration in native ground water was about 15 to 18 mg/L. Total dissolved iron was quite high (19.5 mg/L) and well above the upgradient concentration of 2.1 mg/L. Methane was present, although quite low in concentration (0.06 mg/L). These parameters are all supportive of conditions suitable for intrinsic biodegradation of the chlorinated solvents. While some chemical transformation of TCA was indicated (0.4 mg/L), biotransformation was quite extensive, as indicated by a 1,1-DCA concentration of 7.2 mg/L compared with the TCA concentration of 5.5 mg/L. Some CA was also present (0.19 mg/L). Transformation was also indicated for PCE and TCE, which remained at concentrations of only 0.016 mg/L and 1.5 mg/L, respectively, while the cis-DCE, VC, and

ethene concentrations were 56, 4.2, and 0.076 mg/L, respectively. Only traces of ethane were found. Trans-DCE concentration was only 0.57 mg/L, again providing evidence that cis-DCE is the most common transformation intermediate from TCE and PCE. Downgradient from the lagoon, the dominant products were cis-DCE (4.5 mg/L), VC (5.2 mg/L), and 1,1-DCA (2.1 mg/L). While good evidence for intrinsic biotransformation is provided for this site, the ethene and ethane concentrations appear very low compared with VC concentration, suggesting that biotransformation was not eliminating the chlorinated solvent hazard at the site, although it was producing compounds that may be more susceptible to aerobic co-metabolism.

Evidence for intrinsic biotransformation of chlorinated solvents has also been provided from analyses of gas from municipal refuse landfills where active methane fermenation exists. A summary by McCarty and Reinhard (12) of data from Charnley et al. (13) indicated average gaseous concentrations in parts per million by volume from eight refuse landfills to be: PCE, 7.15; TCE, 5.09; cis-DCE, not measured; trans-DCE, 0.02; and VC, 5.6. While these averages indicate that, in general, transformation was not complete, the presence of high VC indicates the transformation was significant. For TCA, gaseous concentrations were: TCA, 0.17; 1,1-DCE, 0.10; 1,1-DCA, 2.5; and CA, 0.37. These data indicate that TCA biotransformation was quite extensive, with the transformation intermediate, 1,1-DCA, present at quite significant levels, as is frequently found in ground water.

Perhaps the most extensively studied and reported intrinsic chlorinated solvent biodegradation is that at the St. Joseph, Michigan, Superfund site (7, 14-17). Ground-water concentrations of TCE as high as 100 mg/L were found present, with extensive transformation to cis-DCE, VC, and ethene. A high but undefined COD (400 mg/L) in ground water, resulting from waste leaching from a disposal lagoon, provided the energy source for the co-metabolic reduction of TCE. Nearly complete conversion of the COD to methane provided evidence of the ideal conditions for intrinsic bioremediation (7). Extensive analysis near the source of contamination indicated that 8 percent to 25 percent of the TCE had been converted to ethene, and that up to 15 percent of the reduction in COD in this zone was associated with reductive dehalogenation (15). Through more extensive analysis of ground water farther downgradient from the contaminating source, Wilson et al. (17) found a 24-fold reduction in CAHs across the site. A review of the data at individual sampling points indicated that conversion of TCE to ethene was most complete where methane production was highest and removal of nitrate and sulfate by reduction was most complete.

References

1. McCarty, P.L., and L. Semprini. 1994. Ground-water treatment for chlorinated solvents. In: Norris, R.E., ed. Handbook of bioremediation. Boca Raton, FL: Lewis Publishers, Inc. pp. 87-116.

2. Council, N.R. 1993. *In situ* bioremediation: When does it work?. Washington, DC: National Academy Press.

3. Haag, W.R., and T. Mill. 1988. Effect of subsurface sediment on hydrolysis of haloalkanes and epoxides. Environ. Sci. Technol. 22:658-663.

4. Cline, P.V., and J.J. Delfino. 1989. Transformation kinetics of 1,1,1-trichloroethane to the stable product 1,1-dichloroethene. In: R.A. Larson, ed. Biohazards of drinking water treatment. Chelsea, MI: Lewis Publishers, Inc. pp. 47-56.

5. Jeffers, P., L. Ward, L. Woytowitch, and L. Wolfe. 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propanes. Environ. Sci. Technol. 23(8): 965-969.

6. Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21:722-736.

7. McCarty, P.L., and J.T. Wilson. 1992. Natural anaerobic treatment of a TCE plume, St. Joseph, Michigan, NPL site. In: U.S. EPA. Bioremediation of hazardous wastes. EPA/600/R-92/126. Cincinnati, OH. pp. 47-50.

8. Freedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55(9):2,144-2,151.

9. de Bruin, W.P., et al. 1992. Complete biological reductive transformation of tetrachloroethene to ethane. Appl. Environ. Microbiol. 58(6):1,996-2,000.

10. Major, D.W., W.W. Hodgins, and B.J. Butler. 1991. Field and laboratory evidence of *in situ* biotransformation of tetrachloroethene to ethene and ethane at a chemical transfer facility in North Toronto. In: Hinchee, R.E., and R.F. Olfenbuttel, eds. Onsite bioreclamation. Boston, MA: Butterworth-Heinemann. pp. 147-171.

11. Fiorenza, S., et al. 1994. Natural anaerobic degradation of chlorinated solvents at a Canadian manufacturing plant. In: Hinchee, R.E., A. Leeson, L. Semprini, and S.K. Ong, eds. Bioremediation of chlorinated and polycyclic aromatic hydrocarbon compounds. Boca Raton, FL: Lewis Publishers, Inc. pp. 277-286.

12. McCarty, P.L., and M. Reinhard. 1993. Biological and chemical transformations of halogenated aliphatic compounds in aquatic and terrestrial environments. In: Oremland, R.S., ed. The biogeochemistry of global change: Radiative trace gases. New York, NY: Chapman & Hall, Inc.

13. Charnley, G., E.A.C. Crouch, L.C. Green, and T.L. Lash. 1988. Municipal solid waste landfilling: A review of environmental effects. No. Meta Systems, Inc.

14. Haston, Z.C., P.K. Sharma, J.N. Black, and P.L. McCarty. 1994. Enhanced reductive dechlorination of chlorinated ethenes. In: U.S. EPA. Bioremediation of hazardous wastes. San Francisco, CA.

15. Kitanidis, P.K., L. Semprini, D.H. Kampbell, and J.T. Wilson. 1993. Natural anaerobic bioremediation of TCE at the St. Joseph, Michigan, Superfund site. In: U.S. EPA. Symposium on bioremediation of hazardous wastes: Research, development, and field evaluations (abstracts). EPA/600/R-93/054. Washington, DC (May). Cincinnati, OH. pp. 47-50.

16. McCarty, P.L., et al. 1991. *In situ* methanotrophic bioremediation for contaminated ground water at St. Joseph, Michigan. In: Hinchee, R.E., and R.G. Olfenbuttel, eds. Onsite bioreclamation processes for xenobiotic and hydrocarbon treatment. Boston, MA: Butterworth-Heinemann. pp. 16-40.

17. Wilson, J.T., J.W. Weaver, and D.H. Kampbell. 1994. Intrinsic bioremediation of TCE in ground water at an NPL site in St. Joseph, Michigan. Presented at the U.S. EPA Symposium on Intrinsic Bioremediation of Ground Water, Denver, CO (August 30 to September 1).

Contamination of Ground Water With Trichloroethylene at the Building 24 Site at Picatinny Arsenal, New Jersey

Mary Martin and Thomas E. Imbrigiotta
U.S. Geological Survey, West Trenton, NJ

Abstract

Ground water at the Building 24 site at Picatinny Arsenal in Morris County, New Jersey, is contaminated with trichloroethylene (TCE). Estimated average linear ground-water flow velocities are 0.3 to 1.0 m/d, and estimated travel time from the source area to Green Pond Brook is 2 y to 5 y. The total mass of dissolved TCE within the 130,000-m^2 plume area is estimated to be 970 kg. About 65 percent of the mass is in areas where TCE concentrations exceed 10,000 μg/L, whereas about 30 percent is in areas where TCE concentrations are 1,000 to 10,000 μg/L.

The average flux of TCE discharged to Green Pond Brook from the plume area, estimated from measured TCE concentrations in samples of water from the unconfined aquifer and measured base-flow discharge in Green Pond Brook, is 1 to 2 mg/sec. Biotransformation is the most important mechanism by which dissolved TCE leaves the ground-water system.

Introduction

Picatinny Arsenal, a U.S. Army armament research and development center, is located in a glaciated valley in north-central New Jersey (Figure 1). In 1960, Building 24 was remodeled, and a new metal-plating facility and industrial wastewater treatment plant were installed. From 1960 to 1981, the wastewater treatment system discharged tens of thousands of liters of wastewater daily into two 2.5-m deep, sand-bottomed settling lagoons behind the building (1). The metal-plating wastewater contained trace metals, such as cadmium, chromium, copper, lead, nickel, tin, vanadium, and zinc, and other ions used in plating solutions, such as sodium, potassium, sulfate, chloride, and cyanide (2). From 1973 to 1985, an improperly installed relief system of the degreasing unit allowed pure chlorinated solvents to condense in an overflow pipe and discharge to a 1-m deep dry well in front of Building 24. The condensate from the overflow system contained TCE and, after 1983, 1,1,1-trichloroethane (2).

The infiltration of wastewater from the lagoons and of chlorinated solvents from the dry well has created a plume of contaminated ground water downgradient from Building 24. Most of the contamination is limited to unconfined sediments, where estimated ground-water flow velocities (based on estimated horizontal hydraulic conductivities, measured head gradients, estimated porosities, and results of calibrated solute-transport model simulations) generally range from 0.3 to 1.0 m/d in the plume area. On the basis of these estimated velocities, the residence time within the unconfined aquifer of a conservative solute entering the aquifer near Building 24 and discharging at Green Pond Brook is 2 y to 5 y.

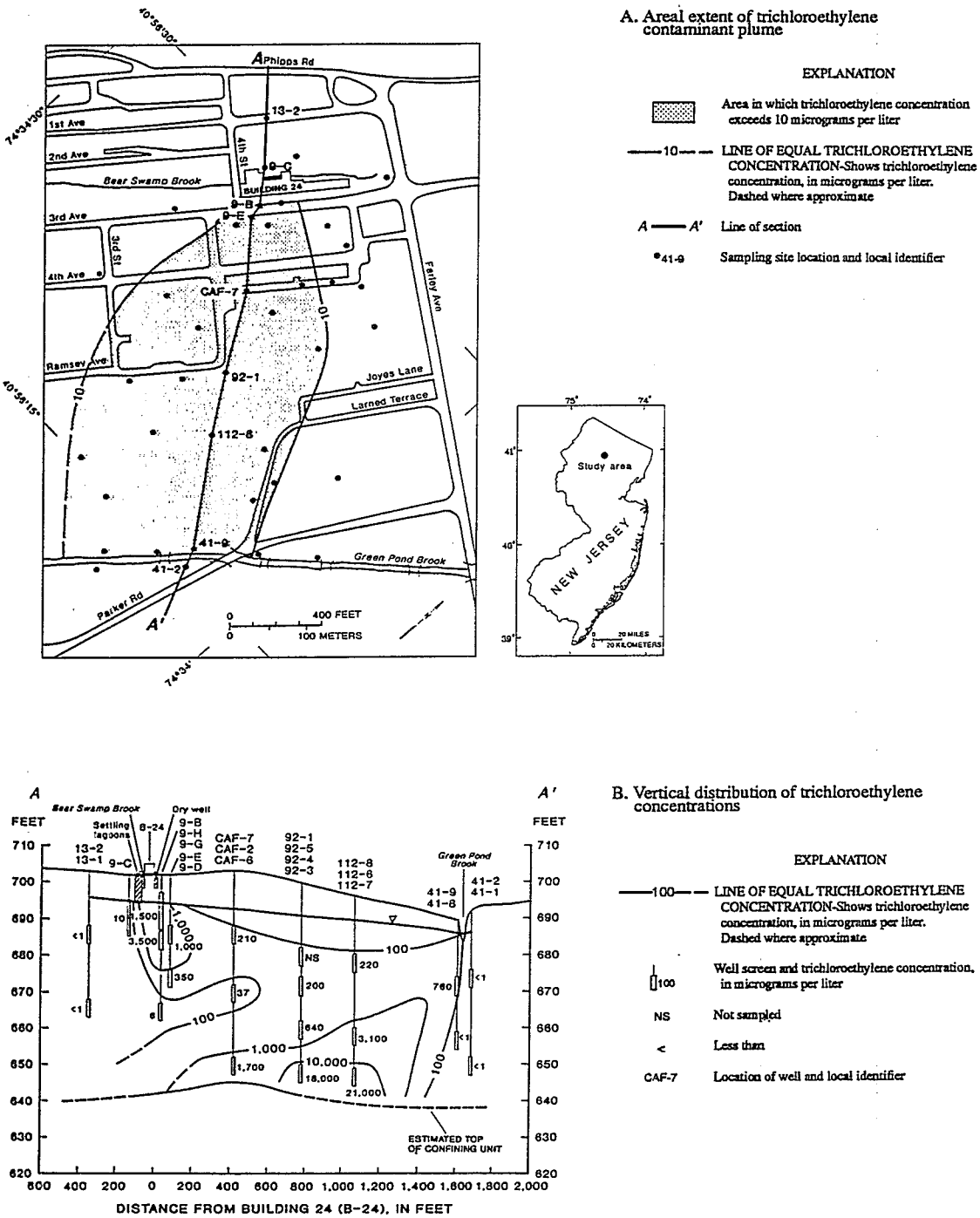


Figure 1. (A) Location of Building 24 study area at Picatinny Arsenal, and areal extent of TCE plume and altitude of water table, January 1993, and (B) vertical distribution of TCE concentrations, October to November 1991. (Location of section A-A′ is shown in Figure 1A.)

Ground-water contamination in the unconfined aquifer has been discussed previously by Sargent et al. (3), Fusillo et al. (2), and Imbrigiotta et al. (4,5). Results of water-quality sampling during 1986 to 1991 confirm that TCE remains the dominant contaminant in the unconfined aquifer and that the extent of the plume of TCE-contaminated ground water has changed little since September 1986. These water-quality measurements also show that 1) Building 24 is the source of the TCE plume; 2) the highest TCE concentrations near Building 24 are found at depths of less than 6 m and within 10 m downgradient from the dry well; 3) the plume extends 500 m from Building 24 to Green Pond Brook and follows the ground-water head gradients as it flows downward through the unconfined aquifer, then upward toward Green Pond Brook; 4) the plume disperses as it moves downgradient, is about 350-m wide where it enters Green Pond Brook, and has an areal extent of about 130,000 m^2; 5) the highest concentrations of TCE are found at the base of the unconfined aquifer midway between Building 24 and Green Pond Brook; and 6) the highest TCE concentrations at Green Pond Brook are found at depths of less than 6 m (Figure 1).

