

Natural Attenuation Strategy for Groundwater Cleanup Focuses on Demonstrating Cause and Effect

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In the 20 years since cleanup of contaminated groundwater has been a high priority in the United States, recognition of both the scope of the problem and the technical difficulties involved has grown steadily. Estimates of the number of hazardous waste sites where groundwater may be contaminated vary between 300,000 and 400,000 nationwide [NRC, 1994]. Legislation passed in the 1980s by Congress and the states generally required that groundwater in contaminated aquifers be restored to background or drinking water standards. Unfortunately, attempts to meet these goals using conventional methods, such as pump and treat systems, frequently have been unsuccessful [NRC, 1994].

Moreover, constructing and operating engineered groundwater cleanup systems is very expensive, with total spending on environmental remediation in the United States estimated at \$9 billion in 1996 alone [NRC, 1997]. Over the last 5 years, the high costs of engineered cleanup systems and their disappointing performance has spurred both a search for alternative remediation strategies and rethinking of remediation

goals and time frames. In this climate, interest in the capabilities of a remediation strategy known as *monitored natural attenuation* has skyrocketed.

The Environmental Protection Agency (EPA) defines natural attenuation as "a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants" [EPA, 1999] (Figure 1).

Use of monitored natural attenuation as a remediation strategy involves filing a formal regulatory application to allow natural biological, chemical, and physical processes to treat groundwater contaminants, and conducting ongoing monitoring to verify that these processes are effective. In many cases, the feasibility of a natural attenuation strategy depends on whether the regulatory goal is to clean up the contaminant plume to drinking water standards or whether a less stringent,

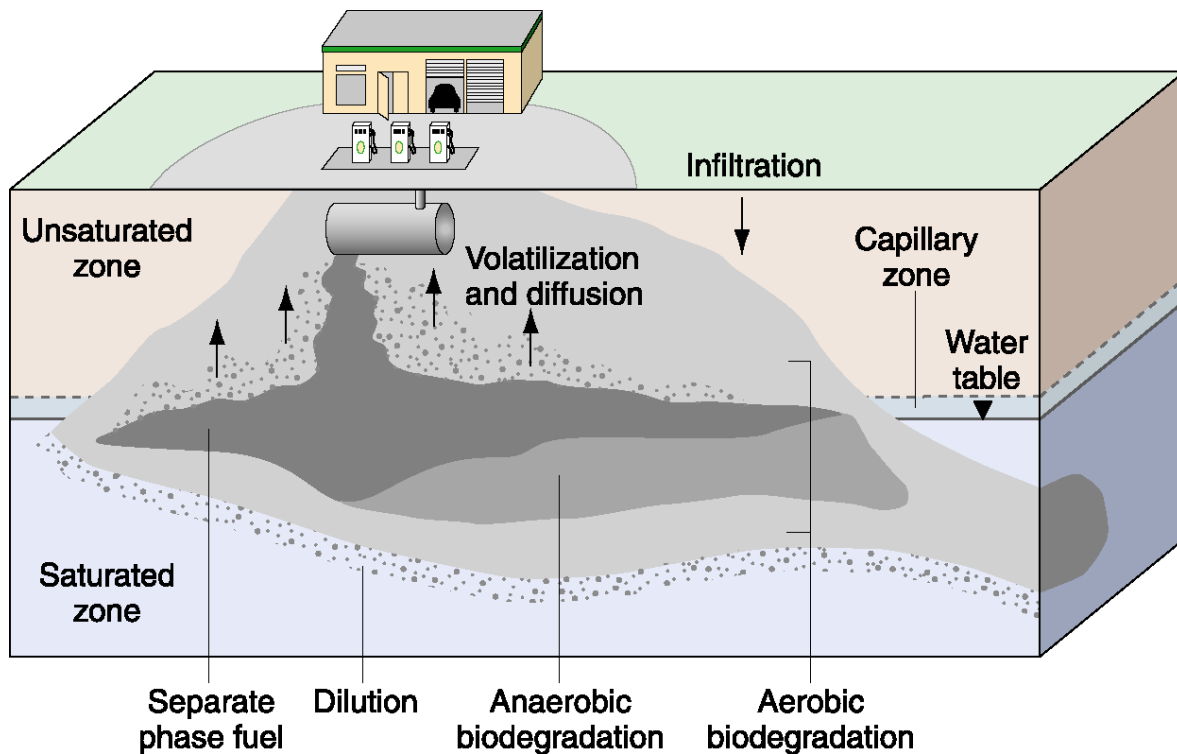


Fig. 1. Conceptual illustration of the important natural attenuation processes that affect the fate of petroleum hydrocarbons in aquifers.

