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Capabilities and Challenges of Natural Attenuation in the Subsurface: Lessons from the U.S. Geological Survey Toxics Substances Hydrology Program

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ABSTRACT

Natural attenuation has been used as a practical method to dispose of wastes throughout human history. However the presumption of natural attenuation as a strategy for disposal of wastes has had serious consequences for human health and the environment in the twentieth century. It is now clear that the environment has a limited ability to assimilate wastes and that this ability depends on the nature and quantity of the waste compounds and the characteristics of the subsurface. Thus, increasing our knowledge of the capabilities and limitations of natural attenuation is of high priority. To this end, the U.S. Geological Survey Toxic Substances Hydrology Program (Toxics Program) conducts studies on the fate of contaminants in the natural environment. Results from the Toxics Program research sites have documented the effectiveness of a variety of individual processes that together contribute to natural attenuation in the subsurface. The site studies also indicate that many challenges remain in our efforts to understand the effectiveness of natural attenuation. These include spatial heterogeneity and slow, rate-limiting processes that result in long time frames for cleanup. The subsurface microbial populations that catalyze biotransformation reactions also are poorly understood. However, recent results have yielded insights into controls on the spatial and temporal distribution of the various microorganisms. Quantitative models have been used successfully at several sites for estimating the relative contribution of each natural attenuation process to the overall mass loss. Future research is needed that targets gaps in our understanding of compound-specific behavior, subsurface microbial ecology, and uncertainties associated with heterogeneities and long time frames.

INTRODUCTION

Total spending on environmental remediation in the United States was estimated to be \$9 billion in 1996 alone (National Research Council, 1997). Furthermore, cleanup of contaminated soil and ground water may ultimately cost \$500 billion to \$1 trillion (National Research Council, 1994). Because of the high cost of remediation, the National Research Council sponsored a study in 1997 to evaluate innovative technologies in ground water and soil cleanup (National Research

Council, 1997). One of the emerging technologies for treatment identified in the study was remediation by natural attenuation (RNA). The 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 ground water. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; and chemical or

biological stabilization, transformation, or destruction of contaminants. (EPA, 1997).

Each of these attenuation mechanisms represents complex interactions among physical, chemical, and in some cases, biological processes and thus many are still subjects of active research.

Although the current level of active research would classify RNA as an emerging technology, its use as a remediation option for hydrocarbon contamination has increased dramatically in recent years. By January, 1998, RNA was permitted as a sole remedy for ground water petroleum hydrocarbon cleanup in 43 states (Martinson, 1998). This rapid increase is due to three main developments. First, an analysis of a large database of empirical observations from gasoline sites suggested that most hydrocarbon plumes have not expanded beyond 250 m (Rice and others, 1995). Second, results from lab and field studies have documented many of the significant mechanisms driving natural attenuation for gasoline compounds (see Wiedemeier and others, 1995, for a summary). Third, performance evaluations of cleanup methods such as pump and treat systems indicate that cleanup to drinking water standards is unrealistic in many cases (National Research Council, 1994). However, as the use of RNA has increased, public concern about potential abuses also has increased.

Concern about RNA is reflected in a widespread attitude that this is a "do nothing" option. Specific issues include the time frame for cleanup, whether the plume extends to a receptor, and whether the contaminant is truly rendered harmless. Addressing these issues requires a thorough understanding of the processes that control contaminant transport and contribute to natural attenuation. Measurement and modeling techniques are needed to determine the effects of each specific process and to design monitoring programs that demonstrate the sustainability of these processes. For chemical and biological reactions, knowledge of the reactants, products, reaction rates, microbial populations, and hydrologic controls on transport are all important. However, it would be prohibitively

expensive to conduct investigations leading to a thorough understanding of the fate of contaminants at every site. The goal of research conducted by the USGS Toxic Substances Hydrology Program (USGS Toxics Program) has been to arrive at general scientific principles to guide investigations, monitoring strategies, and regulatory decisions on ground-water cleanup. The research results from the program are especially relevant to RNA because the primary focus of the studies has been on natural processes.

The first part of this paper summarizes the capabilities of several key attenuation processes that have been described and quantified at sites studied under the USGS Toxics Program. In particular, the role of volatilization and biotransformation in the unsaturated zone and aerobic and anaerobic biodegradation in the saturated zone are well documented. However, many challenges to implementation of RNA still exist. The second section of the paper describes results from the study sites that illuminate these challenges. One challenge concerns the common occurrence in aquifers of sharp geochemical gradients and spatial and temporal variability in flow conditions. These heterogeneous conditions have a profound effect on the fate of the contaminants. Another challenge stems from rate-limiting aspects of contaminant flux including desorption, matrix diffusion, and nonaqueous-phase liquid (NAPL) dissolution. The combined effect of heterogeneity and long time frames make it difficult to predict the future sustainability of RNA processes at a site. Finally the microbial communities that perform biodegradation reactions contributing to natural attenuation are poorly understood and are the focus of research at several of the sites. In assessing the potential for RNA at a site, it is necessary to balance the capabilities against the limitations in knowledge imposed by the various challenges described above. Various types of quantitative analyses can be used to perform such an assessment. The third section of the paper describes how quantitative analyses have been successfully used at the Toxics Program sites to identify the relative contribution of individual processes to the total mass loss of a contaminant and to assess their

sustainability. On the basis of the cumulative knowledge gained under the USGS Toxics Program a set of recommendations for future research on the fate of contaminants in the subsurface is provided at the end of the paper.

CAPABILITIES OF NATURAL ATTENUATION

Natural attenuation is caused by a variety of physical, chemical, or biological processes that include dispersion, dilution, sorption, volatilization, and chemical or biological reactions. The effectiveness of each individual process in the subsurface varies depending on the level of saturation, the geochemical conditions, and the ground-water flow field. The research results summarized below provide general principles that can be used to predict the capabilities of natural attenuation under different subsurface conditions. The capabilities discussed are limited to biodegradation and volatilization because these are the primary attenuation mechanisms at the research sites described. For other sites and particularly for contaminant metals, the most important natural attenuation mechanisms may be sorption and chemical reactions. The discussion is divided according to processes that occur primarily above the water table in the unsaturated zone or below the water table, in the saturated zone.