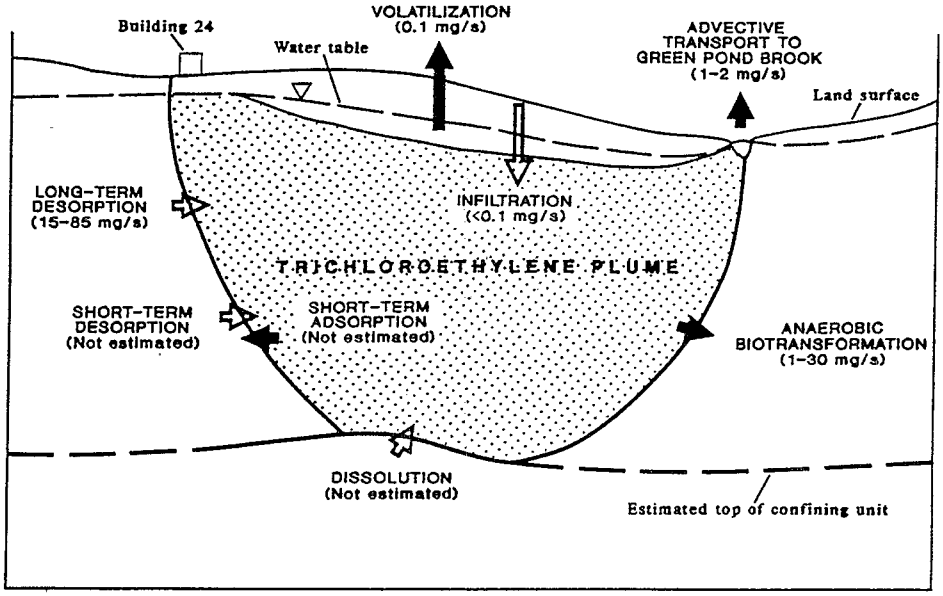
The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by the chlorinated solvents and other contaminants at the Building 24 site at Picatinny Arsenal. The objectives of the study are to 1) describe the chemical, physical, and biological processes that affect the movement and fate of these contaminants, particularly TCE, in the subsurface; 2) determine the relative importance of these processes; and 3) develop predictive models of contaminant transport.

This paper describes a conceptual model of the processes that affect the fate and transport of chlorinated solvents at Picatinny Arsenal research site. A preliminary solute mass balance of TCE in the unconfined aquifer at the site is presented and compared with results of numerical solute-transport simulations.

Conceptual Model

A conceptual model of the physical, chemical, and biological processes that affect the transport and mass balance of TCE within the plume was developed by Imbrigiotta and Martin (6) (Figure 2). TCE is present at the site in several forms: solute phase (dissolved in water), vapor phase (soil gas), and matrix phase (sorbed onto solid surfaces or associated with biota). TCE also may be present as a dense nonaqueous-phase liquid (DNAPL). Nonaqueous-phase flow of TCE from Building 24 to the base of the unconfined aquifer is hypothesized to be the cause of high concentrations of TCE at the base of the unconfined aquifer (5).

Results of chemical analyses of samples of ground water, soil gas, and aquifer sediments from the plume area indicate that the fate and transport of TCE are affected by the physical, chemical, and biological processes at the site. Advection and dispersion in the saturated zone affect the movement of dissolved TCE and cause it to be removed from the system in the discharge to Green Pond Brook. TCE also is removed from the system by anaerobic biotransformation (reductive dehalogenation), volatilization at the water table, and sorption to saturated-zone sediments. Volatilization of TCE to the unsaturated-zone soil gas was measured by Smith and others (7). Transport in the unsaturated zone was determined to be driven principally by molecular diffusion. The detection of the biotransformation products cis-1-2-dichloroethylene (cis-DCE) and vinyl chloride (VC) in water from 75 percent of the wells



NOT TO SCALE

TRICHLOROETHYLENE MASS BALANCE COMPONENTS
[mg/s, milligrams per second; <, less than]

GAINS		LOSSES	
LONG-TERM DESORPTION	15-85 mg/s	ANAEROBIC BIOTRANSFORMATION	1-30 mg/s
INFILTRATION	< 0.1 mg/s	ADVECTIVE TRANSPORT TO GREEN POND BROOK	1-2 mg/s
DISSOLUTION	Not estimated	VOLATILIZATION	0.1 mg/s
SHORT-TERM DESORPTION	Not estimated	SHORT-TERM ADSORPTION	Not estimated

Figure 2. Conceptual model and preliminary mass-balance estimates of TCE fluxes resulting from processes that affect the fate and transport of TCE in the ground-water system at Picatinny Arsenal.

screened within the plume is indicative of biologically mediated, reductive dehalogenation of TCE. The occurrence of methanogenesis is indicated by the detection of dissolved methane in water from 85 percent of the wells in which cis-DCE was detected and in water from 94 percent of the wells in which VC was detected.

Desorption from contaminated sediments is a source of TCE in the ground-water system. If TCE is present as a DNAPL, dissolution will result in a source of dissolved TCE in the ground water. Relatively constant TCE concentrations measured near Building 24 and at the base of the unconfined aquifer from 1986 to 1991 indicate that slow desorption of TCE from contaminated

aquifer sediments, dissolution of DNAPL TCE in the aquifer, or both are a continuing source of dissolved TCE in the ground-water system.

Estimated Mass Distribution of TCE

For a given sample set, the total mass of dissolved TCE below the water table is estimated to be 970 kg or about 660 L of liquid TCE. This estimate was calculated by using results of six sets of water-quality analyses made from 1986 to 1991 (Figure 3). Each measured TCE concentration is assumed to represent the TCE concentration of a volume of ground water extending half the horizontal and vertical distance to the adjacent sampling points. These volumes are limited vertically by the extent of the unconfined aquifer and horizontally by the 10-μg/L maximum TCE concentration line. Aquifer porosity is assumed to be 30 percent. The total volume of dissolved TCE within the ground water outside the 10-μg/L maximum TCE concentration line is estimated to be about 1 L.

The estimated total volume of TCE appears to be unrelated to the total number of samples collected. Four sets of data plotted in Figure 3 (A, C, E, and F) show that about 65 percent of the total volume of TCE is found in ground water that contains TCE concentrations greater than 10,000 μg/L, and about 30 percent is found in areas where TCE concentrations range from 1,000 to 10,000 μg/L. The estimate of the volume of TCE in the water appears to depend mostly on the number of samples that contain relatively high concentrations of TCE and the volume of water each sample is assumed to represent.

The relative amounts of TCE in the dissolved, vapor, and matrix phases in a block of aquifer and unsaturated zone immediately downgradient from Building 24 were estimated on the basis of measured TCE concentrations in samples of all three phases (8) (Figure 4). Most of the mass of TCE in the system near Building 24 is in the matrix phase and is associated with the sediments in both the unsaturated and saturated zones. The mass distribution shown in Figure 4 is based on a representative sample of each TCE phase in the area of Building 24. The ratio of the mass of TCE sorbed to the soil to the mass of dissolved TCE in six sets of samples collected near the water table throughout the site ranged from 2:1 to 5:1. One sample, collected downgradient from the wastewater lagoons, had an unusually high ratio of about 20:1. The amount of DNAPL TCE at the site has not been estimated.

Preliminary Solute Mass Balance

Desorption of TCE from soils that have undergone long-term adsorption (years) and dissolution of DNAPL TCE probably are the processes by which most TCE enters the ground-water system, because the direct release of TCE from Building 24 stopped in 1985. Because the amount of DNAPL TCE has not been estimated, the rate of TCE dissolution cannot be estimated. Three first-order rate constants of TCE desorption from shallow aquifer sediments at the arsenal calculated by Koller et al. (8) ranged from 0.003 to 0.015 per week. The rate constants were measured in laboratory flowthrough columns using uncontaminated water as the influent fluid. Desorption rates in the field, where ground water containing TCE is flowing past the desorbing sediments, probably would be lower. By using an estimated mass of TCE sorbed to the aquifer sediments of three to four times the mass of TCE in the dissolved state, the estimated flux of TCE into the ground-water system through desorption is 15 to 85 mg/sec. This flux estimate is made

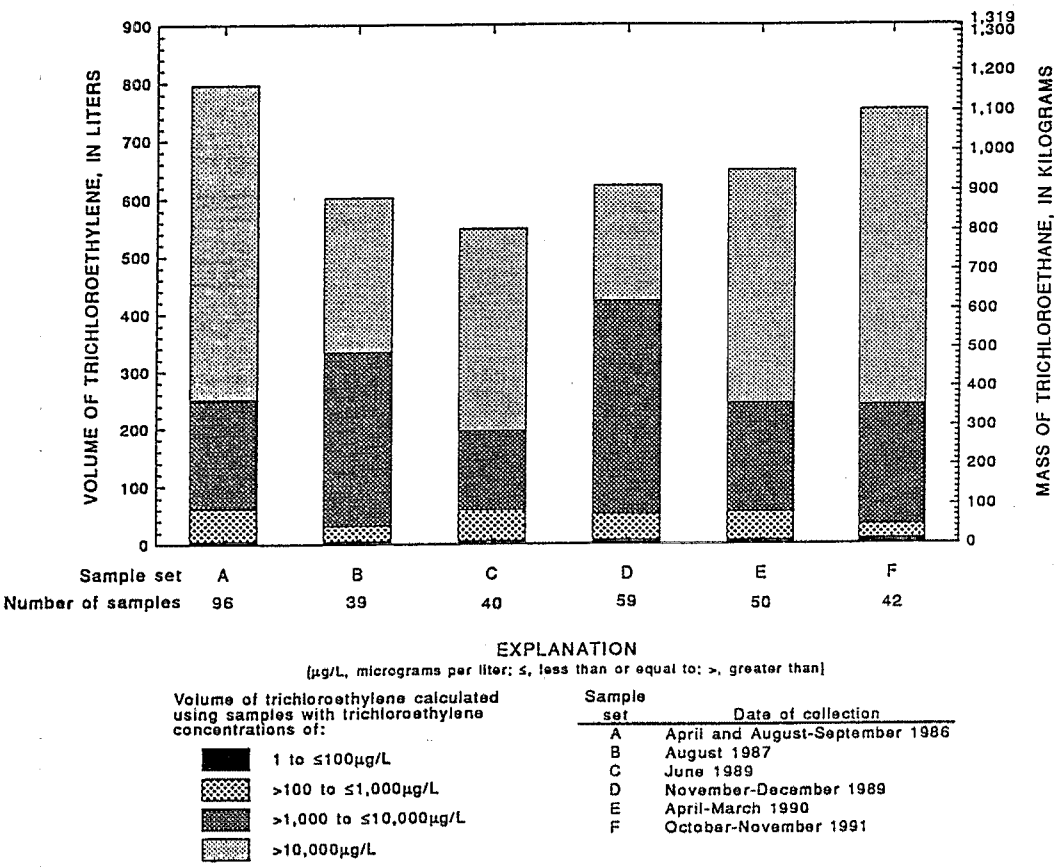
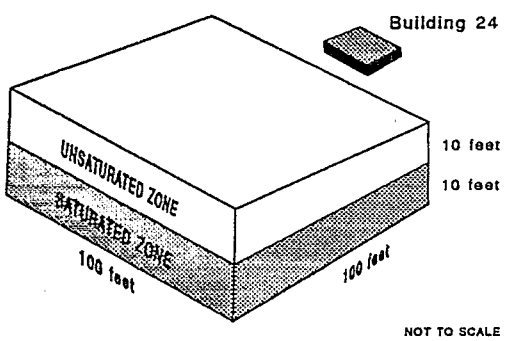


Figure 3. Estimated volume of dissolved TCE in ground water at the Building 24 site at Picatinny Arsenal, 1986-91.



Mass distribution of tricholoroethylene near building 24
[kg, kilogram; <, less than]

	Phase	Mass (kg)	Percent of total
Unsaturated zone	Vapor	0.001	<0.1
	Matrix	3	99.9
Saturated zone	Solute	1	20
	Matrix	4	80

Figure 4. Mass distribution of TCE in the saturated and unsaturated zones immediately downgradient from Building 24 at Picatinny Arsenal.

by assuming that, over long periods (years), the short-term desorption rate (weeks and months) is equal to the short-term adsorption rate, and that soils previously have undergone long-term adsorption, which is no longer occurring.

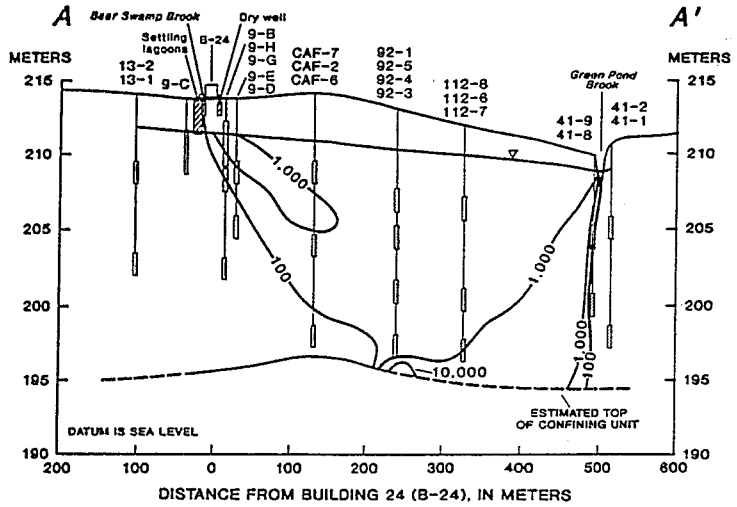
Preliminary estimates of the flux of TCE into and out of the ground-water system at the Building 24 site for each of the mass-balance components are shown in Figure 2. The estimated flux of TCE discharged to Green Pond Brook from the plume area, calculated on the basis of measured TCE concentrations in ground water and measured base-flow discharge in the brook, is 1 to 2 mg/sec. The flux of TCE volatilized from the water table is estimated to be about 0.1 mg/sec on the basis of measured soil-gas TCE concentration gradients and estimates of the physical characteristics of the unsaturated zone.

Biotransformation probably is the mechanism by which most of the dissolved TCE leaves the ground-water system. First-order rate constants for TCE transformation ranging from less than 0.001 to 0.02 per week were estimated by Wilson et al. (9) on the basis of results of laboratory microcosm studies of soil from five sites within the plume area. By using these rate constants and the estimated mass of dissolved TCE, the rate of TCE loss from the plume through biotransformation is calculated to be about 1 to 30 mg/sec. Analogous first-order rate constants for TCE biotransformation calculated by Ehlke et al. (10) from field-measured TCE concentrations and time-of-travel data generally were higher than those measured in the laboratory experiments. Thus, the actual flux of TCE lost through biotransformation may be greater than that shown in Figure 2.