risk-based goal applies, such as preventing the plume from expanding. Since 1995, the use of natural attenuation as a remedial solution for benzene, toluene, ethylbenzene, and xylene (BTEX) has increased dramatically [NRC, 2000]. More recently, natural attenuation has been proposed for chlorinated solvents, nitroaromatics, heavy metals, radionuclides, and other contaminants for which the scientific understanding and field experience are much less robust.

Groundwater remediation by natural attenuation is controversial. Environmental advocates charge that natural attenuation is little more than an excuse for industry to avoid the high costs of building cleanup systems. To address these issues, in 1997 the National Research Council (NRC) appointed the Committee on Intrinsic Remediation to provide guidance on when and how to determine whether natural attenuation is an appropriate remedy for a site. Community leaders interviewed by the NRC committee expressed concern that natural attenuation allows responsible parties to save on cleanup costs while shifting the risks to the community. Furthermore, they expressed mistrust of the multi-process definition of natural attenuation and felt that reductions in contaminant concentration by dilution or transfer to another medium might continue to pose risks.

Community leaders indicated a willingness to accept natural attenuation when responsible parties and regulators can provide solid evidence that natural attenuation processes are transforming the contaminants to harmless products. The NRC committee's recently released report, *Natural Attenuation for Groundwater Remediation* [NRC, 2000], concluded that the key to demonstrating the effectiveness of natural attenuation at a site is establishing the cause-and-effect relationship between loss of contaminant and the mechanism responsible for the loss. This conclusion has important implications for future research and training in the areas of hydrogeology and subsurface biogeochemistry.

The NRC report emphasizes that the success of natural attenuation depends on both the nature of the contaminant and the specific subsurface conditions at a site. In documenting natural attenuation at a contaminated site, a hydrogeologist must develop a substantial degree of understanding of the subsurface processes. Thus, the major expense of the remediation may shift from the design and operation of an active system to detailed investigation and monitoring of the site. The goal of the site investigation is to understand the natural groundwater flow and biogeochemical reactions responsible for controlling the contamination.

The NRC report recommends a varying level of investigation depending on the hydrogeologic complexity of the contaminated aquifer and the nature of the contaminants. More complex environments require a greater degree of characterization and quantitative mass balance. An increased level of characterization also is required when natural

attenuation processes are effective only under specialized geochemical conditions. The processes controlling the subsurface fate of many contaminants are only partially understood and are still topics of active research. Thus, the committee's report emphasizes that broad training in hydrogeology and biogeochemical fundamentals is essential for future employment in the environmental geosciences. This training provides the skills to understand unique contaminants and situations outside the scope of current knowledge.

Much of the theoretical and practical basis for natural attenuation as a remediation strategy has been based on large interdisciplinary studies at field sites. The results of these studies are providing essential insights into the effects of site conditions on the fate of subsurface contaminants. Subsurface geochemical settings that favor natural attenuation for some contaminants are unfavorable for other contaminants. Moreover, geochemical and hydrogeological conditions can change with time and location in the subsurface.

Because of the importance of understanding the effects of site conditions on natural attenuation processes, the NRC committee report states that training of environmental geologists should include descriptions of comprehensive natural attenuation case studies. In accord with this recommendation, the main points of the NRC report are illustrated with results from field studies of natural attenuation processes for a variety of compound classes and sites. Two of the case studies presented in the report are based on results from the U.S. Geological Survey's Toxic Substances Hydrology Program (USGS Toxics Program) research sites. The goal of research conducted by the USGS Toxics Program has been to arrive at general scientific principles to guide investigations, monitoring strategies, and regulatory decisions on the effects of natural processes on environmental contaminants. The remainder of this article reviews the results of two USGS Toxics Program case studies in the context of the NRC committee's recommendations. This is followed by a discussion of the emerging research issues for natural attenuation processes.