Unsaturated Zone Processes

Two of the key processes in natural attenuation are volatilization and biodegradation. Results from USGS Toxics Program study sites in Galloway, NJ, (leaded gasoline) and Picatinny Arsenal, NJ, (solvents) show that these processes are especially rapid in the unsaturated zone. The unsaturated zone is an active area for transfer of contaminants between phases because contaminants may be present in either the vapor, dissolved, or non-aqueous phases. In addition, exchange of gases with the atmosphere can lead to conditions for efficient aerobic biodegradation and also gas-phase transport.

Results from the Galloway site show that transport and biodegradation processes

occurring at the base of the unsaturated zone, near the water table, can contribute significantly to natural attenuation of subsurface spills of gasoline. At this site, leaded gasoline that leaked from an underground storage tank is present as a non-aqueous phase in the unsaturated zone and at the water table (Fischer and others, 1996). The water table is a barrier to the movement of nonaqueous contaminants downward into ground water because gasoline is less dense than water. Fluctuation in the water table elevation over time causes the nonaqueous contaminants to be spread vertically. Constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) volatilize into the air-filled pore space of the capillary zone and migrate upward into the unsaturated zone via diffusion. This pathway combined with microbial degradation results in mass removal of compounds and thus reduces the mass available for solubilization into ground water. The source attenuation is compound-specific and therefore the composition of the remaining product changes over time by processes similar to those described by Baehr (1987).

Although volatilization is most important in the source area, compounds transported downgradient from the source area as solutes in ground water can also volatilize into the unsaturated zone from the ground-water plume. Biodegradation near the water table directly contributes to mass removal and results in sharp concentration gradients that enhance the upward diffusive transport of BTEX compounds into the unsaturated zone. At Galloway, oxygen in the unsaturated zone just above the capillary zone is below atmospheric concentrations but well above zero (about 5 percent) and hydrocarbon concentrations decrease rapidly with distance above the water table. These gradients imply a small vertical zone of active aerobic degradation above the water table. Lahvis and Baehr (1996) used the observed gradients to constrain a model estimating the overall BTEX transformation rates in this zone.

Research results from Picatinny Arsenal show that a significant quantity of trichloroethylene (TCE) volatilizes from water in the capillary fringe into the unsaturated-zone soil gas and is transported to the atmosphere. At

the Picatinny site, improper disposal of wastewater from degreasing operations between 1960 and 1983 resulted in the formation of a trichloroethylene TCE plume in an unconfined, sand-and-gravel aquifer with concentrations as high as 44 mg/L in the ground water (Smith and others, 1996a). Prior to installation of a pump-and-treat system in 1992, the plume extended about 500 m from the source area to a nearby brook. Because the brook acts as the discharge point for the water-table aquifer in the valley, no TCE has been detected in the ground water beyond it. TCE also has been detected in the unsaturated-zone water and soil gas at the site (Smith and others, 1990). Smith and others (1996a) used direct measurements of TCE vapor fluxes from the unsaturated zone to calculate a total TCE vapor flux to the atmosphere of approximately 50 kg/yr. They concluded that natural atmospheric pressure variations cause air flow in the unsaturated zone and lead to advective TCE vapor fluxes that are much greater than diffusive fluxes in the gas phase. However, the rate of volatilization is ultimately controlled by diffusion of dissolved TCE across the water table. Thus, the changing position of the water table at the site also may enhance TCE fluxes to the atmosphere.

Biodegradation in the Saturated Zone

In the saturated zone, aqueous-phase organic contaminants are biodegraded by indigenous microorganisms that have adapted to the conditions in the plume. Results from many of the USGS Toxics Program sites have documented the effectiveness of microbial transformations in reducing contaminant mass and concentrations. The nature and extent of microbial transformations are controlled, to a large degree, by the availability of electron acceptors which, in turn, determines the dominant terminal electron-accepting processes (TEAP) in any given environment. The most common TEAPs are aerobic respiration, denitrification, iron and manganese reduction, sulfate reduction and methanogenesis. Certain contaminants degrade or are transformed best under aerobic conditions, while for others, anaerobic conditions or specific TEAPs are

optimal. Therefore, assessing the potential for microbial transformations requires understanding: (1) which TEAPs are dominant within a contaminated environment (see Smith, 1997); (2) hydrologic factors that affect the supply of TEAP's; (3) geochemical factors that affect TEAP processes; and (4) the fate of each contaminant when subjected to the various TEAPs. Thus, transformation rates depend on a complicated set of interactions between the microbial processes, the environment and the contaminant compounds. Each of these interactions needs to be carefully elucidated, but all are best examined both at field sites and with controlled laboratory experiments that carefully reproduce field conditions. Research results from study sites at Picatinny, Galloway, Bemidji, MN (crude-oil), and Cape Cod, MA (treated sewage effluent), illuminate various issues to consider when assessing the degree of natural attenuation caused by microbial transformation of contaminants in the saturated zone.

Research at Picatinny has demonstrated that biodegradation and volatilization exceed removal rates by pump-and-treat technology. However, even at this well-characterized site, significant uncertainties exist in rate estimations. Anaerobic biotransformation is occurring in the plume by reductive dechlorination of TCE to cis-1,2-DCE and vinyl chloride. Using soil collected from the site, several researchers have documented the biodegradation of TCE in soil-water microcosms under anaerobic conditions (Wilson and others, 1991; Ehlke and others, 1996). Both cis-1,2-dichloroethylene and vinyl chloride have been detected in the plume, even though neither of these chemicals were used at the site. Fitted first-order biotransformation rate constants for TCE range from less than 0.052 to 1.04 yr⁻¹ (Wilson and others, 1991). Using these biotransformation rates and an estimate of the mass of TCE in the aqueous phase in the contaminant plume Imbrigiotta and others (1995) calculated that the rate of TCE biotransformation ranges from less than 52 kg/yr to 1,040 kg/yr. These results indicate the large degree of uncertainty present even at relatively well-understood research sites. In

1995, the rate of TCE withdrawal by the pump and treat system was 70 kg/yr. Thus, the sum of the TCE flux to the atmosphere (50 kg/yr) and the minimum biodegradation loss exceeds removal rate of the pump-and-treat system. Because pump-and-treat systems can be comparatively ineffective at mass removal, they are often used today as a containment strategy in conjunction with natural attenuation processes.