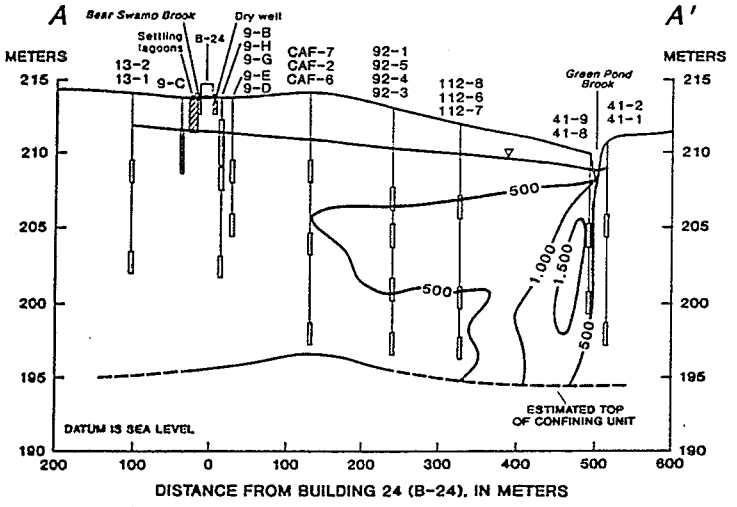
A reactive multispecies transport model of a two-dimensional vertical section along the central axis of the plume is being used to analyze the laboratory and field estimates of the physical and chemical transport characteristics and the estimated TCE mass balance. The model design, calibration, and sensitivity analysis have been described by Martin (11). Transport, desorption, volatilization, and microbial degradation of TCE are simulated. The formation and transport of the degradation products cis-DCE and VC also are simulated. Specified-flux boundary conditions are used to represent ground-water recharge and flows across the horizontal and vertical boundaries of the cross-sectional area. Constant-concentration nodes and desorption within the plume area are solute sources to the simulated system. The constant-concentration solute sources are assumed to represent high rates of desorption or dissolution of TCE near the settling lagoons, at the overflow dry well, and near the base of the unconfined aquifer 230 m downgradient from Building 24.

The simulations were designed to represent average steady-state flow conditions and virtually steady-state transport conditions after 1985. Simulated concentrations of TCE and cis-DCE from the calibrated model are shown in Figure 5. Most concentrations were simulated to within an order of magnitude of average concentrations measured in micrograms per liter in water samples from each well. Because the degradation of VC was not simulated, concentrations are higher than measured concentrations and are not shown.

The calibrated model does not provide a unique estimate of the magnitudes of the various mass-balance components of the plume of TCE-contaminated ground water at the Building 24 site; however, sensitivity simulations were used to test hypotheses concerning the fate of TCE in ground water. Results of a series of sensitivity simulations discussed by Martin (11) support the general conceptual model as defined by the estimated solute mass balance presented above.



(A) Trichloroethylene



(B) cis-1-2-Dichloroethylene

EXPLANATION

—100— LINE OF EQUAL SOLUTE CONCENTRATION-Shows solute concentration, in micrograms per liter.

Location of well screen

CAF-7 Location of well and local identifier

Figure 5. Simulated concentrations from calibrated model with simulated desorption, volatilization, and microbial degradation: (A) TCE and (B) cis-DCE. (Location of section A-A' is shown in Figure 1A.)

Results of sensitivity simulations made with various desorption and degradation rates typically showed that use of the laboratory estimates resulted in reasonable simulated concentrations. Although volatilization is not a major mass-balance component, this process was shown to be an important mechanism for removing solutes and thereby affecting solute concentrations near the water table. The overall flux of TCE into and out of the system was not simulated well because the total simulated mass of TCE in the system was too low. Increasing the simulated solute-source area near the base of the unconfined aquifer might result in a reasonable simulated TCE mass balance.

Summary

Infiltration of wastewater from the lagoons and chlorinated solvents from the dry well at Building 24 at Picatinny Arsenal, New Jersey, has created a plume of contaminated ground water downgradient from the building. TCE is the predominant contaminant in the 130,000 m^2 plume, which extends 500 m to Green Pond Brook. Ground-water velocities typically range from 0.3 to 1.0 m/d.

Results of water-quality sampling conducted from 1986 through 1991 show that the TCE contaminant plume has changed little since September 1986, and that the highest TCE concentrations are found near the water table near Building 24 and near the base of the unconfined aquifer about midway between Building 24 and Green Pond Brook. TCE is present at the site in several phases: dissolved in water, as a vapor in the soil gas, and sorbed onto solid surfaces or associated with biota. TCE also may be present as a DNAPL. The total volume of dissolved TCE below the water table is estimated to be about 660 L, but most of the mass of TCE in the system is associated with the sediments in the saturated and unsaturated zones.

A conceptual model of the physical, chemical, and biological processes that affect the transport and mass balance of TCE within the plume includes 1) transport of TCE from the Building 24 source area to Green Pond Brook by advection and dispersion; 2) loss of dissolved TCE from the ground-water system by discharge to Green Pond Brook, biotransformation, and volatilization; and 3) gain of dissolved TCE by slow desorption from contaminated aquifer sediments and possibly from dissolution of DNAPL TCE in the aquifer. Preliminary estimates of the flux of dissolved TCE discharged to Green Pond Brook from the plume is 1 to 2 mg/sec. Most dissolved TCE leaves the ground-water system by means of biotransformation. The estimated flux of TCE out of the system by this process may be about an order of magnitude greater than the flux of TCE discharged to Green Pond Brook. Although the estimated flux of TCE out of the ground-water system by volatilization is estimated to be about an order of magnitude less than the flux of TCE discharge to Green Pond Brook, volatilization is an important mechanism for removing solutes and thereby affecting solute concentrations near the water table.

References

1. Benioff, P.A., M.H. Bhattacharyya, C. Biang, S.Y. Chiu, S. Miller, T. Patton, D. Pearl, A. Yonk, and C.R. Yuen. 1990. Remedial investigation concept plan for Picatinny Arsenal, Vol. 2. Descriptions of and sampling plans for remedial investigation sites. Argonne, IL: Argonne National Laboratory, Environmental Assessment and Information Sciences Division. pp. 22-1 to 22-24.

2. Fusillo, T.V., T.A. Ehlke, M. Martin, and B.P. Sargent. 1987. Movement and fate of chlorinated solvents in ground water: Preliminary results and future research plans. In: Franks, B.J., ed. Proceedings of the U.S. Geological Survey Program on Toxic Waste—Ground-Water Contamination, Pensacola, FL (March 23-27). U.S. Geological Survey Open File Rep. 87-109. pp. D5-D12.

3. Sargent, B.P., J.W. Green, P.T. Harte, and E.F. Vowinkel. 1986. Ground-water-quality data for Picatinny Arsenal, New Jersey, 1958-85. U.S. Geological Survey Open File Rep. 86-58. 66 pp.

4. Imbrigiotta, T.E., M. Martin, B.P. Sargent, and L.M. Voronin. 1989. Preliminary results of a study of the chemistry of ground water at the Building 24 research site, Picatinny Arsenal, New Jersey. In: Mallard, G.E., and S.E. Ragone, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Phoenix, AZ (September 26-30, 1988). Water Res. Invest. Rep. 88-4220. pp. 351-359.

5. Imbrigiotta, T.E., T.A. Ehlke, and M. Martin. 1991. Chemical evidence of processes affecting the fate and transport of chlorinated solvents in ground water at Picatinny Arsenal, New Jersey. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15). Water Res. Invest. Rep. 91-4034. pp. 681-688.

6. Imbrigiotta, T.E., and M. Martin. 1991. Overview of research activities on the movement and fate of chlorinated solvents in ground water at Picatinny Arsenal, New Jersey. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15). Water Res. Invest. Rep. 91-4034. pp. 673-680.

7. Smith, J.A., C.T. Chiou, J.A. Kammer, and D.E. Kile. 1990. Effect of soil moisture on sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. Environ. Sci. Technol. 24(5):676-683.

8. Koller, D., T.E. Imbrigiotta, A.L. Baer, and J.A. Smith. 1994. Desorption of trichloroethylene from aquifer sediments at Picatinny Arsenal, New Jersey. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

9. Wilson, B.H., T.A. Ehlke, T.E. Imbrigiotta, and J.T. Wilson. 1991. Reductive dechlorination of trichloroethylene in anoxic aquifer material from Picatinny Arsenal, New Jersey. In: Mallard, G.E., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Monterey, CA (March 11-15). Water Res. Invest. Rep. 91-4034. pp. 704-707.

10. Ehlke, T.A., B.H. Wilson, J.T. Wilson, and T.E. Imbrigiotta. 1994. *In situ* biotransformation of trichloroethylene and cis-1,2-dichloroethylene at Picatinny Arsenal, New Jersey. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

11. Martin, M. 1994. Simulation of transport, desorption, volatilization, and microbial degradation of trichloroethylene in ground water at Picatinny Arsenal, New Jersey. In: Morganwalp, D.W., and D.A. Aronson, eds. Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program, Colorado Springs, CO (September 20-24, 1993). Water Res. Invest. Rep. 94-4014. In press.

Intrinsic Bioremediation of TCE in Ground Water at an NPL Site in St. Joseph, Michigan

John T. Wilson, James W. Weaver, and Don H. Kampbell
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK

Introduction

The ground water at the St. Joseph, Michigan, National Priority List (NPL) site is contaminated with chlorinated aliphatic compounds (CACs) at concentrations in the range of 10 mg/L to 100 mg/L. The chemicals are thought to have entered the shallow sandy aquifer either through waste lagoons that were used from 1968 to 1976 or through disposal of trichloroethene (TCE) into dry wells at the site (1). The contamination was determined to be divided into eastern and western plumes, as the suspected sources were situated over a ground-water divide. Both plumes were found to contain TCE, cis- and trans-1,2-dichoroethene (c-DCE and t-DCE), 1,1-dichloroethene (1,1-DCE), and vinyl chloride (VC).

Previous investigation of the site indicated that natural anaerobic degradation of the TCE was occurring, because transformation products and significant levels of ethene and methane (2, 3) were present. The purpose of this presentation is to present the results of later sampling of the western plume near Lake Michigan, to estimate the contaminant mass flux, and to estimate apparent degradation constants. The estimates are based on visualization of the data that represent each measured concentration by a zone of influence that is based on the sample spacing. The presentation of the data is free from artifacts of interpolation, and extrapolation of the data beyond the measurement locations is controlled.

Data Summary

In 1991, three transects (1, 2, and 3 on Figure 1) were completed near the source of the western plume (2). The three transects consisted of 17 borings with a slotted auger. In 1992, two additional transects (4 and 5 on Figure 1) were completed, consisting of 9 additional slotted auger borings. In each boring, water samples were taken at roughly 1.5 m (5 ft) depth intervals. Onsite gas chromatography was performed to determine the width of the plume and find the point of highest concentration. Three of the transects (2, 4, and 5) are roughly perpendicular to the contaminant plume. Of the remaining transects, transect 1 crosses the plume at an angle and transect 3 lies along the length of the plume. The perpendicular transects form logical units for study of TCE biotransformation.

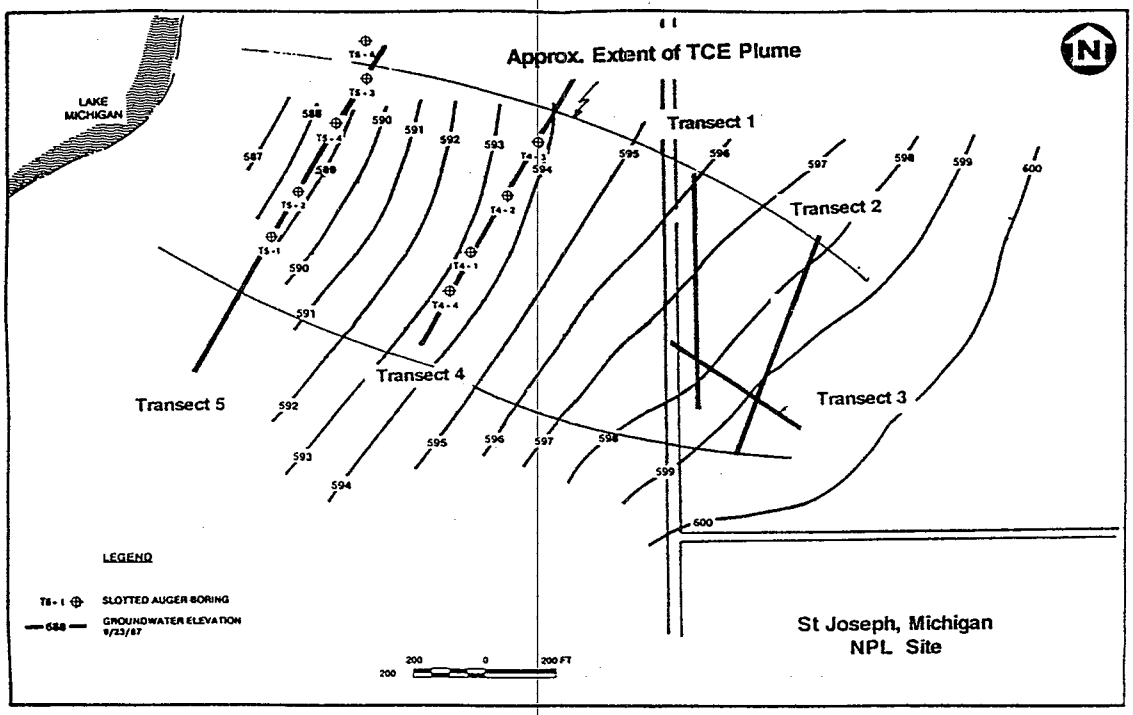


Figure 1. Site plan, St. Joseph, Michigan, NPL site.

The site data from the transects are visualized as sets of blocks that are centered around the measurement point. The blocks are defined so that the influence of a particular measured concentration extends halfway to the next measurement location both horizontally and vertically. Thus, presentation of the data is simple and direct. The visualization of the data is performed on a Silicon Graphics Indigo workstation using a two-dimensional version of the fully three-dimensional field-data analysis program called SITE-3D that is under development at the Robert S. Kerr Environmental Research Laboratory.

The mass of each chemical per unit thickness and the advective mass flux of each chemical are calculated by summing over the blocks. By following this procedure, the measured chemical concentrations are not extrapolated into the clay layer under the site, nor are they extrapolated beyond a short distance from the measurement locations (5 ft vertically and 50 ft to 100 ft horizontally). Other interpolation schemes such as inverse distance weighting or kriging could also be used to estimate the concentration field and perform the mass estimates. Figures 2 and 3 show the distributions of the VC and TCE at transect 5 using a logarithmic, black-and-white "color" scale. Notably, the maximum VC concentration at transect 4 was 1,660 μg/L and at transect 5 was 205 μg/L. The maximum TCE concentration at transect 4 was 8,720 μg/L and at transect 5 was 163 μg/L. As noted previously for other portions of the site (2, 4), the contamination is found near the bottom of the aquifer. The highest concentrations of VC and TCE do not appear to be co-located. In Table 1, mass estimates are presented for the perpendicular transects ordered from farthest upgradient (transect 2) to farthest downgradient (transect 5). The data in Table 1 represent the mass in a volume of aquifer that has an area equal to the cross-sectional area of the transect and is 1.0-m thick in the direction of groundwater flow.