Case Studies

Detailed case studies illustrate how site investigations can reduce uncertainty and document the natural attenuation processes responsible for the reduction of contaminants. The contaminants at the USGS Toxics Program subsurface research sites cover a range of contaminant classes (Table 1). The fate of each contaminant class in the subsurface is determined by its chemical properties and the environmental conditions at a site. A major distinction exists between organic chemicals and metals. While naturally occurring biodegradation can completely convert some organic contaminants to harmless products, metals can only be transformed to forms that are less mobile or toxic.

Table 1: Sites where USGS researchers and university collaborators are conducting intensive field investigations of representative cases of subsurface contamination and solute transport as part of the USGS Toxics Substances Hydrology Program.

Site	Contaminant	Date study started
Galloway, NJ	Gasoline	1987
Bemidji, MN	Crude oil	1983
Pensacola, FL	Creosote	1981
Laurel Bay, SC	MTBE	1997
Picatinny, NJ	TCE	1986
Pinal Creek, AZ	Mine drainage	1984
Upper Arkansas River	Mine Drainage	1986
Cape Cod, MA	Sewage Effluent	1979
Norman, OK	Landfill leachate	1995
Amargosa Desert, NV	Radioactive waste in arid environments	1976
Mirror Lake, NH	None; Fractured rock flow and transport	1990

To illustrate this point, we present two case studies: one on the fate of organic contaminants and another on the fate of metals. Frequently, the effectiveness of natural attenuation can be documented using "footprints" of the underlying mechanisms. Footprints are changes in concentrations of reactants and products that are diagnostic of specific biogeochemical reactions acting to transform or immobilize the contaminant. Coupling the observed loss of contaminant to the measurement of several footprints demonstrates which natural attenuation processes may be responsible for contaminant loss. At sites where the contaminant source will be present for many years into the future, it may be necessary to determine the quantities of important natural attenuation reactants in the aquifer. A mass balance is then performed to ensure natural attenuation is sustainable for the lifetime of the source.

The Fate of Crude Oil

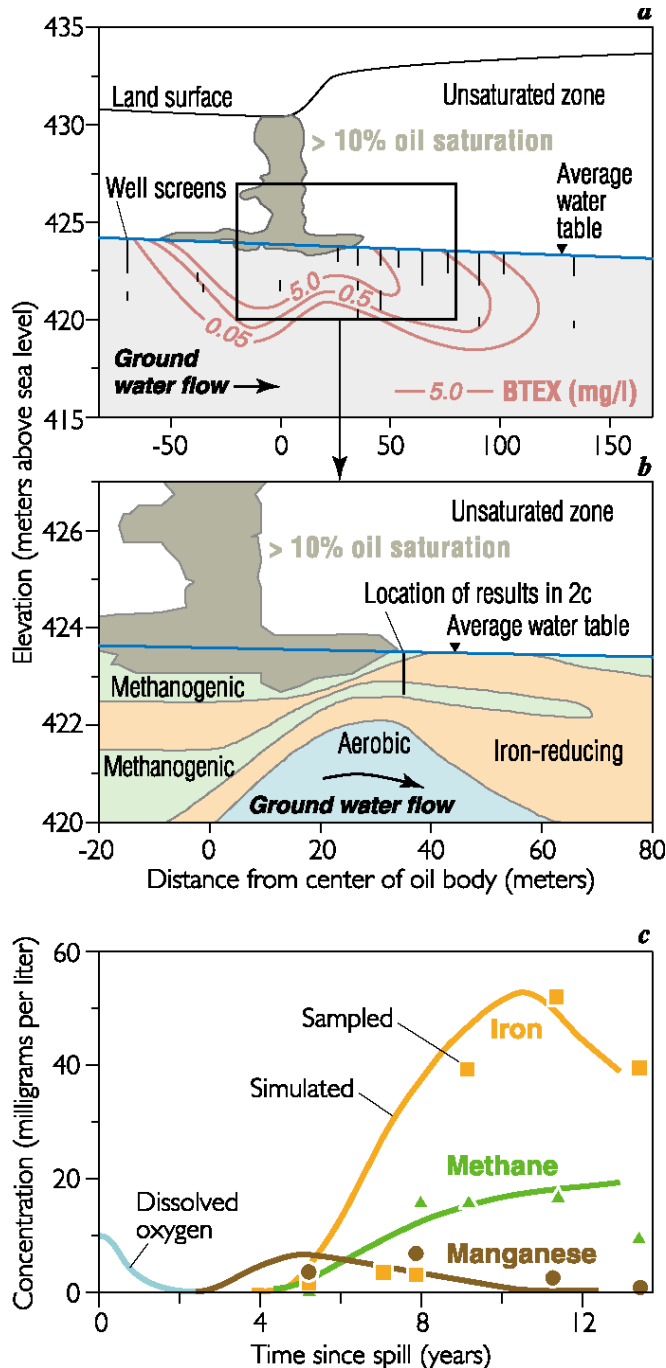
A buried oil pipeline located in a glacial outwash plain near Bemidji, Minnesota, ruptured in 1979 and an estimated 3,200 barrels of spilled oil infiltrated the subsurface. The oil forms a long-term, continuous source of hydrocarbon contaminants that dissolve in and are transported with the groundwater (Figure 2a). Microbial degradation of the petroleum hydrocarbons in