Research at the Galloway site has explored the intricate relationships between aquifer mineralogy, aqueous geochemistry and TEAPs, and has found that many significant processes occur in very narrow zones. At this site, the primary attenuation mechanism of hydrocarbons below the water table is anaerobic degradation. In the absence of oxygen, the oxidized forms of other inorganic species available in subsurface environments are utilized by bacteria to mediate the oxidation of hydrocarbons. Cozzarelli (1993) described the predominant reaction mechanisms and their spatial scale. The presence of a narrow zone at the water table where nitrate is transformed to N_2O and ammonia indicates that nitrate entering in the recharge water is rapidly utilized. Below the water table, a zone of iron-reduction is present. However, the depletion of microbially reducible solid iron-oxyhydroxides in narrow zones has allowed sulfate reduction to begin at small spatial scales. Reduced iron and sulfide are elevated in the plume and have combined to form the mineral pyrite on the aquifer solids. The presence of reaction products such as reduced iron, sulfide, and resulting minerals in concentrations that exceed background values is one line of evidence indicating that anaerobic biodegradation has contributed to mass loss at the site.

Important results from the Bemidji crude oil site are (1) the rate and extent of biotransformation reactions under different redox conditions; (2) the documented effects of organic contaminant chemistry on aquifer geochemistry; (3) the slow evolution of conditions in the plume from aerobic to iron-reducing to methanogenic conditions. These results frequently are cited in protocols that summarize our knowledge of petroleum hydrocarbon natural attenuation processes (see,

for example, Wiedemeier and others, 1995). The Bemidji site became contaminated in 1979 when a pipeline broke spilling 10,000 barrels of crude oil on the land surface (Hult, 1984). After cleanup operations, about 40 percent of the oil remained and subsequently infiltrated into the sand-and-gravel glacial outwash aquifer. The oil is present in residual concentrations in the unsaturated zone and as two floating oil bodies on the water table. An aqueous plume emanating from the northern oil body has been extensively studied under the USGS Toxics Program.

Baedecker and others (1993) found that geochemical conditions in the Bemidji plume could be classified into three zones corresponding to anaerobic, transition, and aerobic conditions. In the anaerobic zone, degradation of the hydrocarbons by iron reduction initially dominated (Lovley and others, 1989). However, as ferric iron has been depleted, narrow methanogenic zones have formed in areas of high contaminant flux (Bekins and others, 1999). Reduced iron and methane concentrations are elevated in the plume along with aliphatic and aromatic organic acids. The organic acid composition and concentration shifts as the dominant TEAP evolves from iron reduction to methanogenesis (Cozzarelli and others, 1994). In the anaerobic portion of the plume, concentrations of benzene and alkylbenzenes decrease relatively slowly compared to other hydrocarbons. However, in the transition zone between anaerobic and aerobic conditions, the concentrations of hydrocarbons decrease rapidly (Eganhouse and others, 1993). Anderson and others (Anderson and others, 1998) showed that rapid degradation of benzene occurred over a narrow region at the downgradient edge of the Fe(III) reduction zone in an area associated with elevated numbers of *Geobacter* species. The microbial degradation reactions lead to significant perturbations in the inorganic as well as the organic chemistry of the water and the aquifer material (Bennett and others, 1993). Changes in the aquifer include formation of authigenic minerals (Baedecker and others, 1992; Bennett and others, 1993; Tuccillo, 1998) and dissolution of aquifer

mineral phases (Hiebert and Bennett, 1992; Rogers and others, 1998).

Nitrate is the most prevalent anthropogenic groundwater contaminant. In aqueous solution, it is generally a stable compound that is transported conservatively after entering the subsurface. However, when significant concentrations of organic carbon lead to anaerobic conditions, denitrification reduces nitrate to nitrogen gas. This reaction has resulted in significant natural attenuation of nitrate at the Cape Cod, MA, USGS Toxics Program site. A long-term study of the site has included: a) factors that control occurrence of denitrification in an aquifer (Smith and Duff, 1988); b) measurement of in situ rates (Smith and others, 1996b); c) the effect on ground water nitrogen geochemistry (Smith and others, 1991b); d) identification and characterization of unique subsets of the denitrifying microbial population in the aquifer (Smith and others, 1994); and e) the inability of certain soils techniques to assess denitrification in the subsurface (Brooks and others, 1992). The ground water at the Cape Cod site has been contaminated with secondarily treated sewage effluent from rapid infiltration ponds located on Otis Air Force Base. The sewage-contaminated ground water has formed a plume more than 6 km long containing chlorinated hydrocarbons, detergents, metals, microbes, and nitrate.

At the Cape Cod site denitrification is electron-acceptor limited throughout the center of the contaminant plume, having completely consumed the source nitrate. However, it is electron-donor limited in a 5- to 7-m thick zone that extends for several kilometers downgradient from the contaminant source. Denitrification occurs primarily in the aquifer under suboxic conditions within the 10-30 μM region of the oxygen gradient. In high nitrate zones, nitrite and nitrous oxide are present. Concentrations of these intermediates can vary significantly on a meter scale (both vertically and laterally), though neither persists with downgradient transport on the kilometer scale. Elevated concentrations of nitrogen gas also are present within the aquifer, particularly in zones in which denitrification is electron-acceptor limited. Natural gradient tracer tests with ^{15}N -

enriched nitrate have demonstrated that unequal amounts of N (and electron equivalents) pass through the individual steps of the denitrification pathway. A comprehensive picture of the interacting processes that may limit denitrification rates in an aquifer is emerging from the Cape Cod results.

CHALLENGES OF NATURAL ATTENUATION

The potential success of natural attenuation as a remedial strategy is complicated or limited by several aspects of the subsurface environment. The physical and chemical properties of subsurface rocks and sediments can be highly variable within a single site. Moreover, the subsurface flow fluctuates temporally. Ground-water flow rates are typically very slow and dissolution and desorption rates are limited by the small flux of clean ground water contacting concentrated sources of contaminants. Natural chemical fluxes into the subsurface from the surface also are limited and this affects the number and diversity of subsurface microbial populations. The sections below describe how these various aspects of the subsurface have complicated and limited the processes controlling the natural attenuation of contaminants at several of the Toxics Program sites. The discussion is divided into sections on spatial and temporal variability, slow time frames, and microbial ecology.