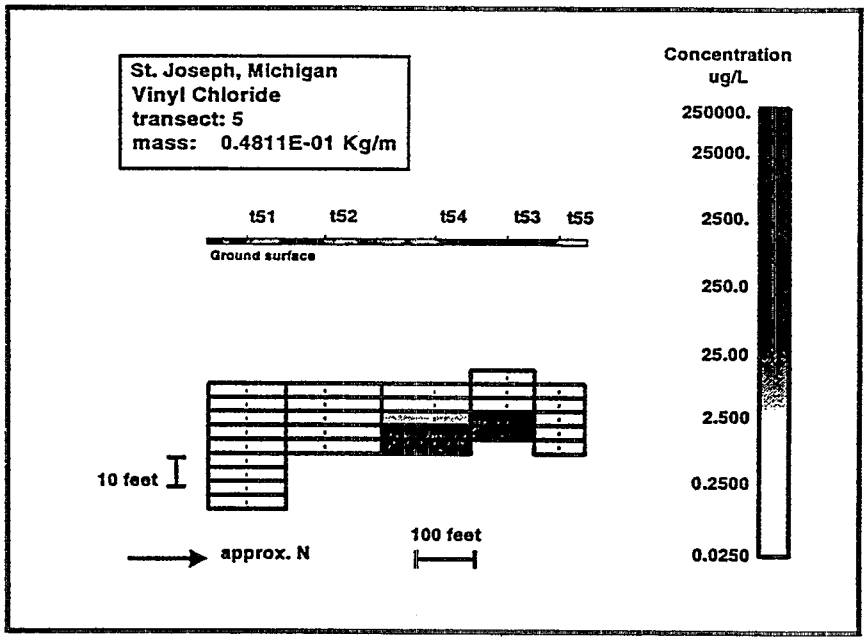


Figure 2. VC distribution at transect 5.

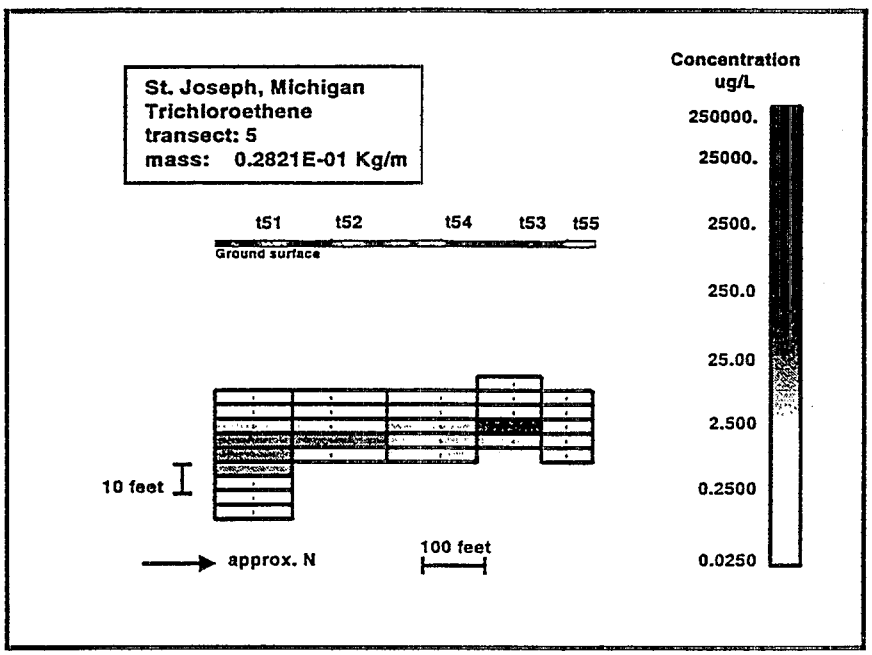


Figure 3. TCE distribution at transect 5.

Table 1. Mass per Unit Thickness (kg/m) at St. Joseph, Michigan

Chemical	Transect			
	2	1	4	5
Vinyl chloride	1.523	1.8969	0.4868	0.04811
1,1-DCE	0.2377	0.0816	0.01451	0.001047
t-DCE	0.566	0.5059	0.03628	0.007041
c-DCE	12.32	5.1127	1.890	0.2832
TCE	10.67	5.5804	1.397	0.02821
Methane	5.855	5.4826	4.620	1.373
Ethene	0.6847	0.8925	0.1747	0.004901
Ethane	No data	No data	0.2085	0.001689
TOC	No data	No data	12.63	8.314
Chloride	129.9	148.8	213.1	156.2
Sulfate	37.05	34.376	95.78	66.19
NO_3-Nitrogen	2.904	2.471	4.421	8.247
NH_4-Nitrogen	1.835	2.5609	0.4562	0.2256
TKN-Nitrogen	2.987	3.8357	0.6353	0.3646

Advective Mass Flux Estimates

Results from the calibrated MODFLOW model of Tiedeman and Gorelick (4) were used to estimate the ground-water flow velocity at each transect. The estimate is an upper bound because the modeled vertical component of flow was neglected in the present analysis. The head drop from one location to the next was assumed to generate horizontal flow only. Tiedeman and Gorelick (4) also represented the aquifer by single values of hydraulic conductivity and porosity. They gave, however, 95 percent confidence limits for the hydraulic conductivity. Well yields estimated for each sample location indicate declining hydraulic conductivity toward the west (i.e., towards Lake Michigan and transects 4 and 5). Thus, using the single parameter values from the MODFLOW simulations may overestimate the flux of water into the lake.

As would be expected, the advective mass fluxes decline toward the downgradient edge of the plume (Table 2). There the concentrations are lower, due to either transient flow or degradation of the TCE. Notably the mass fluxes using the average hydraulic conductivity result in a total flux of 13 kg/y of TCE, c-DCE, t-DCE, 1,1-DCE, and VC at transect 5. This value contrasts with the total flux of these CACs of 310 kg/y at transect 2 near the source of contamination. Thus, there is a 24.4-fold decrease in mass flux of CACs across the site. Using the 95 percent confidence

limits on the hydraulic conductivity determined by Tiedeman and Gorelick (4), the range total of mass flux of these five chemicals ranges from 205 kg/y to 420 kg/y at transect 2 and from 8.4 kg/y to 17 kg/y at transect 5. The range of fluxes at transect 5 is an upper bound on, and best estimate of, the flux into Lake Michigan.

Table 2. Mass Flux (kg/y) at St Joseph, Michigan

Chemical	Transect			
	2	1	4	5
Vinyl chloride	18.81	36.03	10.69	1.676
1,1-DCE	2.934	1.551	0.3185	0.03648
t-DCE	6.995	9.609	0.7963	0.2453
c-DCE	152.1	97.11	41.48	9.868
TCE	131.7	106.0	30.67	0.9829
Methane	72.29	104.1	101.4	47.86
Ethene	8.453	16.95	3.836	0.1708
Ethane	No data	No data	4.577	0.05885
TOC	No data	No data	277.2	289.7
Chloride	1604	2826	4678	5444
Sulfate	457.4	652.9	2102	2306
NO_3-Nitrogen	35.85	46.93	97.05	287.4
NH_4-Nitrogen	22.66	48.64	10.01	7.861
TKN-Nitrogen	36.88	72.85	13.95	12.70

Apparent Degradation Constants

The mass per unit thickness of TCE at transects 2, 4, and 5 was used to estimate apparent first-order degradation constants. The constants are estimated by applying the first-order rate equation

$$\ln\left[\frac{c_{j+1}}{c_j}\right] = \lambda \Delta t \qquad (1)$$

to the site data, where c_j is the average concentration in the transect j, c_{j+1} is the average concentration in the downgradient transect j+1, Δt is the advective travel time for TCE to move

between the transects, and λ is the apparent degradation constant. The mass per unit thickness data for TCE and the cross-sectional area were used to determine the average concentrations c_i and c_{i+1} in the up- and downgradient transects. The porosity, bulk density, fraction organic carbon, organic carbon partition coefficient (5), ground-water gradient, and distance between the transects were used to determine the advective travel times. The values used in equation 1 are given in Table 3. From these quantities, the apparent degradation constant for TCE was determined to be -0.0076/wk from transect 2 to 4 and -0.024/wk from transect 4 to 5.

Table 3. Chemical and Hydraulic Values Used in Estimating Apparant Degradation Rates

Transect	Area with nonzero TCE concentration (m^2)	Mass per unit thickness from SITE-3D (kg/m)	Average TCE concentration in the transect (kg/m^3) c_i and c_{i+1} in equation 1	Distance between transects (m)	Gradient estimated from Tiedeman and Gorelick (1993)	Retarded seepage velocity for TCE[a] (m/d)	Estimated travel time between transects (weeks) Δt in equation 1
2	1592	10.67	6.70e-3				
				260	7.3e-3	0.11	340
4	2774	1.397	5.04e-4				
				160	1.1e-2	0.156	145
5	1943	0.0282	1.44e-5				

[a]Constants used in seepage velocity calculation:
Hydraulic conductivity: 7.5 m/d
Retardation factor for TCE: $1.78 = 1 + K_{oc}f_{oc}\rho_b/\theta$
Porosity, θ: 0.30
Bulk density ρ_b: 1.86 g/cm^3
K_{oc}: 126 mL/g, f_{oc}: 0.001

References

1. Engineering Science, Inc. 1990. Remedial investigation and feasibility study, St. Joseph, MI, phase I technical memorandum. Liverpool, NY.

2. Kitanidis, P.K., L. Semprini, D.H. Kampbell, and J.T. Wilson. 1993. Natural anaerobic bioremediation of TCE at the St. Joseph, Michigan, Superfund site. In: U.S. EPA. Symposium on bioremediation of hazardous wastes: Research, development, and field evaluations. EPA/600/R-93/054. Washington, DC (May). pp. 57-60.

3. McCarty, P.L., and J.T. Wilson. 1992. Natural anaerobic treatment of a TCE plume, St. Joseph, Michigan, NPL site. In: U.S. EPA. Bioremediation of hazardous wastes. EPA/600/R-92/126. pp. 47-50.

4. Tiedeman, C., and S. Gorelick. 1993. Analysis of uncertainty in optimal ground-water contaminant capture design. Water Resour. Res. 29(7):2,139-2,153.

5. U.S. EPA. 1990. Subsurface remediation guidance table 3. EPA/540/2-90/011b.

Poster Session

Technical Protocol for Implementing the Intrinsic Remediation With Long-Term Monitoring Option for Natural Attenuation of Fuel-Hydrocarbon Contamination in Ground Water

Todd H. Wiedemeier
Engineering-Science, Inc., Denver, CO

John T. Wilson and Donald H. Kampbell
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK

Ross N. Miller and Jerry E. Hansen
U.S. Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks AFB, TX

This paper presents a brief overview of the technical protocol, currently under development by the U.S. Air Force Center for Environmental Excellence (AFCEE), Technology Transfer Division, for data collection, ground-water modeling, and exposure assessment in support of intrinsic remediation (natural attenuation) with long-term monitoring for restoration of fuel-hydrocarbon contaminated ground water (1). The material presented herein was prepared through the joint effort of AFCEE, the Bioremediation Research Team at the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma, and Engineering-Science, Inc., to facilitate implementation of intrinsic remediation at fuel-hydrocarbon contaminated sites. Specifically, this protocol is designed to evaluate the fate of dissolved-phase fuel hydrocarbons having regulatory maximum contaminant levels (MCLs). The intended audience for this document is U.S. Air Force (USAF) personnel, scientists, consultants, regulatory personnel, and others charged with remediating fuel-hydrocarbon contaminated ground water at USAF facilities.

Intrinsic remediation is achieved when naturally occurring attenuation mechanisms, such as biodegradation (aerobic and anaerobic), bring about a reduction in the total mass of a contaminant dissolved in ground water. During intrinsic remediation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide and water), not just transferred to another phase or location within the environment. Intrinsic remediation results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Destructive processes include biodegradation, abiotic oxidation, and hydrolysis. Nondestructive attenuation mechanisms include sorption, dilution (caused by dispersion and infiltration), and volatilization.

In some cases, intrinsic remediation reduces dissolved-phase contaminant concentrations to below MCLs before the contaminant plume reaches potential receptors, even if little or no source removal or reduction takes place. In situations where intrinsic remediation will not reduce contaminant concentrations to below regulatory MCLs, in an acceptable time frame, less stringent cleanup goals may be implemented. This is especially likely if it can be demonstrated that intrinsic remediation will result in a continual reduction in contaminant concentrations over time such that calculated risk values are reduced.

Intrinsic remediation is gaining regulatory acceptance and has been implemented at several sites over the past few years (2-5). In addition to bringing about complete mineralization of contaminants, intrinsic remediation is nonintrusive and allows continuing use of infrastructure during remediation. The main limitation is that intrinsic remediation is subject to natural and institutionally induced changes in local hydrogeologic conditions. In addition, aquifer heterogeneity may complicate site characterization as it will with any remedial technology.

Evaluating the effectiveness of intrinsic remediation requires the quantification of ground-water flow and solute transport and transformation processes, including rates of natural attenuation. Quantification of contaminant migration and attenuation rates, and successful implementation of the intrinsic remediation option, requires completion of the following steps, each of which is discussed in the following sections and outlined in Figure 1:

1. Review existing site data.

2. Develop a preliminary conceptual model for the site, and assess the potential significance of intrinsic remediation.

3. Perform site characterization in support of intrinsic remediation.

4. Refine the conceptual model based on site characterization data, complete premodeling calculations, and document indicators of intrinsic remediation.

5. Model intrinsic remediation using numerical fate and transport models that allow incorporation of a biodegradation term (e.g., Bioplume II or Bioplume III).

6. Conduct an exposure assessment.

7. Prepare a long-term monitoring plan, long-term monitoring wells at the site, and point-of compliance wells.

8. Present findings to regulatory agencies, and obtain approval for the intrinsic remediation with long-term monitoring option.

Collection of an adequate database during the iterative site characterization process is an important step in the documentation of intrinsic remediation. At a minimum, the site characterization phase should provide data on the location and extent of contaminant sources; data on the location, extent, and concentration of dissolved-phase contamination; ground-water geochemical data; geologic data on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential contaminant migration pathways to human or ecological receptors. Contaminant sources include nonaqueous-phase liquid (NAPL) hydrocarbons present as mobile NAPL (NAPL occurring at sufficiently high saturations to drain, under the influence of gravity, to a well) or residual NAPL (NAPL occurring at immobile residual saturations that are unable to drain to a well by gravity).