the plume has resulted in the growth of aquifer microbial populations dominated by iron-reducers, fermenters, methanogens, and aerobes (Figure 2b). The biodegradation reactions cause a number of geochemical changes or diagnostic footprints near the aqueous plume. These include decreases in concentrations of oxygen and hydrocarbons and increases in concentrations of dissolved iron, manganese, and methane (Figure 2c). Characterizing the various biodegradation processes occurring in the aquifer is important because each process results in different degradation rates for the individual hydrocarbon compounds.

Simulations of the evolution of redox zones and microbial populations in the plume provide important insights, including estimates of losses due to each biodegradation process and the long-term sustainability of the hydrocarbon degradation. A vertical cross-section parallel to the direction of groundwater flow was simulated from the time of the spill in 1979 until September 1992 using the code BIOMOC [Essaid and Bekins, 1997]. In the model, aerobic, Mn and Fe reducing, and methanogenic aquifer microbes degrade the dissolved hydrocarbons. Aerobic degradation takes place first, and oxygen inhibits anaerobic processes. As oxygen is consumed and an anoxic zone develops, the Mn/Fe reducers and methanogens begin to grow, consuming solid-phase Mn(IV) and Fe(III), and releasing dissolved Mn(II), Fe(II), and methane.

The model calibration involved balancing the observed spatial and temporal variations of hydrocarbons against the other degradation reactants and the observed microbial populations. Steady-state flow was assumed, and literature values, theoretical estimates, and field biomass measurements were used to obtain reasonable estimates of the transport and biodegradation parameters. Simulated concentrations and data in Figure 2c illustrate how the evolution of redox zones results in changes in water chemistry over time. The simulation predicts that 60% of the hydrocarbon degradation occurs anaerobically (Mn reduction: 5%, Fe reduction: 19%, methanogenesis: 36%) and 40% occurs aerobically. The field data, modeling, and microbial population results illustrated in Figure 2 suggest that the natural attenuation capacity of the aquifer near the oil is being slowly consumed. This has been confirmed by monitoring of the site over the 20 years since the spill [Cozzarelli *et al.*, 2001].

Fig. 2. At the crude oil study site near Bemidji, Minnesota, aerobic and anaerobic biodegradation are the most important natural attenuation processes affecting the hydrocarbon plume. a) Contour plot of 1995 total BTEX concentration in the Bemidji plume for a vertical cross-section along the plume axis [modified from Cozzarelli et al., in press, 2001]. b) Cross-section showing the distribution of physiologic types of microorganisms inferred from most probable number data [modified from Bekins et al., 1999]. The areas contaminated by separate-phase oil are predominantly methanogenic in both the saturated and unsaturated zones. c) Simulated and observed concentrations versus time for a water table well located 36 m down gradient from the center of the oil body. The loss of oxygen and production of reduced electron acceptors (Fe(II), Mn(II), and methane) illustrate the temporal evolution of redox conditions in the aquifer [modified from Essaid et al., 1995].