Spatial and Temporal Variability

Ground-water contaminant plumes are characterized by longitudinal and vertical gradients of both naturally-occurring and contaminant solutes. These heterogeneities are due to various combinations of: a) changes in contaminant source; b) differential rates of transport; c) physical and chemical heterogeneity of aquifer properties; d) geochemical and microbiological processes; and e) changes in hydrologic conditions along the flow path. As geochemical conditions change in space and time, the carbon sources, electron acceptors, and other environmental variables that limit microbial degradation in the

subsurface also change. These changes complicate attempts to monitor or predict remediation outcomes. Nevertheless, it is clear that proper evaluation of the effects of spatial and temporal changes are necessary in order to monitor, predict, or model either specific or composite processes at sites proposed for RNA. Efforts to characterize the effects of heterogeneity on natural attenuation have been an important aspect of Toxics Program research at the Cape Cod, Bemidji, and Galloway sites and at Wurtsmith Air Force Base, MI (mixed wastes). The results indicate that changes in redox conditions on small spatial scales and over short time frames are common and that these changes have profound effects on the fate of contaminants in the subsurface.

At the Cape Cod site, small vertical dispersivity limits vertical mixing and maintains sharp gradients in oxygen and other solutes even after several kilometers and several decades of transport (Smith and others, 1991a). Studies with large-scale tracer tests have estimated the vertical dispersivity in the aquifer to be 0.15 cm, or >600 times smaller than longitudinal dispersivity (Garabedian and others, 1991). Concomitant with the large concentration gradients are large changes over a vertical distance of a few meters in bacterial abundance, growth rates, and heterotrophic activity, as well as cell morphology (Smith and others, 1991a). In the horizontal direction, the plume character changes more gradually with increasing recalcitrance in the residual DOC downgradient (Harvey and Barber, 1992) and increasing importance of autotrophic processes (such as nitrification) as oxygen-consuming mechanisms (Ceazan, 1987; Ceazan and others, 1988) over a scale of kilometers.

Dramatic spatial and temporal changes in TEAP zonation (Chapelle and others, 1996; McGuire and others, 1999), microbial community composition, and bacterial population abundance (Haack and Reynolds, 1999; Reynolds and Haack, 1999) also have been observed in Toxics Program research at the former Wurtsmith Air Force base. Fire training exercises conducted at the site from 1958 until 1986, resulted in dispersal of waste fuel, solvents, and fire-fighting compounds to a

shallow water table aquifer composed of glacial deposits of gravel, sand, silt and clay (USGS, 1991; Huffman and others, 1995). The contaminant plume extends about 500 m downgradient from the central site of fire-training activities and the majority of the contaminants are located on the aquifer solids near the water table. The water table ranges from 5-8 m below land surface and water levels fluctuate 0.3-1 m annually. The average ground-water velocity is 0.1-0.3 m per day.

The research at the Wurtsmith site had three primary objectives: (1) determine spatial and temporal heterogeneity in TEAPs, microbial communities and TEAP-related microbial populations; (2) relate spatial and temporal heterogeneity in these parameters to evidence of biodegradation in the contaminant plume; and (3) evaluate the significance of spatial and temporal heterogeneity for intrinsic remediation. In October 1995, June 1996, and October 1996, the dominant TEAP was assessed at specific locations and depths in the aquifer by determining the ground-water redox chemistry and hydrogen gas concentration. Aquifer sediments were then collected from specific depths, and assigned a TEAP based on analyses from a well less than 4 m upgradient of the sediment collection site. Preliminary results indicate that TEAPs and microbial communities and populations vary over spatial scales of less than 1 m and over temporal scales of months. Changes in microbial communities and populations were related to gradients in aquifer water chemistry at the site. Current research focuses on relating these gradients to patterns of biodegradation products within the plume. It is likely that specific biodegradation reactions occur only at certain locations within the Wurtsmith plume, or only at certain times.

Data from the Bemidji site confirm that the potential for degradation of specific hydrocarbons and also reaction rates vary with redox zone (Baedecker and others, 1993; Eganhouse and others, 1993; Cozzarelli and others, 1994; Anderson and others, 1998). Moreover, the spatial extent of the reaction zones was found to be especially narrow at both the Galloway gasoline site and the Bemidji crude-oil site, where maximum hydrocarbon

contamination within the plumes corresponded to anoxic zones of only one to two meters in thickness. Within the anoxic zones, observations of submeter-scale intervals of sulfate reduction at the Galloway site (Cozzarelli, 1993) and methanogenesis at the Bemidji site (Tuccillo, 1998; Bekins and others, 1999) are associated with depletion of microbially reducible solid iron-oxyhydroxides. Interpretation of reaction processes is complicated by mixing of degradation products from different redox zones. At the Galloway site, the mixing of end products of different biogeochemical reactions was enhanced by fluctuations in the water table and the small spatial scale of the reaction zones (Cozzarelli, 1993).

In summary, results from the USGS Toxics Program sites show that understanding whether environmental conditions favor biodegradation depends on our ability to measure these processes at an appropriate scale. Ground-water samples obtained from wells with long screens have little relevance if the chemistry of the composite sample does not exist anywhere in the aquifer. Thus, sample intervals and well-screen lengths must be matched to the steepness of the subsurface gradients. Research conducted by the USGS Toxics program has made extensive use of short-interval sampling, and provides exceptional examples of the significance of scale. A variety of innovative technologies have been used to achieve this objective. At the USGS Cape Cod study site, multilevel samplers (MLSs) were constructed with short vertical intervals between ports making them particularly useful for sampling across steep gradients (LeBlanc and others, 1991; Smith and others, 1991a). Currently the Cape Cod site has ~2000 15-port MLSs in place to study the sewage-derived contaminant plume. At the Wurtsmith site, a hydropunch was used in conjunction with short well screens to study the relationship between TEAPs and microbial communities. Unprecedented spatial resolution for studying the relationship between pore water chemistry and adjacent sediments and microbial populations was possible at the Bemidji site using a freezing drive shoe designed by Murphy and Herkelrath (1996). Using the drive shoe,

hundreds of cores containing both the aquifer material and pore fluids collected from the plume and the oil body have enhanced understanding of the effects of spatial variability on natural attenuation at the Bemidji site.