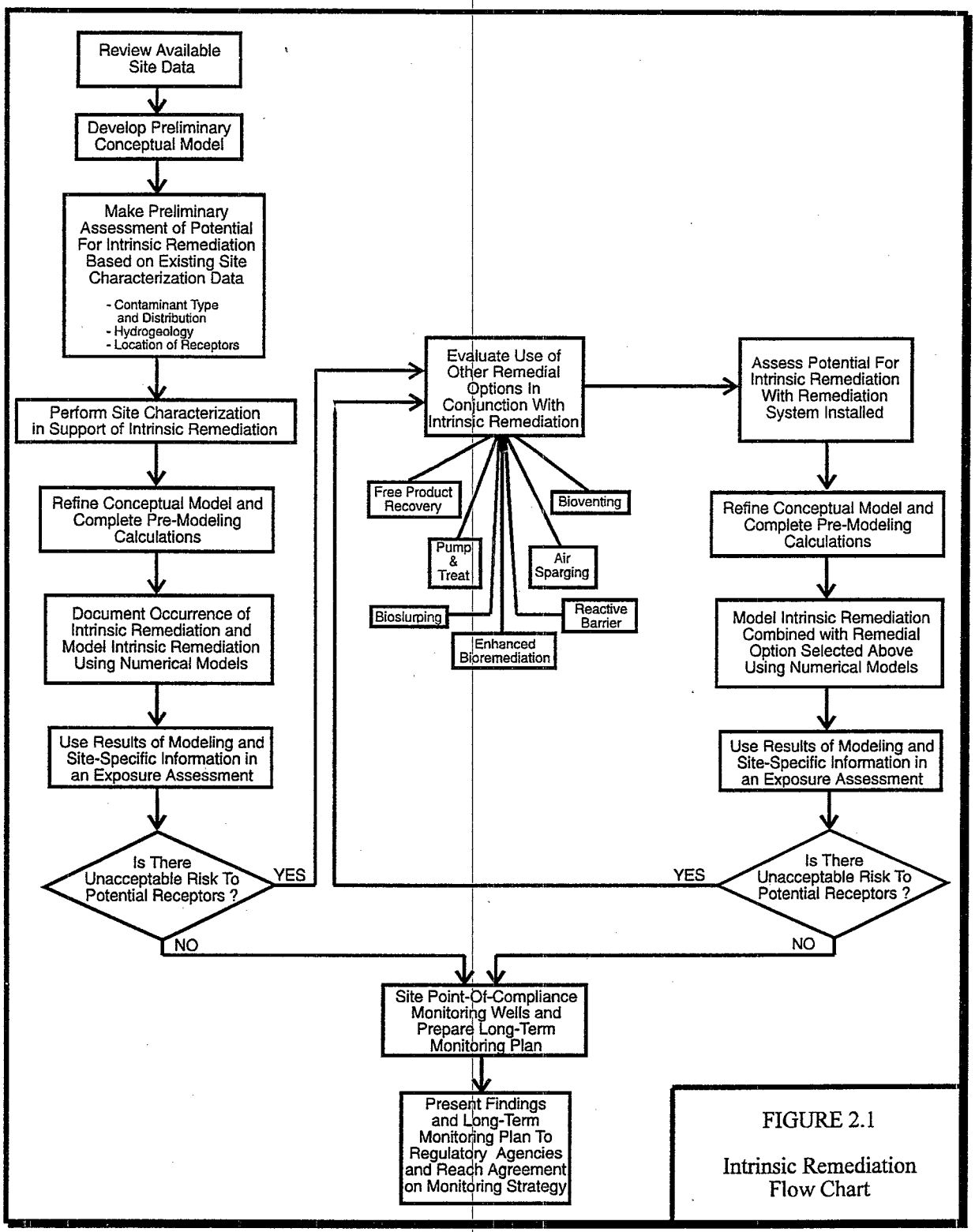


Figure 1. Intrinsic remediation flow chart.

The following analytical protocol should be used for analysis of soil and ground-water samples. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and biodegradation (aerobic and anaerobic) of fuel hydrocarbons. Soil samples should be analyzed for total volatile and extractable hydrocarbons, aromatic hydrocarbons, and total organic carbon. Ground-water samples should be analyzed for dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, alkalinity, nitrate, sulfate, sulfide, ferrous iron, carbon dioxide, methane, chloride, total petroleum hydrocarbons, and aromatic hydrocarbons. The extent and distribution (vertical and horizontal) of contamination and electron acceptor and metabolic byproduct concentrations and distributions are of paramount importance in documenting the occurrence of biodegradation of fuel hydrocarbons and in numerical model implementation. Dissolved oxygen concentrations below background in an area with fuel-hydrocarbon contamination are indicative of aerobic hydrocarbon biodegradation. Similarly, nitrate and sulfate concentrations below background in an area with fuel-hydrocarbon contamination are indicative of anaerobic biodegradation through denitrification and sulfanogenesis. Contour maps can be used to provide visible evidence of these relationships. Elevated concentrations of metabolic byproducts in areas with fuel-hydrocarbon contamination are indicative of hydrocarbon biodegradation. As iron II and methane concentrations increase during iron (III) reduction and methanogenesis (anaerobic processes), BTEX concentrations should be seen to decrease. Contour maps can be used to provide visible evidence of these relationships.

To support implementation of intrinsic remediation, the property owner must scientifically demonstrate that degradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment. Three lines of evidence can be used to support intrinsic remediation: 1) documented loss of contaminants at the field scale, 2) the use of chemical analytical data in mass balance calculations of microbial metabolism, and 3) laboratory microcosm studies using aquifer samples collected from the site.

The first line of evidence involves using measured dissolved-phase concentrations of biologically recalcitrant tracers found in fuels in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in the total mass of contaminants is occurring at the site. The second line of evidence involves the use of chemical analytical data in mass balance calculations to show that a decrease in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations. This evidence can be used to show that electron acceptor concentrations are sufficient to degrade dissolved-phase contaminants. Numerical models can be used to aid mass-balance calculations and to collate information on degradation. The third line of evidence, the microcosm study, involves studying site aquifer materials under controlled conditions in the laboratory to show that indigenous biota are capable of degrading site contaminants and to confirm rates of contaminant degradation measured at the field scale.

The primary objective of the intrinsic remediation investigation is to determine if natural processes of degradation will reduce contaminant concentrations in ground water to below regulatory standards before potential exposure pathways are completed. This requires that a projection of the potential extent and concentration of the contaminant plume in time and space is made based on governing physical, chemical, and biological processes. This projection should be based on historic variations in—and the current extent and concentration of—the contaminant plume, as well as on the measured rates of contaminant attenuation.

The data collected during site characterization can be used to model the fate and transport of contaminants in the subsurface. Such modeling allows an estimate of the future extent and concentration of the dissolved-phase plume to be made. Several models, including Bioplume II (6), have been used successfully to model dissolved-phase contaminant transport and attenuation. Additionally, a new version of the Bioplume model, Bioplume III, is under development by AFCEE. The intrinsic remediation modeling effort has three primary objectives: 1) to estimate the future extent and concentration of a dissolved-phase contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the possible risk to potential downgradient receptors; and 3) to provide technical support for the natural attenuation remedial option at postmodeling regulatory negotiations.

Microorganisms generally utilize dissolved oxygen and nitrate in areas with dissolved-phase fuel-hydrocarbon contamination at rates that are instantaneous relative to the average advective transport velocity of ground water. This results in the consumption of these compounds at a rate approximately equal to the rate at which they are replenished by advective flow processes. For this reason, the use of these compounds as electron acceptors in the biodegradation of dissolved-phase fuel hydrocarbons is a mass-transport-limited process (7, 8). The use of dissolved oxygen and nitrate in the biodegradation of dissolved-phase fuel hydrocarbons can be modeled using Bioplume II. Microorganisms generally utilize sulfate, iron III, and carbon dioxide (used during methanogenesis) in areas with dissolved-phase fuel-hydrocarbon contamination at rates that are slow relative to the advective transport velocity of ground water. This results in the consumption of these compounds at a rate slower than the rate at which they are replenished by advective flow processes. Therefore, the use of these compounds as electron acceptors in the biodegradation of dissolved-phase fuel hydrocarbons is a reaction-limited process that can be approximated by first-order kinetics. The Bioplume II model utilizes a first-order rate constant to model such biodegradation. First-order decay constants can be determined by simple calculations based on ground-water chemistry or through the use of laboratory microcosm studies. In addition, the use of radiolabeled materials in a microcosm study can be used to provide evidence of the ultimate fate of the contaminants.

The results of the modeling effort are not in themselves sufficient proof that intrinsic remediation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model and the model itself. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent to provide sufficient evidence to demonstrate that the mechanisms of intrinsic remediation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of conservative input parameters and numerous sensitivity analyses so that consideration is given to all plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently supports the natural reduction and removal of the dissolved-phase contaminant plume. In some cases, simple calculations of contaminant attenuation rates are all that are required to successfully support intrinsic remediation.

Upon completion of the fate and transport modeling effort, model predictions can be used in an exposure assessment. If intrinsic remediation is sufficiently active to mitigate risks to potential receptors, the proponent of intrinsic remediation has a reasonable basis for negotiating this option with regulators. The exposure assessment allows the proponent to show that potential exposure pathways will not be completed.

The long-term monitoring plan consists of locating ground-water monitoring wells and developing a ground-water sampling and analysis strategy. This plan is used to monitor plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on the results of a numerical model such as Bioplume II.

Point-of-compliance (POC) monitoring wells are wells that are installed at locations downgradient of the contaminant plume and upgradient of potential receptors. POC monitoring wells are generally installed along a property boundary or at a location approximately 5 yr downgradient of the current plume at the seepage velocity of the ground water of 1 yr to 2 yr upgradient of the nearest downgradient receptor, whichever is more protective. The final number and location of POC monitoring wells depends on regulatory considerations.

Long-term monitoring wells are wells that are placed upgradient of, within, and immediately downgradient of the contaminant plume. These wells are used to monitor the effectiveness of intrinsic remediation in reducing the total mass of contaminant within the plume. The final number and location of long-term monitoring wells depends on regulatory considerations. Figure 2 shows a hypothetical long-term monitoring scenario. The results of a numerical model such as Bioplume II can be used to help site both the long-term and POC monitoring wells.

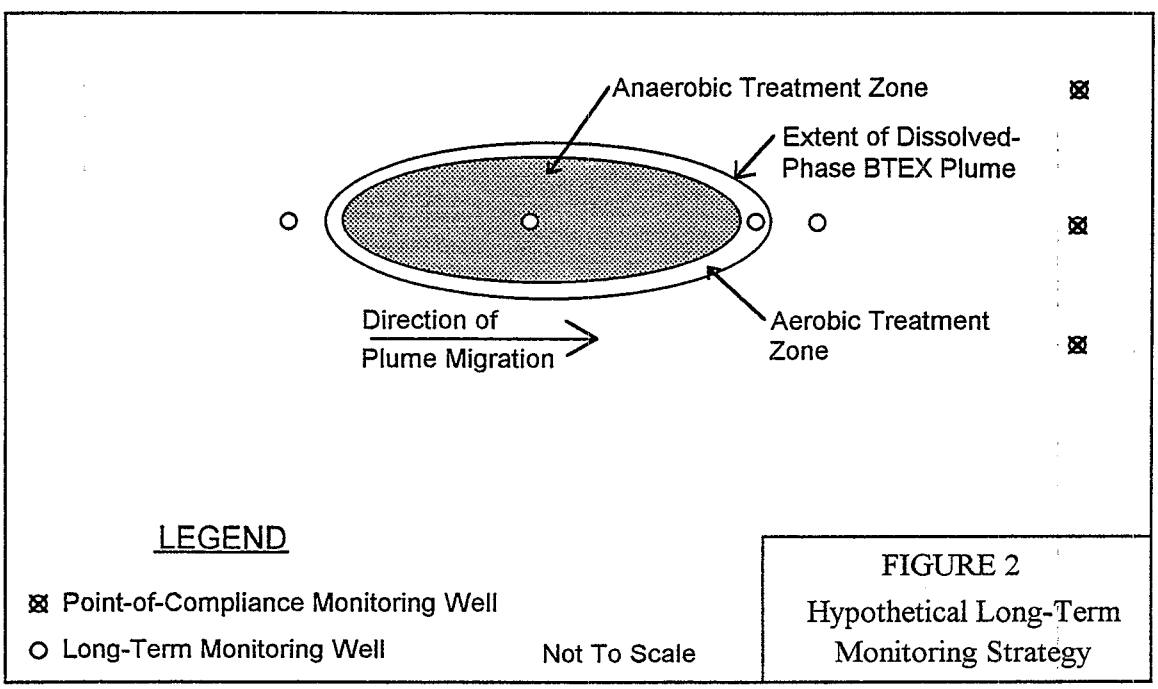


Figure 2. Hypothetical long-term monitoring strategy.

References

1. Wiedemeier, T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1994. Draft technical protocol for implementing the intrinsic remediation with long-term monitoring option for natural attenuation of dissolved-phase fuel contamination in ground water. U.S. Air Force Center for Environmental Excellence, Technology Transfer Division.

2. Klecka, G.M., J.W. Davis, D.R. Gray, and S.S. Madsen. 1990. Natural bioremediation of organic contaminants in ground water—Cliffs-Dow Superfund site. Ground Water 28(4):534-543.

3. Downey, D.C., and M.J. Gier. 1991. Supporting the no-action alternative at a hydrocarbon spill site. In: Proceedings of the USAF Environmental Restoration Technology Symposium, San Antonio, TX (May 7-8). Section U. pp. 1-11.

4. Wiedemeier, T.H., P.R. Guest, R.L. Henry, and C.B. Keith. 1993. The use of Bioplume to support regulatory negotiations at a fuel spill site near Denver, Colorado. In: Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference. NWWA/API. pp. 445-459.

5. Wiedemeier, T.H., B. Blicker, and P.R. Guest. 1994. Risk-based approach to bioremediation of fuel hydrocarbons at a major airport. In: Proceedings of the 1994 Federal Environmental Restoration III and Waste Minimization Conference and Exhibition, New Orleans, LA. Hazardous Materials Control Resources Institute. pp. 51-60.

6. Rifai, H.S., P.B. Bedient, J.T. Wilson, K.M. Miller, and J.M. Armstrong. 1988. Biodegradation modeling at aviation fuel spill site. J. Environ. Eng. 114(5):1,007-1,0029.

7. Borden, R.C., and P.B. Bedient. 1986. Transport of dissolved hydrocarbons influenced by oxygen limited biodegradation—theoretical development. Water Resour. Res. 22(13):1973-1982.