The Fate of Metals from Mine Waste

Acidic drainage from former mine sites is the most frequent cause of metal-contaminated groundwater, with an estimated 20,000-50,000 affected sites nation-wide. In the Pinal Creek Basin of central Arizona, large-scale copper mining since the late 1880s and related activities have resulted in contamination of an alluvial aquifer by acid mine drainage. The plume of acidic water extends 25 km down gradient from the location of mining operations at the head of the basin (Figure 3) and contains excessive concentrations of iron, manganese, copper, zinc, aluminum, cobalt, and nickel. The source of the plume probably had a pH of 2-3 and iron and sulfate concentrations exceeding 2000 and 19,000 mg/L, respectively.

Reactions between the acid mine drainage plume and the aquifer materials have resulted in several footprints of natural attenuation processes. These include carbonate and manganese oxide dissolution, pH increase, increase in calcium, and decreases in concentrations of iron, copper, and aluminum. As the plume migrates through the aquifer, oxidation of reduced iron by sediment manganese oxides results in iron precipitation and release of more dissolved manganese. In addition, reaction of the acidic water with carbonate minerals and sorption of hydrogen ions on the precipitated iron increases the pH to 5-6 [Stollenwerk, 1994]. The sorption reactions of aqueous copper, cobalt, nickel, and zinc depend strongly on pH. Thus, at the location where the pH increases in the plume, sorption by iron oxides removes substantial quantities of copper from the groundwater and the migration rates of cobalt, nickel, and zinc are retarded. The pH increase also causes aluminum to precipitate onto the aquifer solids. Because chloride was present in the plume source water, it is possible to assess the role of dilution in decreasing the contaminant concentrations. Chloride concentrations indicate that in the first 2 km of migration, mixing with uncontaminated water along the sides and base of the plume accounts for a 60% decrease in metal concentrations.

The acidity of the plume has resulted in depletion of the carbonate in the aquifer and related