Time Frame

The decision to rely on natural attenuation processes at a site is simplified when it is clear that the contamination will be degraded or immobilized within the foreseeable future. Some state regulators have expressed a concern that the predicted cleanup time by natural attenuation not exceed a few decades. However, slow rates of matrix diffusion, desorption, and nonaqueous-phase liquid (NAPL) dissolution may result in natural attenuation time frames much longer than can be planned for in a regulatory process or predicted with models. Results from three very different USGS Toxics Program sites illustrate situations where the time frame of natural attenuation is very long and our ability to predict the future sustainability may be questionable. At the Mirror Lake, NH (fractured rock), site rate-limiting aspects of matrix diffusion in fractured rock aquifers have been the focus of several studies. At the Picatinny site, it is estimated that slow desorption will result in a substantial long-term mass flux of TCE from the aquifer solids into the ground water. Finally, an analysis of the dissolution rate of nonaqueous-phase oil at the Bemidji crude oil spill suggests that contamination will persist for hundreds of years. The results of these studies show that a clear understanding of the expected progress of natural attenuation over long time frames will be crucial for guiding remediation decisions about certain types of contaminant sources and aquifer conditions.

Results from the Mirror Lake site, show that matrix diffusion and (or) "effective" matrix diffusion acts as a "storage" and "release" mechanism in heterogeneous formations. Initially matrix diffusion is an uptake mechanism that reduces the concentration in the mobile phase. Later, when concentration gradients are conducive for transfer from the "immobile" to the "mobile" phase the stored

contaminants are slowly released from the formation matrix. The geology of the Mirror Lake site is characterized by fractured metamorphic and igneous rocks overlain by a thin veneer of glacial drift. Although the site is uncontaminated, research has focused on developing and testing methods for characterization of the physical properties of the fractured network that affect the advective and dispersive movement of dissolved chemicals in ground water.

Investigations at Mirror Lake have included tests on multiple scales ranging from meters to kilometers and emphasized integration of geologic, hydrologic, geophysical, and geochemical methods to characterize and simulate ground-water flow and transport. Laboratory-scale studies of fractured rocks from the Mirror Lake site show that granite and schist have an intrinsic interconnected porosity that is capable of transporting dissolved constituents (in this case ^{137}Cs) by diffusion over several centimeters in a period of 100 days (Wood and others, 1996). ^{137}Cs is highly retarded so the effect on a conservative constituent would be much greater. Field-scale investigations were conducted using an injection of a tracer (sodium-bromide) under controlled hydraulic conditions (Shapiro, 1994). In addition, regional-scale investigations of chemical migration were inferred from tritium and CFC concentrations in ground-water samples (Shapiro, 1996).

In both the field and regional-scale investigations at Mirror Lake, fitting the chemical data required including an "effective" matrix diffusion orders of magnitude larger than the value from the laboratory investigation (Shapiro, 1996). The reason for this increase is that at the laboratory scale, the flow regime (in this case only diffusion) is known explicitly, while at the field and regional scales, the intricacies of the flow regime are not known. In addition to diffusion of dissolved constituents into the rock matrix, there also are advective processes that give the appearance of "matrix diffusion" when considered over larger dimensions. For example, dissolved constituents can be advected from a higher-permeability region into a lower-permeability region and then

eventually back into a high-permeability region. If this process occurs over a small distance, it gives the appearance of "diffusing" into an "immobile" flow regime and then back into a "mobile" flow regime. In these investigations, this effect could not be represented by dispersion alone. Similar processes to those observed in fractured rock at the Mirror Lake site will also arise in other geologic environments where there are contrasts in the hydraulic properties, such as clay lenses within a sand and gravel aquifer, sand stringers within till, etc.

Matrix diffusion and (or) "effective" matrix diffusion can contribute significantly to the inefficiency of pump-and-treat remediation in heterogeneous formations. While a contaminant is present in the "mobile" or high-permeability flow regime there is a large chemical gradient driving the constituent into the "immobile" or low-permeability flow regime. After pumping has started, however, the contaminant is first removed from the high permeability regions, increasing the chemical gradient driving the constituent back to the "mobile" flow regime. The chemical gradient from the "immobile" to the "mobile" flow regime, however, is small in comparison to the original gradient driving the contaminant into the low-permeability region. Thus, the time-frame for diffusive migration out of the low-permeability region will always be significantly longer than the period of untreated contamination. In other words, the diffusive exchange between "immobile" and "mobile" flow regimes will control the rate at which contaminants can be removed by pump-and-treat technology, regardless of the pumping rate employed. Contrasts in hydraulic properties similarly will affect flushing technologies (steam, co-solvents, surfactants, etc.) used in treatment of NAPL's. Contact between the NAPL and water occurs mainly in the "mobile" high permeability flow regime whereas NAPL's may have infiltrated lower-permeability regions or water flow may be limited through areas of high NAPL saturation.

Storage and release can account for a major percentage of the ground-water contamination source. This behavior has been

observed and quantified at the Picatinny Arsenal study site where desorption from the solid phase is a significant source of TCE transfer to the ground water. Imbrigiotta and others (1995) estimate that approximately 3,000 to 4,000 kg of TCE are sorbed to the aquifer sediments and that this quantity is 3-4 times greater than the estimated total mass of TCE in the ground water at the site. Recent studies have concluded that the rate of TCE desorption from the aquifer sediments is slow relative to other processes such as advection (Koller and others, 1996; Sahoo and others, 1998). Koller and others (1996) quantified TCE soil-water mass transfer coefficients for contaminated soil collected from the site using laboratory soil-column experiments with native ground water. These mass-transfer coefficients can be used to estimate the mass flux of TCE from the contaminated aquifer sediments to the ground water using a first-order mass-transfer relation. On the basis of best estimates of the mass of contaminated soil, the water and soil TCE concentrations, soil density, porosity, and coefficients for mass transfer and sorption, the estimated TCE mass flux from soil to water at the site ranges from 474 kg/yr to 2,300 kg/yr. Because the measurements of mass-transfer coefficients were made in the laboratory on disturbed soil samples from the site, it is reasonable to assume that the estimated desorption fluxes have a large degree of uncertainty relative to other fluxes at the site. Nevertheless, the minimum estimated value exceeds the sum of minimum estimates of removal rates by volatilization (50 kg/yr), anaerobic degradation (52 kg/yr), and pump and treat (70 kg/yr).