8. Wilson, J.T., J.F. McNabb, J.W. Cochran, T.H. Want, M.B. Tomson, and P.B. Bedient. 1985. Influence of microbial adaptation on the fate of organic pollutants in ground water. Environ. Toxicol. Chem. 4:721-726.

Wisconsin's Guidance on Naturally Occurring Biodegradation as a Remedial Action Option

Michael J. Barden
Wisconsin Department of Natural Resources, Emergency and Remedial Response Section, Madison, WI

In February 1993, the Wisconsin Department of Natural Resources issued an interim guidance on naturally occurring biodegradation as a remedial action option for contaminated sites. The focus of this guidance was primarily on soil contamination by petroleum hydrocarbons and on the requirements for site characterization and monitoring necessary to use this approach. Subsequent implementation of the interim guidance has resulted in further refinement to make this an effective approach for both soil and ground-water contamination.

The application of naturally occurring biodegradation as a remedial action requires that the site be adequately characterized and that an adequate monitoring program be developed and implemented. This is a long-term remediation option, likely requiring years or decades to effect adequate cleanup. From a regulatory perspective, the primary concerns are that the site conditions are amenable to naturally occurring biodegradation and that the process is effective in reducing contaminant concentrations to acceptable levels within a reasonable period with respect to potential contaminant migration or impacts to receptors.

Adequate site characterization is required during the site investigation so that naturally occurring biodegradation can be evaluated with other possible remedial action options. This also provides baseline information for the potential application of enhanced bioremediation as well, because the basic site characterization requirements are essentially the same. Characterization involves identification of 1) the contaminants present and their concentrations and biodegradability, 2) physical and chemical parameters affecting availability of oxygen and alternative electron acceptors, 3) nutrients, and 4) microbiological parameters indicating the presence and viability of appropriate microbial populations. A sufficient number of samples should be used to represent the extent of contamination and site heterogeneity. The guidance provides a framework for interpretation and evaluation of the results.

If site conditions are favorable, a monitoring plan must be developed and implemented. Monitoring indicates that contaminant concentrations are decreasing over time, ensures that no unexpected contaminant migration is occurring, and provides information regarding the nature and rate of biodegradation at the site. A variety of monitoring approaches and techniques are available for soil and ground water. In general, monitoring changes in contaminant concentrations and/or concentrations of co-reactants are appropriate.

Experience with implementation indicates that many responsible parties are unlikely to select this option due to the long time frame involved. This suggests that naturally occurring biodegradation is more viable as an option for stable entities where time is not an issue. The availability of the guidance, however, has encouraged consideration of bioremediation in general as a viable remedy due to perceived regulatory acceptance of the technology and because the required consideration of biodegradation potential provides baseline site information that can be used in the evaluation and design of enhanced bioremediation systems.

Assessing the Efficiency of Intrinsic Bioremediation

Francis H. Chapelle
U.S. Geological Survey, Columbia, SC

Abstract

The efficiency of intrinsic bioremediation to contain contaminant migration in ground-water systems can be quantitatively assessed by comparing rates of contaminant transport with rates of biodegradation. If transport rates are *fast* relative to rates of biodegradation, contaminants can migrate freely with ground-water flow and possibly reach a point of contact with human or wildlife populations. Conversely, if transport rates are *slow* relative to biodegradation rates, contaminant migration will be more confined and less likely to reach a point of contact. In either case, the efficiency of intrinsic bioremediation can be assessed by evaluating the presence or absence of contaminant transport to predetermined points of contact. Thus, this assessment includes hydrologic (rates of ground-water flow), microbiologic (rates of biodegradation), and sociopolitical (points of contact) considerations.

The U.S. Geological Survey, in cooperation with the Naval Facilities Engineering Command, has developed a framework for assessing the efficiency of intrinsic bioremediation that is based on these three considerations. In this framework, hydrologic and microbiologic information is synthesized using a solute-transport code (SUTRA) and used to estimate rates of contaminant transport to predefined points of contact (adjacent water supply wells or surface water bodies). This framework is applied to two sites, in Beaufort and Hanahan, South Carolina, contaminated with aviation fuel. At the Beaufort site, rates of biodegradation are slow due to anaerobic conditions (K_{bio} ~0.01 d-1), but because rates of ground-water flow are low (~0.02 ft/d), soluble contaminants are effectively contained and are not transported to adjacent points of contact. At the Hanahan site, biodegradation rates are similarly slow under the ambient anaerobic conditions (K_{bio} ~0.01 d^{-1}), but because rates of ground-water flow are relatively high (~1.0 ft/d), contaminants are transported to multiple points of contact with humans. These examples illustrate the complex interplay that develops between hydrologic, microbiologic, and sociopolitical considerations, and show that the efficiency of intrinsic bioremediation can only be assessed on a site-by-site basis.

A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water

Paul M. McAllister and Chen Y. Chiang
Shell Development Company, Houston, TX

The extent of natural attenuation is an important consideration in determining the most appropriate corrective action at sites where ground-water quality has been affected by releases of petroleum hydrocarbons or other chemicals. The objective of this presentation is to provide guidelines for evaluating natural attenuation based on easily obtainable field and laboratory data.

The primary indicators that can be used to evaluate natural attenuation include dissolved oxygen (DO) levels in ground water and plume characteristics. Background DO levels greater than 1 to 2 mg/L and inverse correlation between DO and soluble hydrocarbon concentration have been identified through laboratory and field studies as key indicators of aerobic biodegradation. Several unique plume characteristics include 1) plumes migrate more slowly than expected; 2) plumes reach a steady state; and 3) plumes decrease in extent and concentration, which may indicate the effects of natural attenuation.

When DO is depleted in an aquifer, anaerobic conditions prevail. For biodegradation to occur, an alternative electron acceptor such as nitrate, carbonate, or iron III must be available. Between aerobic and anaerobic conditions (i.e., 0.1 ppm to 2 ppm), there is a region sometimes labeled the hypoxic zone. Studies in the hypoxic zone have indicated that biodegradation of benzene, toluene, ethylbenzene, and the xylenes (BTEX) may occur at relatively low DO levels provided a secondary electron acceptor is available.

Other secondary indicators (e.g., geochemical data) and more intensive methods (e.g., contaminant mass balances, laboratory microcosm studies, and detailed ground-water modeling) can be applied to demonstrate natural attenuation as well. The recommended approach for evaluating natural attenuation is to design site assessment activities so that required data such as DO levels and historical plume flow path concentrations are obtained. With the necessary data, the primary indicators should be applied to evaluate natural attenuation.

The Use of Low Level Activities To Assist Intrinsic Bioremediation

Robert D. Norris
Eckenfelder Inc., Nashville, TN

Jeffrey C. Dey
Resource Control Corporation, Rancogas, NJ

Daniel P. Shine
Sun Company, Inc., Aston, PA

Intrinsic bioremediation as discussed in the recent report of the National Academy of Sciences Committee on Bioremediation (1) can reduce the concentrations of some common contaminants to levels generally considered protective of human health. Since the observations of the role of biodegradation in limiting the extent of the ground-water plume at the Conroe, Texas, wood-preserving site (2), many other sites have been observed to have undergone natural attenuation at sufficient rates to limit the size of contaminant plumes; in several instances, contaminant levels decreased to below cleanup levels.

The use of intrinsic bioremediation, while generally attractive from a cost perspective, may actually be desirable environmentally because secondary effects of active remediation are avoided. Intrinsic bioremediation, however, has several costs associated with its use. These include some level of documentation that biological degradation of constituents of concern is taking place and costs associated with monitoring and management of the site. Managing a small plume, such as is frequently found at service stations, includes sampling and reporting to the responsible environmental agency. At one typical site (3), the annual environmental management costs have been approximately $11,900 per year, consisting of site visits and sampling ($1,000), chemical analysis ($7,200), reporting ($2,400), and consulting ($1,300). At other sites, costs have exceeded these values by 50 percent or more. Documenting that biodegradation is occurring adds substantially to these costs.

Intrinsic bioremediation will be effective where the electron acceptor requirements are relatively small. While oxygen may reach the affected zones at rates sufficient to prevent and shrink contaminant plumes, and thus eventually achieve remedial goals, the time frame may be unacceptably long from the site owner's perspective because of long-term monitoring costs and management burdens.

Addition of appropriate electron acceptors would accelerate reduction in constituents such as monoaromatic hydrocarbons. In some cases where intrinsic bioremediation is technically feasible, it may not be the most cost-effective approach. To evaluate the concept of applying limited engineering solutions at sites where intrinsic bioremediation appears to be slowly reducing the contaminant mass, we are testing the use of air sparging wells (3). The air sparging wells are placed immediately outside the plumes and operated intermittently at low flow. The cost of installing three shallow air sparging wells, routine maintenance, limited additional sampling, and reporting was budgeted at $8,500 per site for each of the three sites. If the time to reach closure is shortened by 1 yr or more, the cost of treatment will have been less than the cost that would have been incurred by only monitoring and managing the site.

Another approach to providing electron acceptors is to add aqueous solutions of hydrogen peroxide or nitrate to wells located within or immediately upgradient of the plume; however, nitrate addition has not been shown to be effective for degradation of benzene, and introduction of hydrogen peroxide is more labor intensive and thus more costly than air sparging. Alternatively, a slow-release oxygen compound such as magnesium peroxide can be placed in wells and oxygen allowed to diffuse into the formation.

Regulatory acceptance for natural attenuation may be more easily attained if a migration barrier is created along the downgradient edge of the plume. Migration barriers can be created through a series of low-flow air-sparging wells. Alternatively, a row of wells containing a slow-release oxygen compound can be placed perpendicular to the ground-water gradient near the downgradient edge of the plume. As demonstrated by Bob Borden (4) of the University of North Carolina at a commercial site in North Carolina and by Doug Mackay (5) of Stanford University in tests conducted at the Borden Landfill in Canada, this approach can successfully prevent migration of monoaromatic hydrocarbons.

Intrinsic bioremediation should be viewed as one approach in a continuum of methods of utilizing biodegradation processes to remediate soil and ground water. It should be used alone, in combination with other approaches, or as a polishing step based on evaluation of the site conditions, regulatory issues, technical feasibility, implementability, and cost.

This poster session will present cost and analytical data from three New Jersey service stations during the monitoring-only phase, site maps, diagrams of the air sparging systems that have been installed, costs of installation and operation, and analytical data available at the time of the meeting. The cost of adding hydrogen peroxide at two similar sites will be discussed. Additionally, the costs and relative advantages of the use of slow-release oxygen compounds and air sparging will be presented.

References

1. National Research Council. 1993. *In situ* bioremediation: When does it work? Washington, DC: National Academy Press.

2. Wilson, J.T., J.F. McNabb, J. Cochran, T.H. Wang, M.B. Tomson, and P.B. Bedient. 1985. Influence of microbial adaptation on the fate of organic pollutants in ground water. Environ. Toxicol. Chem. 4:721-726.

3. Norris, R.D., J.C. Dey, and D.P. Shine. 1993. The advantages of concerted bioremediation of lightly contaminated sites compared to intrinsic bioremediation. Presented at the American Chemical Society I&E Special Symposium, Atlanta, GA.

4. Kao, C.-M., and R.C. Borden. 1994. Enhanced aerobic bioremediation of a gasoline contaminated aquifer by oxygen-releasing barriers. In: Hydrocarbon bioremediation. Boca Raton, FL: Lewis Publishers.

5. Bianchi-Mosquera, G.C., R.M. Allen-King, and D.D. Mackay. 1994. Enhanced degradation of dissolved benzene and toluene using a solid oxygen-releasing compound. Ground Water Monitor. Rev. pp. 120-128.

Natural Attenuation of Jet Fuel in Ground Water

Greg Doyle, Dwayne Graves, and Kandi Brown
International Technologies Corporation, San Bernardino, CA

Natural attenuation is a minimum action remedial strategy that permits the biodegradation of organic contaminants under natural, *in situ* conditions. Mechanisms that act to affect contaminant biodegradation include aerobic biodegradation at the plume boundary and various anaerobic processes within the plume. Nitrate, iron, manganese, and sulfate reduction and methanogenesis are thought to support contaminant biodegradation. Naturally occurring levels of nitrate, sulfate, oxidized iron and manganese, and carbonates support anaerobic biodegradation.

Natural attenuation was proposed as a feasible remedial alternative for the dissolved jet fuel plume at George Air Force Base in Victorville, California. The plume, covering approximately 1.1 million square feet, was located in a poorly yielding perched aquifer, 120 ft below the ground surface. Ground-water flow rate was approximately 20 ft/yr, and the edge of the plume was about 2,000 ft from the property line. The ground water in the affected aquifer was not being used. Because of subsurface conditions, slow migration, poor water yield, and lack of use, natural attenuation represented the most efficient and cost-effective approach for remediating dissolved jet fuel at this site.

A separate-phase layer of jet fuel floated on the water table near the center of the plume. An aggressive skimming operation was employed to remove all recoverable separate-phase jet fuel from the subsurface. Bioventing will be used to further remediate contaminated vadose zone soil in areas where jet fuel was detected and removed.

Natural attenuation for aerobic and aerobic/anaerobic conditions was modeled using BIOPLUME II. The BIOPLUME II model simulates the transport of dissolved hydrocarbons under the influence of oxygen-limited biodegradation. Using BIOPLUME II with site specific parameters, various treatment scenarios were evaluated. Assuming that 60 percent of the separate-phase product was removed, both anaerobic and aerobic biodegradation occurred, and residual jet fuel diffused into the water based on Fick's Law of Diffusion, a remediation time of 42 yr was determined. This treatment time was adequate to remediate the plume before it migrated off site.

Based on this prediction and the cost savings realized by applying natural attenuation, a 5-yr performance period was established prior to the issuance of a finalized record of decision. Joint efforts by the Air Force, the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory, and IT will provide data verifying the accuracy of the BIOPLUME II model predictions and demonstrating the level of natural biological activity occurring in the ground water. These efforts are expected to lead to regulatory acceptance of natural attenuation for the full-scale remediation of the jet fuel plume on site.

Evaluation of Intrinsic Bioremediation at an Underground Storage Tank Site in Northern Utah

R. Ryan Dupont, Darwin L. Sorensen, and Marion Kemblowski
Utah Water Research Laboratory, Utah State University, Logan, UT

A 2-yr field study was initiated by the Utah Water Research Laboratory for the U.S. Environmental Protection Agency's Office of Underground Storage Tanks at two former underground storage tank (UST) sites in northern Utah: a U.S. Air Force site at Hill Air Force Base (AFB) near Ogden, Utah, and a private site in Layton, Utah. The study sought to evaluate rapid site assessment techniques and data collection and summary methods that could be used to provide a comprehensive description of the potential for intrinsic bioremediation at UST sites. This poster presentation focuses on the Hill AFB site, where tank and line leaks from an 18,000 gal UST, removed in 1989, were the probable sources of observed ground-water contamination. Total dissolved petroleum hydrocarbon contaminant mass at the beginning of the study was estimated to be 950,000 mg, while approximately 6,000 mg of benzene and 8,000 mg of toluene were quantified in the plume underlying the site. The site was covered with a permeable gravel surface layer during the study, and dissolved oxygen concentrations at a number of locations in uncontaminated areas surrounding the plume were over 2 mg/L.