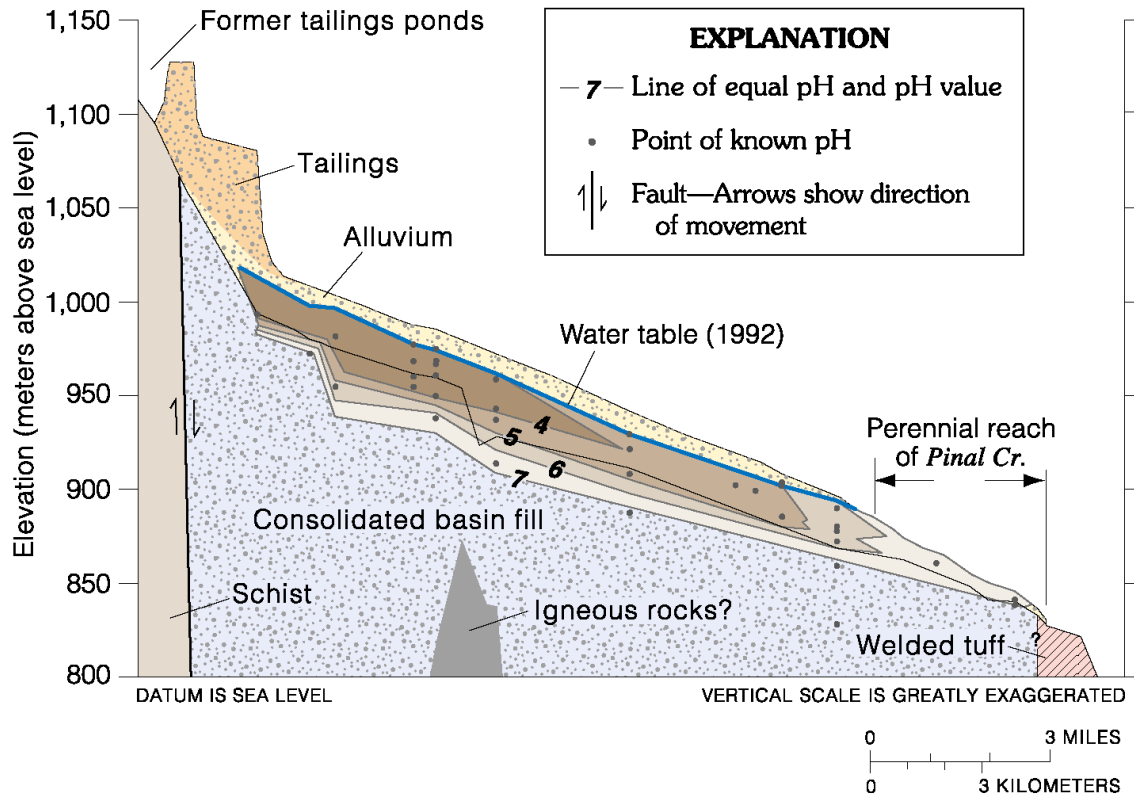


Fig. 3. Cross-section of Pinal Creek Basin showing the pH of the groundwater contaminant plume migrating from the former location of mining and related activities at the far left [modified from Stollenwerk, 1994]. Groundwater flowing beneath the contaminant source area has a pH less than 4 (as shown on the dashed line marked 4), but farther down gradient the pH increases to 5-6 as carbonate minerals neutralize the acidity. The low-pH region corresponds to the region with high concentrations of dissolved metals. Attenuation of the dissolved metals by sorption and precipitation occurs as the pH increases. Oxidation or sorption of metals in the streambed further attenuates metals that reach the perennial stream.

slow migration of the front edge of the low pH plume at a rate of about one-seventh of the advective groundwater flow. The metal sorption reactions are reversible, causing remobilization of the metal contaminants as the pH front migrates down gradient. Although the acidic front of the plume has not yet reached Pinal Creek, the leading edge of the neutralized plume, containing elevated concentrations of manganese, cobalt, nickel, and zinc, discharges into the perennial reach of the creek. Within the creek, the pH and dissolved oxygen of the contaminated water increase due to gas exchange with the atmosphere. Precipitation of manganese oxides on the stream sediments is enhanced by the presence of manganese-oxidizing bacteria, which immobilizes about 20% of the dissolved manganese flowing out of the drainage basin [Harvey and Fuller, 1998].

Sorption onto the manganese oxides also reduces the dissolved mass of nickel, zinc, and cobalt in the stream by 12-68% depending on the type of metal [Fuller and Harvey, 2000]. Dilution over a 7-km perennial reach of the stream results in an additional

20% decrease in concentrations of the dissolved metals. Although natural attenuation in the aquifer and stream decreased metal transport, the size of the plume and the longevity of the source of contamination at Pinal Creek Basin have overwhelmed the intrinsic remediation capacity of the aquifer. However, similar processes govern the fate of metals at other acid mine sites, substantially reducing the mobility of metals in aquifers and streams that receive metal-contaminated, groundwater discharge.

Emerging Research Issues

With the dramatic increase in the use of natural attenuation, there are many issues that require further study to ensure that this strategy is protective of public health and the environment. These fall into three broad categories: poorly understood chemical classes, uncertainty posed by subsurface heterogeneity, and long-term sustainability. An important conclusion of the NRC report is that natural attenuation has been demonstrated to be effective most of the time for only a few compounds. There are many compounds for which

the natural attenuation potential has not yet been established. For example, the gasoline oxygenate MTBE is highly mobile in the environment and the rates of physical, chemical, and biological processes controlling its environmental fate are the subject of active research by the USGS Toxics Program and others. Another important area of research is the natural attenuation potential for mixtures of contaminants such as those found in the Norman landfill plume (Table 1).