Nonaqueous-phase liquids that enter the subsurface may act as long-term sources of ground-water contamination as the organic constituents dissolve from the nonaqueous phase. The amount and rate of dissolution depends on many factors, including the flow field in the vicinity of the oil body. To examine the flow of water and resulting dissolution rate at the Bemidji, MN site, Essaid and others (1995b) simulated steady-state water flow through the oil bodies and used particle-tracking to determine the volumetric water flux through

the oil body and the resulting dissolution of contaminants. Water relative hydraulic conductivities used in the model were computed from kriged oil saturation and hydraulic conductivity data. The effective solubility of a hydrocarbon was determined by multiplying the mole fraction of the component in the oil times the solubility of the component. Assuming that concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) in the water are in equilibrium with the oil, the total mass flux of a hydrocarbon component from the oil body can be estimated by multiplying the volumetric water flux through the oil times the effective solubility. Finally, the time to completely dissolve the BTEX can be estimated by dividing the total mass of each component in the oil by the mass flux of the component due to dissolution. These simulations suggested that the total dissolution time for the Bemidji oil body is on the order of 100 years for benzene, 500 years for toluene, and 1000 years for ethylbenzene and xylene (H. I. Essaid and W. N. Herkelrath, pers. comm., 1999). These calculations are approximate because they do not account for the changing composition of the oil body during dissolution. Nevertheless, they indicate that non-aqueous phase sources may persist for time frames that exceed the current regulatory framework.

Microbial Ecology of Contaminant Plumes

The potential for significant biotransformation of contaminants depends on the capabilities and numbers of indigenous microorganisms that mediate the reactions. A microbial population must be present that is capable of degrading the contaminants under the geochemical conditions in the aquifer. Moreover, as conditions in the plume change, the microbial population must also change. Despite the critical role of microorganisms in natural attenuation, knowledge of how the active degrading microorganisms become established and function in a plume is limited (Madsen, 1998). For example, total counts of bacteria do not correlate with contaminant degradation (Madsen and others, 1991).

Moreover, the specific organisms that carry out the degradation reactions are rarely known. In many cases, cooperation of several populations within a microbial community is required but the mechanisms of the community interactions are poorly understood. The results of studies of the active microbial populations at Wurtsmith Air Force Base, together with results from the Bemidji, Pensacola, FL (wood-treatment wastes), and Cape Cod USGS Toxics Program sites have contributed to an increased understanding of these issues and provide a sense of the current level of knowledge.

Research conducted by the USGS Toxics Program at the former Wurtsmith Air Force Base in Michigan used new methods in microbial ecology based on analysis of the nucleic acids DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) extracted from aquifer materials to examine in situ microorganisms. Sediment samples taken from specified TEAP zones in two (field replicate) cores exhibited similar community DNA compositions, suggesting similar community structure and demonstrating the reproducibility of both procedures. Cluster analysis of community DNA patterns indicated five major community groups (Haack and Reynolds, 1999). Current work is focused on defining the environmental gradients associated with these groupings. Preliminary data based on RNA analysis suggest that populations of methanogens (or other *Archaea*) are most abundant in sediments where the TEAP indicates methanogenesis or sulfate reduction during most of the year (Reynolds and Haack, 1999). Samples from the capillary fringe exhibited the largest amount of total bacterial RNA. The capillary fringe also was found to be an area of enhanced bacterial activity by Bone and Balkwill (1988) in a study of a pristine aquifer in Lula, Oklahoma. Dramatic changes in methanogen (or other *Archaea*) abundance occurred over vertical intervals of less than 1 m on each tested date. RNA analysis demonstrated spatial and temporal correlations between in situ abundance of a "TEAP - active population" (methanogens) and geochemical indications of methanogenesis (H_2 and CH_4 concentration). Additional population studies by Dojka and others (1998)

also documented that methanogens were important populations in samples taken from zones at Wurtsmith where methane (CH_4) was in highest concentration in October 1996. However, this research also demonstrated that TEAP zones defined as iron-reducing or sulfate-reducing by H_2 gas analysis did not harbor significant populations of currently known iron- or sulfate-reducing bacteria. In fact, this research, employing DNA-based methods, demonstrated that there exist numerically dominant and (as of yet) uncultured, and therefore unknown, populations of microbes at this site.

Results from the Bemidji site provide insight into the microbial ecology of the anaerobic portion of a crude-oil plume. Lovley and others (1989) isolated an organism from the site that can degrade a variety of aromatic organic compounds under iron-reducing conditions. Bekins and others (1999) analyzed microbial populations, pore water chemistry, sediment grain sizes, and extractable iron at 15-30 cm intervals from cores containing both sediment and pore water. The most probable number method (MPN) was used to characterize the spatial distribution of six physiologic types of microorganisms: aerobes, denitrifiers, iron reducers, heterotrophic fermenters, sulfate reducers, and methanogens. Areas in the plume that have changed from iron-reducing to methanogenic conditions are clearly indicated by lower numbers of iron-reducers and the presence of culturable methanogens, heterotrophic fermenters, and sulfate reducers. These conditions are found in areas of high contaminant flux either in the vicinity of the nonaqueous oil or in the dissolved plume where higher concentrations are associated with local increases in aquifer permeability. In the older part of the plume under the oil body, the methanogenic niche spans 50 percent of the vertical thickness of the dissolved plume. At 30 m downgradient where the change to methanogenic conditions is more recent, the methanogenic niche spans 25 percent of the vertical thickness of the plume.