Initial site assessment activities utilized cone penetrometry for rapid collection of subsurface soil stratigraphic data and for the placement of more than 60 small-diameter ground-water sampling points at the two shallow field sites. Ambient temperature headspace analyses were conducted using a polyethylene bag method developed by the Utah Water Research Laboratory in addition to a commercial Lag-in-a-Bag apparatus to provide rapid field-determined measurements of ground-water total hydrocarbons. Field total petroleum hydrocarbon (TPH) measurements were collected on a near real-time basis to guide the initial placement of ground-water monitoring points along and perpendicular to the axis of the contaminant plume at each site. These field methods proved that the original conceptual model of the nature and extent of contamination and of the potential contaminant migration pathways at the Hill AFB site, based on conventional site assessment techniques (soil gas survey, collection of limited soil core samples, and placement of more limited numbers of large-diameter ground-water monitoring wells), was greatly in error. The model could be improved significantly with these cost-effective field techniques, which are now widely available to the consulting community.

Seven field sampling events, beginning in April 1992, were conducted over the 2-yr study period as part of a proposed intrinsic bioremediation strategy developed in the project. Ground-water quality data were collected from the small-diameter sampling points and existing ground-water monitoring wells to assess the distribution and transport of contaminants, along with the predominant microbial reactions taking place within the contaminant plume. Ground-water quality data collected included field measurements of pH, dissolved oxygen, temperature, and ambient headspace total hydrocarbon concentrations; laboratory determinations included nitrate-N, sulfate, dissolved iron and manganese, total hydrocarbons (purge and trap and semivolatile constituents), specific organic contaminants (C-6 to C-15 alkanes and benzene, toluene, ethylbenzene, p-xylene, naphthalene, and methylnaphthalene), and contaminant boiling point split concentrations.

Ground-water data were used to generate total and specific compound dissolved contaminant and dissolved electron acceptor mass data for each sampling period. The location of the center of the mass of contaminants and electron acceptors were evaluated, and changes in these parameters over time, with respect to bulk ground-water flow, were used to assess the rate and magnitude of natural degradation processes taking place at each site.

Over the 2-year study period, the mass of TPH showed exponential decay, while all specific constituents displayed zero-order decay rates. Dissolved TPH mass declined to less than 1,000 mg (>99.9 percent removal) by the end of the 630-d monitoring period, while dissolved benzene and toluene mass remaining in the contaminant plume declined to less than 200 mg (97 percent removal). TPH, benzene, and toluene mass decay rates were found to be -0.013/d ($p = 0.03$, $r^2 = 0.933$), -11.2 mg benzene/d ($p = 0.01$, $r^2 = 0.976$), and -14.2 mg toluene/d ($p = 0.01$, $r^2 = 0.998$), respectively. Mass center data indicate that while ground-water velocities at the site through the study period averaged 0.45 ft/d, the net movement of contaminants was attenuated significantly, with measured center of mass velocities of TPH, benzene, and toluene being 0.03 ft/d, 0.05 ft/d, and 0.07 ft/d, respectively. Corresponding utilization of oxygen and other terminal electron acceptors occurred across the plume.

Intrinsic bioremediation of the dissolved plume at the Hill AFB site successfully attenuated and removed the residual hydrocarbon mass existing at the site at the beginning of the study. In January 1994, only 1 of 34 monitoring well/piezometer ground-water samples contained a benzene concentration (20.7 μg/L) above regulatory concern, and the site is expected to be eligible for closure at the next routine, semiannual sampling event.

This poster session will detail the physical/chemical characteristics of the field sites and the rapid site assessment techniques and typical results collected, as well as highlight the data collection/reduction/interpretation methodology developed in this study. Finally, more complete results demonstrating natural degradation of hydrocarbon contaminants at this site will be presented, along with a summary of a natural attenuation decision support system to aid investigators in assessing the viability of intrinsic bioremediation for the selection of a "no action"/natural attenuation monitoring alternative at their sites.

Case Studies of Field Sites To Demonstrate Natural Attenuation of BTEX Compounds in Ground Water

Chen Y. Chiang and Paul M. McAllister
Shell Development Company, Houston, TX

The most definitive indicators of natural attenuation such as plume characteristics and dissolved oxygen (DO) concentrations are based on actual concentrations obtained during periodic monitoring events. Based on appropriate data from monitoring wells, the following parameters can be used to indicate and demonstrate that natural attenuation is occurring: 1) the mass of benzene, toluene, ethylbenzene, and the xylenes (BTEX) present and 2) the extent and rate of migration and distribution of BTEX concentrations. Data collected from two field sites will be used to demonstrate natural attenuation mechanisms.

The first site is characterized by 42 monitoring wells to show the relationship between soluble BTEX and DO plumes. Results from 10 sampling periods over 3 years show a significant reduction in total BTEX mass with time in ground water. These reduction and leakage rates from sources are determined from material balance and nonlinear least-squares analyses. The natural attenuation rate is calculated to be 0.95 percent/d. Spatial relationships between DO and total BTEX are shown to be strongly correlated by statistical analyses and solute transport modeling. In addition, laboratory microcosm biodegradation experiments are performed to determine possible threshold limits for aromatic hydrocarbon oxidation under varying levels of DO. The results are remarkably consistent with field data on the presence of high or low levels of BTEX and DO in several monitoring well-water samples.

The second site data will be used to demonstrate natural attenuation from a cost-effectiveness perspective through evaluation of plume characteristics over time. The benzene concentrations along the primary flow path at this site are observed to decrease from 2,600 ppb at the source to 2.7 ppb at a distance 1,425 ft downgradient. The decrease in concentrations with distance from the source is a direct indication that some degree of natural attenuation is occurring. If no natural attenuation was occurring, then concentrations would remain relatively constant out to the leading edge, where a sharp front would be observed. It is emphasized that natural attenuation also includes other mechanisms than biodegradation: dispersion, sorption, volatilization, and chemical transformation.

Demonstrating Intrinsic Bioremediation of BTEX at a Natural Gas Plant

Keith Piontek and Tom Sale
CH2M Hill, St. Louis, MO, and Denver, CO

Steve de Albuquerque and John Cruze
Phillips Petroleum Company, Bellaire, TX, and Bartlesville, OK

Intrinsic bioremediation is being characterized at the site of a former natural gas plant. Gas plant operations resulted in the release of nonaqueous-phase liquid (NAPL) to the eolian deposits beneath the site. Ground water beneath the site contains benzene, toluene, ethylbenzene, and xylene (BTEX) constituents of the NAPL. The rate and extent of BTEX biodegradation that occurs under natural conditions is being characterized to provide for more realistic assessment of potential risks posed by the site, and to support long-term site management decision-making.

The characterization of intrinsic bioremediation is being conducted in general accordance with the protocol proposed by Dr. John Wilson of the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory. Key parameters being assessed include seasonal variations in ground-water flow direction and velocity, changes in hydrocarbon concentrations, and changes in the concentrations of electron acceptors. These data, together with knowledge of the stoichiometry of hydrocarbon biodegradation under various redox conditions, are used to confirm that BTEX biodegradation is occurring at the site and to estimate the BTEX biodegradation rate.

The characterization of intrinsic bioremediation at this site is under way. Ground-water samples are collected and analyzed on a quarterly basis. Two ground-water sampling events have been performed, and two additional sampling events are planned. To date, findings include the following:

- The extent of the dissolved hydrocarbon plume is smaller than would be expected if the hydrocarbons were not being biodegraded. BTEX concentrations decrease by five orders of magnitude within a lateral, downgradient distance of 300 ft from the NAPL zone.

- While some oxygen flux into the plume occurs, the majority of contaminant mass removal occurs under anoxic conditions. Naturally high concentrations of sulfate in the ground water provide an essentially infinite supply of electron acceptor for biodegradation under sulfate-reducing conditions. Site data suggest that sulfate is the most significant electron acceptor in terms of hydrocarbon mass removal, with over 90 percent of the hydrocarbon mass removal attributable to sulfate reduction.

- Additional hydrocarbon mass removal is attributable to reduction of nitrate, iron, carbon dioxide, and oxygen.

- Elevated concentrations of bicarbonate downgradient of the plume, associated with hydrocarbon mineralization, confirm the role of intrinsic bioremediation in limiting plume migration and provide evidence that the plume has reached its steady-state extent.

The poster paper will present information on the site setting, monitoring and data evaluation methodology, evidence of intrinsic bioremediation mechanisms and rates, and impact of observed biodegradation on plume migration.

Demonstrating the Feasibility of Intrinsic Bioremediation at a Former Manufactured Gas Plant

Ian D. MacFarlane
EA Engineering, Science, and Technology, Sparks, MD

Edward J. Bouwer
The Johns Hopkins University, Baltimore, MD

Patricia J.S. Colberg
University of Wyoming, Laramie, WY

A former manufactured gas plant (MGP) in Baltimore, Maryland, is the subject of an investigation to assess natural, *in situ* biodegradation for the purposes of basing remediation decisions on intrinsic bioremediation and engineered, enhanced bioremediation. Tar, a byproduct of the former gas manufacturing operation, is found in the site's subsurface to depths as great as 100 ft. The tar is a dense nonaqueous-phase liquid (DNAPL) that contains monocyclic aromatic hydrocarbons (MAHs), such as benzene and toluene, and polycyclic aromatic hydrocarbons (PAHs), such as naphthalene and benzo(a)pyrene. The tar DNAPL acts as a long-term source of aromatic hydrocarbons to ground water, and concentrations in ground water over much of the 70-acre site are close to theoretical effective solubilities.

Laboratory and field data were collected to evaluate biodegradation. The first phase of the laboratory investigation, consisting of tests on 16 soil samples from various depths, was to discern whether or not microbes existed in the subsurface, if they could use MGP-tar as a carbon source, and if relationships could be established between hydrogeology, contaminant distribution, and microbiological characteristics. Aerobic and anaerobic enumerations were performed, followed by fatty acid analyses to identify the microbes. Viable aerobic bacteria were detected in all subsurface samples. Bacteria were grown in the samples plated under anaerobic conditions, but at counts of 10 percent to 50 percent less than the corresponding aerobic counts. Tar-degrading bacteria were detected in 7 of the 16 samples.

The second laboratory phase consisted of more detailed microcosm studies performed by the Johns Hopkins University (JHU) and the University of Wyoming (UW). JHU used 49 soil samples from five boreholes with site ground-water and individual radiolabeled target substrates (benzene, naphthalene, phenanthrene, and acetic acid) in sealed vials to make microcosms that mimicked *in situ* redox conditions (i.e., oxygenated or unoxygenated). Viable bacteria were enumerated, and total cell counts were performed by the acridine orange direct-count method. Similar microcosm studies are being performed by UW under sulfidogenic, iron-reducing, and methanogenic conditions using phenol, benzene, toluene, naphthalene, and phenanthrene as the targeted radiolabeled compounds. Benzene, naphthalene, and phenanthrene were observed to mineralize 6 percent to 24 percent, 8 percent to 43 percent, and 3 percent to 31 percent, respectively, in JHU aerobic microcosms over a 4-week incubation period. Anaerobic naphthalene mineralization (7 percent to 13 percent) was observed in two JHU samples in the presence of NO_3. Half-lives calculated from first-order degradation rates typically ranged from tens to hundreds of days, with a lower half-life in the initial stages of incubation followed by a slower rate presumably indicative of oxygen- or nutrient-limiting conditions. Under sulfate-

reducing conditions, phenol mineralized 13 percent to 18 percent in 200 d, but benzene, naphthalene, and phenanthrene showed less than 1 percent mineralization in the same period, and toluene showed less than 1 percent mineralization in 165 d. The apparent limited transformation may, in fact, be due to the small inoculum sizes used, a phenomenon documented by others.

Field investigations for natural *in situ* biodegradation included aqueous phase redox conditions, biogenic product analyses, and apparent attenuation of model contaminants. Ground-water quality data generally showed reduced conditions with little or no measurable oxygen, low redox potential (-70 mV average), high biochemical oxygen demand in source zones (>200 mg/L), elevated sulfate (2,200 mg/L average), and elevated iron (570 mg/L average). Biogenic gases (CO_2, H_2S, and CH_4) were detected at levels greater than atmospheric in 11 of the 16 wells measured.

Apparent degradation rates were calculated using the first-order model by regressing the natural log of constituent concentrations (adjusted for dilution) by estimated *in situ* travel time. Because no nonreactive, conservative tracers are unique to the tar sources, dilution was estimated by considering dissolved carbon (organic plus inorganic) as a tracer. While the use of carbon as a tracer is prone to error due to its reactive nature, its use is conservative in that observed carbon concentrations would tend to be less than actual anthropogenic carbon, resulting in overestimates of dilution and underestimates of degradation rates. Half-lives for benzene, toluene, ethylbenzene, xylenes, and naphthalene were calculated to be 729, 660, 877, 855, and 2,166 d, respectively. Half-lives for the three-ring and greater PAHs were not calculated due to the poor regression correlation coefficients. Degradation estimates showed that toluene is the most preferred aromatic substrate studied and that naphthalene appears to degrade the slowest as predictable from the literature. Surprisingly, the benzene rate was only slightly less than the toluene rate.

Laboratory investigations have shown that 1) microbes exist in the subsurface, 2) microbes are capable of using tar as a carbon source, 3) various redox conditions can be established with site consortia, and 4) site bacteria can degrade selected aromatic constituents under aerobic and anaerobic conditions. Field evidence showing various redox conditions and biogenic products of organic degradation gives clues to the possible fate of aromatic hydrocarbons, but this indirect evidence can only be used to support more definitive evidence in demonstrating intrinsic bioremediation. Although estimates of *in situ* constituent decay are based on numerous assumptions and are fraught with uncertainty, this evidence is needed to show real attenuation of aromatic hydrocarbons. In this case, enough geochemical and hydrogeologic data were available to segregate dilution (an important "attenuation" process) from degradation processes. The task of estimating apparent degradation was facilitated by the relatively simple hydraulics and the aged system to allow assumption for negligible sorption. The attenuation assessment demonstrated that contaminant loss was observed over time along the aqueous plume travel path (i.e., travel time, rather than at one point over time) and degradation, probably biotic, was measured for target contaminants.

The combined laboratory and field evidence point to natural *in situ* biodegradation as an active process in the site's low oxygen, subsurface environment. Intrinsic bioremediation, albeit slow due to mass transfer limitations from the tar to the aqueous phase, may be technically viable for controlling aqueous aromatic hydrocarbon contamination emanating from MGP-tar sources. Laboratory studies are continuing to explore compound-specific biodegradation under various conditions, and plans are being formulated now for an *in situ* biodegradation pilot study.