Because the migration paths and degradation potential of groundwater contaminants are strongly affected by subsurface physical and chemical heterogeneity, the NRC report recommends that increased effort is needed to document the effectiveness of natural attenuation where the subsurface is highly heterogeneous. Thus, strategies for characterizing the effects of subsurface heterogeneity on natural attenuation and reducing uncertainty in contaminant risk assessments are also fertile areas of research. The application of quantitative modeling at many USGS Toxics Program sites is providing examples of how uncertainty can be assessed and used to guide new data needs. Because documenting the fate of solutes in fractured rock aquifers is particularly difficult, developing new methods for characterizing flow and transport in fractured rock is the goal of research at the Mirror Lake study site (Table 1).

Finally, the NRC report stresses that many practical issues regarding the performance of natural attenuation over long time frames are still unclear. These include the effects of active remediation efforts on the natural attenuation processes; the design of long-term monitoring networks to verify that natural attenuation is working as expected; and the natural attenuation capacity of the aquifer over the lifetime of the source. The effect of source removal on natural attenuation processes is the focus of USGS Toxics Program research efforts at the Bemidji crude oil and the Cape Cod treated sewage plume sites.

As natural attenuation sites nationwide are monitored over the coming decades, the results of detailed process studies from the USGS Toxics Program and other field-based research efforts will provide a framework for assessing the continued sustainability of natural attenuation. Further information on the USGS Toxics Program, site summaries, and reference lists may be found at <http://toxics.usgs.gov/>. The NRC report is available at <http://books.nap.edu/>.

Authors

Barbara A. Bekins, U. S. Geological Survey, Menlo Park, Calif., USA; Bruce E. Rittmann, Department of Environmental Engineering, Northwestern University, Evanston, Ill., USA; and Jacqueline A. MacDonald, RAND Corporation, Pittsburgh, Penn., USA. For additional information, contact Barbara Bekins, U.S. Geological Survey, MS 496, 345 Middlefield Rd.,

Menlo Park, CA 94025, USA; E-mail: babekins@usgs.gov

References

- Bekins, B. A., E. M. Godsy, and E. Warren, Distribution of microbial physiologic types in an aquifer contaminated by crude oil, *Microbial Ecol.*, 37, 263-275, 1999.
- Cozzarelli, I. M., B. A. Bekins, M. J. Baedecker, G. R. Aiken, R. P. Eganhouse, and M. E. Tuccillo, Progression of natural attenuation processes at a crude-oil spill site I. Geochemical evolution of the plume, *J. Contam. Hydrol.*, in press, 2001.
- Environmental Protection Agency, Use of monitored natural attenuation at Superfund, RCRA Corrective Action, and underground storage tank sites, *Directive 9200.4-17P*, 32 pp., EPA, Office of Solid Waste and Emergency Response, Washington, D.C., 1997.
- Essaid, H. I., and B. A. Bekins, BIOMOC, A Multispecies Transport Model with Biodegradation, *Water-Resources Investigations Report 97-4022*, 68 pp., U.S. Geological Survey, Washington, D.C., 1997.
- Essaid, H. I., B. A. Bekins, E. M. Godsy, E. Warren, M. J. Baedecker, and I. M. Cozzarelli, Simulation of aerobic and anaerobic biodegradation processes at a crude oil spill site, *Water Resour. Res.*, 31, 3309-3327, 1995.
- Fuller, C. C., and J. W. Harvey, Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona, *Environ. Sci. Tech.*, 34, 1150-1156, 2000.
- Harvey, J. W., and C. C. Fuller, Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, *Water Resour. Res.*, 34, 623-636, 1998.
- National Research Council, *Alternatives for Groundwater Cleanup*, 315 pp., National Academy Press, Washington, D.C., 1994.
- National Research Council, *Innovations in groundwater and soil cleanup: From concept to commercialization*, 265 pp., National Academy Press, Washington, D.C., 1997.
- National Research Council, *Natural Attenuation for Groundwater Remediation*, 292 pp., National Academy Press, Washington, D.C., 2000.
- Stollenwerk, K. G., Geochemical interactions between constituents in acidic groundwater and alluvium in an aquifer near Globe, Arizona, *Appl. Geochem.*, 9, 353-369, 1994.