At the Pensacola USGS Toxics Program site, creosote wastes from a wood treatment facility operated from 1898-1982 have migrated

from unlined impoundment ponds into a deltaic sand aquifer. Conditions in the contaminant plume are primarily methanogenic and concentrations of DOC decreased from 357 mg/L at the impoundment ponds to 50 mg/L at 100 m down gradient. The presence of methane and organic acids in the plume provide evidence that methanogenic degradation was active in the aquifer (Goerlitz and others, 1985). Godsy and others (1992) found a 100-fold increase in culturable methanogens within the plume compared to the uncontaminated background. Modeling of the degradation processes by Bekins and others (1993) indicated that observations of a steady-state plume are consistent with a steady-state microbial population. One possible explanation for lack of growth in the microbial population is the toxicity of the creosote compounds. Laboratory studies indicate that enriched cultures of acetate-utilizing methanogens from the field site are inhibited by the soluble fraction of the creosote compounds (Bekins and others, 1997).

Results from microbiological studies at the Cape Cod study site demonstrate that 60 years of discharge of treated sewage to a highly-permeable, unconfined, sandy aquifer has resulted in a diverse and dynamic microbial community within the resultant 5 km-long contaminant plume. In spite of the long-term input of organic material into the aquifer, denitrification in the contaminant plume is limited with respect to organic carbon (Smith and Duff, 1988) and the bacteria therein appear to be metabolically stressed (Metge and others, 1993). A large (up to 10^6 /mL) community of unattached bacteria is being advected downgradient along with the dissolved organic contaminants that they are degrading (Harvey and Barber, 1992) and the partitioning of the bacteria to the aqueous phase increases steadily with decreasing distance from the loading beds. Abundance of unattached bacteria correlates strongly with dissolved organic carbon (DOC) within the first 3 km and with the more readily-degraded (non-alkyl benzene sulfonate) DOC in the more distal portion of the plume.

Bacterial abundance within the Cape Cod contaminant plume also appears to be strongly controlled (Kinner and others, 1997) by a

diverse (Novarino and others, 1997) protistan community that includes a number of species that are hitherto undescribed (Novarino and others, 1994). Large numbers of protozoa (up to 10^5 /g) have been observed in both the oxic and suboxic zones of the contaminant plume (Kinner and others, written communication, U. of New Hampshire). Results from laboratory clearance rate studies suggest that the protistan community may be completely consuming the unattached population of bacteria immediately downgradient from the loading beds every few days (Kinner and others, 1998). Furthermore, the presence of protozoa appears to be causing a marked increase in the growth rate of the unattached bacteria within the plume (Kinner and others, written communication, U. of New Hampshire), thus promoting a greater efficiency in organic contaminant degradation. The community of protozoa is dominated by 2-3 μm nanoflagellates that feed selectively on the 0.8-1.5 μm size class of unattached bacteria (Kinner and others, 1998) that constitute much of the pore water biomass within the plume (Harvey and Garabedian, 1991). Although often weakly associated with grain surfaces, *in situ* and laboratory studies suggest the nanoflagellates are capable of a high degree of mobility within the aquifer (Harvey and others, 1995). This appears to be due, in part, to their strong motility, optimal size for transport (Harvey and Garabedian, 1991), and low buoyant density (Harvey and others, 1997), which contributes to their observed ability to respond quickly to spatial and temporal changes in DOC within the aquifer (Kinner, written communication, U. of New Hampshire).

THE ROLE OF MASS BALANCE

One of the desirable steps in demonstrating the efficacy of natural attenuation at a site is to quantify the relative contribution of individual processes to the total mass loss. In some cases a quantitative analysis may be required by the state regulators (for example, Minnesota Pollution Control Agency, 1996). In addition, the ability to demonstrate the magnitude of specific attenuation mechanisms strengthens public confidence in an RNA

decision. Depending on the goals of the analysis and the complexity of the site, a range of quantitative approaches can be used. An effective approach used for the Picatinny site combines simple rate laws with a range of estimates of parameters or fluxes. The results give a sense of both the role of individual processes and also the uncertainty in each of the values. A more complex approach was used at the Bemidji crude-oil site. In this case, a model of two-dimensional flow and transient transport with biodegradation reactions provided an estimate of the relative mass loss from each of the important biotransformation reactions. The Bemidji example illustrates how concentrations of reaction products can be used to constrain the contribution of a specific reaction to the observed attenuation. Regardless of whether the approach used is simple or complex, it is important that the quantification be based on measured data from the sites as in both the Picatinny and Bemidji examples. Another key aspect is that each of these site analyses is based on a careful understanding of the hydrologic processes controlling transport of the contaminants.

Using simple rate laws and parameter estimates, researchers at Picatinny Arsenal estimated the mass losses from several natural remediation processes and compared their effectiveness to a pump-and-treat system. Table 1 summarizes the estimated mass flux for contaminants at Picatinny Arsenal due to vapor flux, anaerobic biotransformation, desorption, and discharge into Green Pond Brook. Discharge of TCE dissolved in ground water into nearby Green Pond Brook and subsequent volatilization into the atmosphere also was an important mass sink prior to installation of the pump-and-treat system. Using the TCE concentration in ground-water and the average, base-flow ground-water discharge rate, Imbrigiotta and others (1995) estimated that between 32 and 63 kg/yr of TCE were discharged into the brook. It is apparent from these data that the pump-and-treat system is ineffective relative to natural remediation processes. The table shows that the sum of the flux of TCE to Green Pond Brook, the TCE flux to the atmosphere, and losses from anaerobic

biodegradation processes may be several times greater than the flux of TCE from the pump-and-treat system. The mass balance exercise clarifies the emerging picture that pump-and-treat systems frequently are more useful for containment than for mass removal.

It should be noted that several possibly significant TCE sources and sinks have not been estimated. Specifically, no estimate has been made for the rate of TCE dissolution from a nonaqueous phase. To date, no positive confirmation of a nonaqueous TCE phase has been made, let alone estimates of TCE dissolution rates. No estimate of TCE transport across the unconfined aquifer's lower confining unit has been made, despite the fact that TCE has been detected in the deeper, confined aquifer. Lack of adequate concentration data and information on the physicochemical properties of the confining layer prevent a meaningful calculation. Lastly, estimates of TCE desorption and biodegradation rates are based on laboratory experiments using soil and ground water from the field site. These estimates likely have more uncertainty than the direct field estimates of TCE removal by volatilization, pump-and-treat extraction, and discharge to Green Pond Brook.