Natural and Enhanced Bioremediation of Aromatic Hydrocarbons at Seal Beach, California: Laboratory and Field Investigations

Harold A. Ball, Gary D. Hopkins, Eva Orwin, and Martin Reinhard
Western Region Hazardous Substance Research Center, Stanford, CA

Introduction

The objective of this study was to develop our understanding of environmental factors that are important for intrinsic anaerobic biodegradation of aromatic hydrocarbons in contaminated ground-water aquifers, and to determine methods to enhance this process. The focus of the investigation was a site at the Seal Beach Naval Weapons Station in southern California, where a significant gasoline spill resulted in contamination of the ground-water aquifer (1). In the field, nitrate was present at about 5 mg/L in background wells and approached detection levels (<0.1 mg/L) in the contaminated wells. There was a high natural background sulfate concentration of about 85 mg/L in the ground water, and methane was detected in the contaminated well headspace. The distribution of aromatics present in the contaminated ground water differs from that expected from dissolution of pure gasoline (2). This suggests that natural biotransformation of several organic species is occurring at the site. The project was divided into laboratory and field components, which were interrelated. The goals of both the laboratory and field experiments were to determine the capability of the native aquifer microbial community to transform aromatic hydrocarbon compounds under anaerobic conditions and to understand the effect of alternate environmental conditions on the transformation processes. Field experiments were carried out on site at Seal Beach. At the field site, experimental monitoring of biotransformation under natural (presumed sulfate-reducing) and nitrate-enhanced conditions have been carried out.

Approach and Results

Laboratory Study

In a laboratory microcosm experiment (3), we evaluated several factors which were hypothesized to influence *in situ* biotransformation processes. Individual monoaromatic compounds (e.g., benzene, toluene, ethylbenzene, and m-, p-, and o- xylene) were the primary substrates. In replicate bottles during the first 52 d of the study, toluene and m+p-xylene (here, m-xylene and p-xylene were measured as a summed parameter) were biotransformed in the unamended ground-water samples under presumed sulfate-reducing conditions. Addition of nitrate to the ground water increased rates of toluene biotransformation coupled to nitrate reduction, stimulated biotransformation of ethylbenzene, and inhibited the complete loss of m+p-xylene that was observed when nitrate was not added and sulfate-reducing conditions prevailed. Addition of the nutrients ammonia and phosphate had no effect on either the rate of aromatics transformation or the distribution of aromatics transformed. When Seal Beach sediment was placed into nitrate-reducing media, ethylbenzene was transformed first, followed by toluene. When the sediment was placed into sulfate-reducing media, lag times were increased, but toluene and m-xylene were ultimately transformed just as in the microcosms with ground water

alone. Although methane had been detected in the field, there appeared to be no transformation of aromatic compounds in the methanogenic microcosms during the period of the experiment.

Bioreactor Study

A pilot-scale facility consisting of 90-L reactors was constructed at the Seal Beach site (4-6). The facility was designed for the operation of three anaerobic *in situ* bioreactors. The reactors consisted of aquifer-sediment-filled, stainless steel cylindrical vessels with the capability to control and monitor both hydrodynamic flow and supplements to the composition of the native groundwater influent. Initial operation of the three anoxic/anaerobic reactors focused on evaluating anaerobic bioremediation strategies for aromatic hydrocarbons under natural (presumed sulfate-reducing) and enhanced denitrifying conditions.

Bioreactor results were consistent with the laboratory microcosm experiments. Toluene and m+p-xylene were degraded in both the unamended and nitrate-amended bioreactors. Degradation of ethylbenzene was stimulated by nitrate addition. There was no evidence that benzene or o-xylene was transformed in either reactor. The final percentage removal efficiency appeared to be higher in the unamended bioreactor, where flow was slower.

Field Study

Field experiments have been conducted to assess aromatic biotransformation in a test zone within the contaminated aquifer at the Seal Beach site. Initial work focused on evaluation of intrinsic bioremediation as evidenced by the distribution of aromatic species in background wells. Subsequent experiments to determine our ability to enhance this biotransformation have been conducted using a slug test experimental design in which a single well was used for the injection of the "slug" or test pulse and the same well was used to extract the test pulse. Since the native ground water contained a variety of electron acceptors and the water used for the injected pulses was water that had previously been extracted from the test zone, the ground water was treated to control the concentration of all electron acceptors and organics during the injection of the test pulse. Before injection, the desired salts were added back to the deoxygenated injection stream, and the stream was metered into the injection well. Sodium bromide was added as a conservative tracer. Under this scenario, the different electron acceptors investigated (e.g., nitrate and sulfate) could be added as desired. During initial tracer studies, the injection water was organics free, and thus the source of the organics was desorption from the *in situ* aquifer solids. In subsequent and ongoing bioremediation studies, benzene, toluene, ethylbenzene, m-xylene, and o-xylene were added with the injection pulse at a concentration of approximately 200 μg/L each.

The initial bromide tracer data showed stable tracer concentrations and indicated no substantial encroachment of native ground water detected in the first 0.4 pore volumes. There was a very small hydraulic gradient at the site, hence recovery of the bromide mass from the test wells ranged from 93 percent to 99 percent with the extraction of three pore volumes over a 103-d period. During the tracer test, the equilibrium desorption concentrations for the aromatic hydrocarbons when the electron acceptors nitrate and sulfate were absent from the ground water were evaluated. Benzene, ethylbenzene, and o-xylene concentrations remained relatively stable and thus appeared to be at an equilibrium. The toluene and m+p-xylene concentrations had a downward trend relative to benzene once the native ground water encroached after approximately 0.4 pore volumes, suggesting that the nitrate and sulfate concentrations available

in the native ground water supported some intrinsic biological activity in the latter part of the experiment for toluene and m+p-xylene removal.

In a nitrate augmentation experiment, nitrate and aromatics were added to the injection pulse, resulting in complete consumption of toluene and m-xylene followed by ethylbenzene within the first 2 wk. o-Xylene was slowly degraded, and its concentration approached zero by day 60. There was no apparent loss of benzene when compared with the inert tracer. The addition of nitrate to the test region appeared to enhance the natural anaerobic denitrifying population. This would confirm that there was already an active nitrate-reducing population in the aquifer whose activity was enhanced by the addition of nitrate. With the exception of o-xylene transformation, these results were comparable with those from the nitrate-amended microcosm and bioreactor experiments, wherein toluene, ethylbenzene, and m-xylene were transformed under denitrifying conditions.

During the tracer study, methane was detected in the test wells. With the encroachment of the native ground water and associated increase in nitrate and sulfate concentrations, the methane concentration decreased to values close to zero, suggesting that nitrate and sulfate inhibit methanogenesis at this site.

Acknowledgment

Funding for this study was provided by the U.S. Environmental Protection Agency's Office of Research and Development, under agreement R-815738-01 through the Western Region Hazardous Substance Research Center. The content of this study does not necessarily represent the views of the Agency. Additional funding was obtained from the Chevron Research and Technology Company, Richmond, California.

References

1. Schroeder, R.A. 1991. Delineation of a hydrocarbon (weathered gasoline) plume in shallow deposits at the U.S. Naval Weapons Station, Seal Beach, California. Water Res. Invest. Rep. 89-4203.

2. Cline, P.V., J.J. Delfino, and P.S.C. Rao. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. Environ. Sci. Technol. 25(5):914-920.

3. Ball, H.A., and M. Reinhard. 1994. Laboratory study of monoaromatic hydrocarbon degradation under anaerobic conditions at Seal Beach, California. In preparation.

4. Ball, H.A., and M. Reinhard, M. 1994. Pilot-scale study of monoaromatic hydrocarbon degradation under anaerobic conditions at Seal Beach, California. In preparation.

5. Huxley, M.P., C. Lebron, M. Reinhard, H. Ball, H.F. Ridgway, and D. Phipps. 1992. Anaerobic and aerobic degradation of aromatic hydrocarbons using *in situ* bioreactors at an unleaded gasoline spill site. Presented at the 18th Environmental Symposium of the American Defense Preparedness Association, Alexandria, VA.

6. Reinhard, M., L.E. Wills, H.A. Ball, T. Harmon, D.W. Phipps, H.F. Ridgway, and M.P. Eisman. 1991. A field experiment for the anaerobic biotransformation of aromatic hydrocarbon compounds at Seal Beach, California. In: Hinchee, R.E., and R.F. Olfenbuttel, eds. *In situ* bioreclamation: Applications and investigations for hydrocarbon and contaminated site remediation. Boston, MA: Butterworth-Heinemann.

The Complete Dechlorination of Trichloroethene to Ethene Under Natural Conditions in a Shallow Bedrock Aquifer Located in New York State

David Major, Evan Cox, and Elizabeth Edwards
Beak Consultants Limited, Guelph, Ontario

Paul W. Hare
General Electric Company, Corporate Environmental Programs, Albany, NY

Introduction

In anaerobic environments, chlorinated ethenes can act as electron acceptors in a process called reductive dehalogenation (specifically, reductive dechlorination). The extent of dechlorination, however, has been shown to vary in anaerobic dechlorination studies depending upon the flow and availability of electrons within the anaerobic microbial community. For example, dechlorinated intermediates such as dichloroethene (DCE) and vinyl chloride (VC) were found to accumulate during the dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE) (1-3). Freedman and Gossett (4), however, were the first to observe the complete dechlorination of PCE to ethene in a methanogenic enrichment culture, and DeBruin et al. (5) showed that PCE could be reduced to ethane. The first field observation of the complete dechlorination of PCE to ethene was documented by Major et al. (6). Their laboratory and field study showed that anaerobic microorganisms in a low-permeability aquifer were capable of naturally dechlorinating PCE in the presence of methanol. This paper documents that microorganisms in a bedrock aquifer unit are also capable of completely dechlorinating TCE to ethene.

Study Site Conditions

The study site is located in the Finger Lakes region of central New York. The property was used from 1951 to 1990 as a manufacturing plant for a variety of electrical components, including high-voltage semiconductors. In the early to mid-1960s waste solvents were disposed of in an unlined evaporation pit. TCE, which was often mixed with acetone or methanol, was among the solvents disposed of in the unlined evaporation pit. As a result, these chemicals are now found in the overburden and bedrock units beneath the study site.

Results

Our study involved collecting representative ground-water samples from 21 existing ground-water monitoring wells, mostly in the shallow bedrock unit, for geochemical and microbiological analyses. 1,2-DCE and VC were detected in ground-water samples, which indicated that TCE was being biodegraded in the subsurface at the site. These TCE degradation products were not used or produced at the site, and thus their presence can only be attributed to the dechlorination of TCE. In addition, the detection of ethene provides evidence that VC is being dechlorinated at the site. Three observations of the relative distribution of TCE and its dechlorination products suggested that the migration of the volatile organic compounds (VOCs) in the shallow bedrock

unit is being controlled by biodegradation. First, the distribution of TCE is much less extensive than the observed distributions for 1,2-DCE, VC, and ethene. Second, the distribution of VC, which should be greater than that of 1,2-DCE as predicted by its mobility in ground water, was essentially the same as the distribution of 1,2-DCE. Third, VC and ethene migrate at similar rates relative to ground-water velocity and should have had similar distributions, but the distribution of VC was less than ethene. The distribution of acetone and methanol is considerably limited in comparison to the distribution of the chlorinated VOCs and ethene. The mobility of acetone and methanol should be approximately the same as the average linear ground-water flow; however, their distribution was less than the distribution of the VOCs. This suggests that acetone and methanol are also being biodegraded.

In addition to the distributions of VOCs, the distributions of inorganic anions, methane and methane isotopes, and volatile fatty acids (e.g., acetate) were used as indirect measures of the activity of functional groups of microorganisms in the bedrock. The depletion of sulfate and the production of methane and acetate indicated that sulfate-reducing, methanogenic, and acetogenic bacteria were active in the bedrock aquifer. Isotopic analysis of methane indicated that the methane was produced biotically. Furthermore, the distribution of methane and methane isotopes clearly showed that the microorganisms were active in the bedrock.

Microbial biomass, composition, and nutritional status were assessed by extracting and analyzing phospholipid fatty acids (PLFAs) and respiratory quinones from microorganisms that were trapped onto 0.22-μm membranes. Analysis of respiratory quinones indicated that the microbial populations at the site are strictly anaerobic. The microbial biomass in the ground water ranged from 1.6×10^2 cells/mL to 4.2×10^4 cell/mL. The total biomass appeared generally to correlate with the presence of VOCs and other nutrients, and was found to be higher in the areas containing acetone and methanol. The total biomass was orders of magnitude higher near VOC source areas, as well as in areas with measurable concentrations of acetone and methanol, than at downgradient or background (upgradient) locations. The microbial biomass distribution suggested that a biologically active zone (BAZ) has developed in response to the presence of VOCs, acetone, and methanol. The microbial populations in the samples generally demonstrated nutritional or environmental stress, as indicated by the ratio of specific PLFAs. Stress may be due to an inadequate supply of nitrogen and phosphorous to support ideal growth. Cluster analysis of the PLFA data showed that three population groups exist at the site. The population groups appear to coincide with observed changes in the concentration and types of VOCs and other geochemical parameters.

Conclusions

This study provides evidence that microbial populations can exist and function in bedrock. Furthermore, these populations possess an intrinsic capability to anaerobically dechlorinate TCE to ethene when suitable substrates are present to support their growth. At this study site, an active and diverse anaerobic microbial community, consisting of sulfate-reducing, methanogenic, and acetogenic bacteria, has been established and is being maintained by acetone and methanol. This anaerobic microbial community is affecting the distribution and migration of TCE, TCE biodegradation products, and other chemicals at the site.

References

1. Bouwer, E.J., and P.L. McCarty. 1983. Transformation of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. Appl. Environ. Microbiol. 45(4):1,286-1,294.

2. Parsons, F., P.R. Wood, and J. DeMarco. 1984. Transformations of tetrachloroethylene and trichloroethylene in microcosms and ground water. J. Am. Water. Assoc. 76:56-59.

3. Wilson, B.H., G.B. Smith, and J.J. Rees. 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. Environ. Sci. Technol. 20(10):997-1,002.

4. Freedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55(9):2,144-2,151.

5. De Bruin, W.P., M.J.J. Kotterman, M.A. Posthumus, G. Schraa, and A.J.B. Zehnder. 1992. Complete biological reductive transformation of tetrachloroethene to ethane. Appl. Environ. Microbiol. 58(6):1,996-2,000.

6. Major, D.M., E.W. Hodgins, and B.J. Butler. 1991. Field and laboratory evidence of *in situ* biotransformation of tetrachloroethene to ethene and ethane at a chemical transfer facility in North Toronto. In: Hinchee, R.E., and R.F. Olfenbuttel, eds. On-site bioremediation, pp. 147-171. Boston, MA: Butterworth-Heinemann.