Table 1. Estimates of TCE sinks and sources for ground water from the Building 24 contamination plume at Picatinny Arsenal, New Jersey.

Process	TCE source or sink	Mass TCE flux, kg/yr
Pump-and-treat system	Sink	70*
Diffusion/advection of TCE vapors through unsaturated zone	Sink	50
Anaerobic biotransformation	Sink	52 to 1040
Desorption from aquifer sediments	Source	474 to 2300
Discharge to Green Pond Brook	Sink	32 to 63

*Based on data from 1995.

In the Bemidji site model created by Essaid and others (1995a), volatile and nonvolatile organic compounds in the petroleum hydrocarbon plume are transported and undergo degradation by three microbial populations; aerobes, Mn and Fe-reducers, and methanogens. The biotransformation reactions in the model consume dissolved oxygen, and solid-phase Fe(III) and Mn(IV). In addition they produce dissolved Fe(II), Mn(II), and methane. Observations of concentrations of these reactants and products in the ground-water plume over the period 1984-1992 were used to constrain the relative contribution of each reaction to the overall mass loss of petroleum hydrocarbons. The simulations were performed with the BIOMOC model code (Essaid and Bekins, 1997). By using an inhibition formulation in the code, iron-reduction was delayed until dissolved oxygen was exhausted. Similarly, methanogenesis was inhibited if solid phase Fe(III) and Mn(IV) were still present. The model results accurately reproduce the temporal and spatial concentration changes in volatile and nonvolatile organic compounds, dissolved Fe(II), Mn(II), and methane. The simulation indicates that, over a distance of 200 m, 46 percent of the total dissolved organic carbon introduced into the aquifer is degraded. Of this, aerobic processes account for 40 percent of the degradation, while the remaining 60 percent is by anaerobic processes (5 percent by Mn reduction, 19 percent by Fe reduction, and 36 percent by methanogenesis). The Bemidji modeling illustrates how concentrations of reaction products can be used to constrain the fraction of the total contaminant mass loss that results from each biotransformation process.

SUMMARY AND FUTURE DIRECTIONS

The increased use of natural attenuation as a remediation strategy in recent years is based on careful study results that document the effectiveness of specific attenuation processes in the field. The goal of the U. S. Geological Survey Toxic Substances Hydrology Program is to better understand the fate of contaminants in the environment in support of improved

strategies for contaminated site assessments, monitoring programs, and decisions regarding remedial options. Results from the program have documented the effectiveness of volatilization and biotransformation as attenuation processes in the subsurface for several types of contaminants. Additional studies of the subsurface microbial populations that transform contaminants have provided insights into the distributions of organisms and some estimates of the biotransformation rates.

Research results also show that a number of problems and research challenges remain for understanding natural attenuation. One of these challenges is the spatial and temporal variability inherent in aquifers and hydrologic systems. This variability is now well documented and several associated research challenges are clear. These include methods to predict the effect of variability on natural attenuation; methods to assess uncertainty in the fate of ground-water plumes associated with incomplete characterization, and designs for optimal monitoring strategies that can provide early warning of failure of the natural attenuation processes. Another challenge is the long time frame over which unrecoverable immobile contaminant phases will continue to act as sources of dissolved contaminants to the ground water. Although the expected longevity is now well documented (National Research Council, 1994), the regulatory community is still grappling with policies for managing this problem with risk-based assessments. An important goal of future research will be to enhance the current understanding of the sustainability of natural attenuation processes into the distant future (hundreds of years). This understanding will be necessary to assess whether a long-term source ultimately poses a threat to human health and the environment.

Research at the USGS Toxics Program study sites has focussed on several classes of compounds including petroleum hydrocarbons, the chlorinated solvent TCE, wood treatment wastes, nitrogen, and sewage wastewater. The results show that natural attenuation processes are highly specific to the individual compounds, interactions among compounds, and the natural geochemistry of the contaminated aquifer. Thus,

another set of challenges is to understand the fate of specific compounds under a variety of redox conditions, the interactions between compounds, and the fate of compounds not yet studied. For example, the recent use of ether-oxygenates such as MTBE as gasoline additives challenges the paradigm of natural attenuation remediation which has developed within a BTEX frame of reference. Compared to BTEX, MTBE is much more soluble and is believed to be less degradable than BTEX in the subsurface. These facts together with field evidence that MTBE solute migration advances ahead of BTEX at gasoline-spill sites (for example, Landmeyer and others, 1996) suggest that volatile losses of MTBE from the source area may be significant in assessing natural attenuation with respect to MTBE.

Understanding the capabilities of subsurface microorganisms that mediate biotransformation reactions represents another challenge to implementing natural attenuation. Many open questions remain with respect to these organisms. These include (1) biotransformation rates under various conditions and what controls them; (2) the extent to which multiple compounds either interfere with or enhance transformation rates; (3) whether the transformations are mediated by single species or consortia; (4) how degradative capabilities are acquired; and (5) how the microbial populations become established in the aquifer and what controls their growth. Finally, work at the USGS Toxics Program study sites has demonstrated the efficacy of quantitative mass balances in understanding the contributions of specific processes to the overall attenuation. The desire for an accounting of the fate of contaminants is emerging as a priority of regulators tasked with site decisions (for example, Minnesota Pollution Control Agency, 1996). Quantitative assessments may be based on a spectrum of approaches. However, regardless of the approach, the value is highly dependent on how well the model represents the processes at the site. Thus a need exists for strategies that increase the use and quality of quantitative mass balances. These may include wider use of parameter estimation techniques, graphical user interfaces, better training of

modelers, and a more iterative approach to modeling.

Continued research work on subsurface processes at the USGS Toxics Program study sites will be directed toward some of these research challenges. Other work in the program focuses on the fate of contaminants in surface waters, acid mine drainage, the regional-scale fate of pesticides, and metals and pesticides in the San Francisco Bay Estuary. More information about the program and the results from individual research sites can be found at the web site at <http://toxics.usgs.gov/toxics/>.

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