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September 1996

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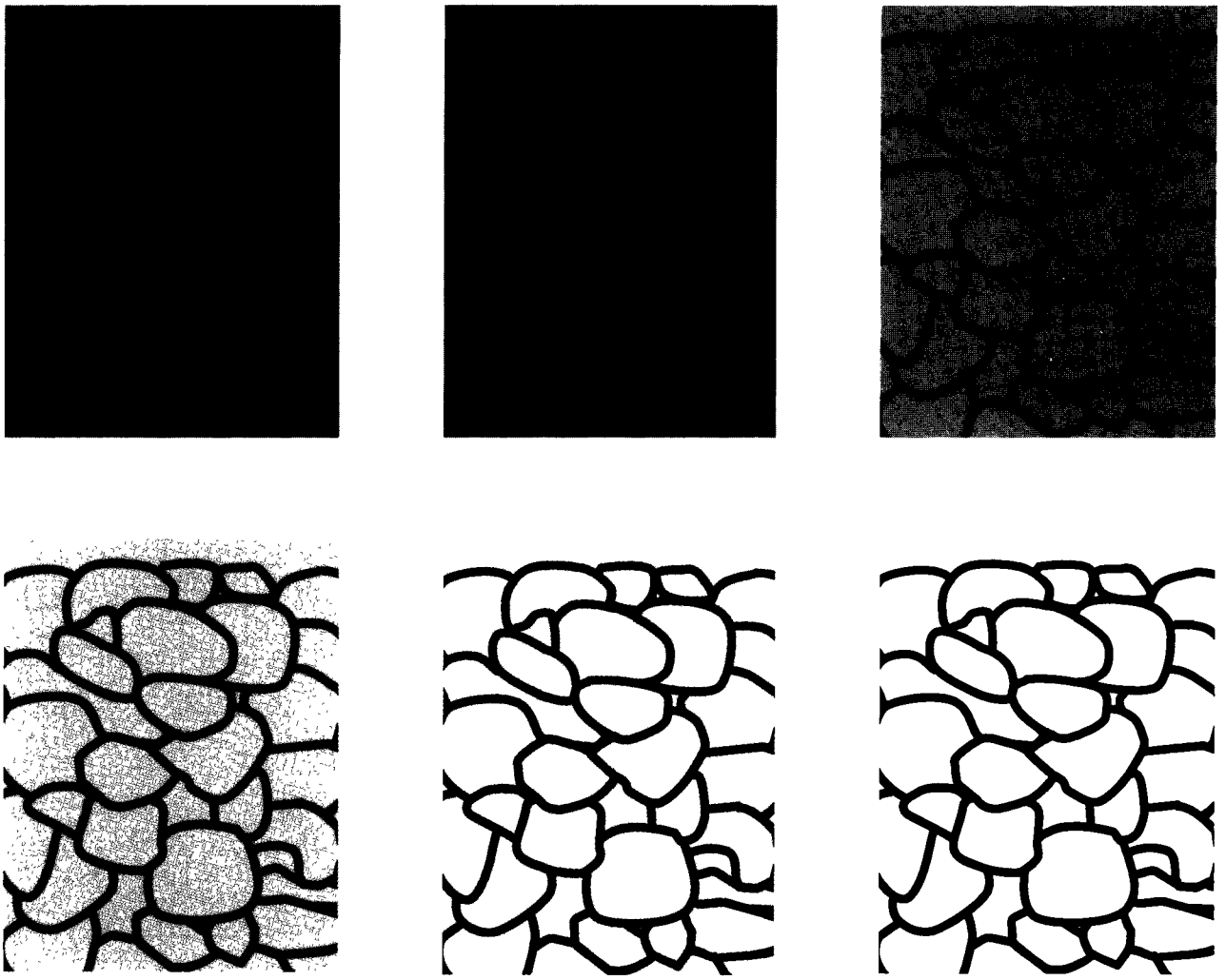
Symposium on Natural Attenuation of Chlorinated Organics in Ground Water

Hyatt Regency Dallas
Dallas, TX
September 11–13, 1996



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Introductory Talk: Where Are We Now? Moving to a Risk-Based Approach

C.H. Ward
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Setting Cleanup Goals for Ground Water

When the Comprehensive Environmental Response, Compensation, and Liability and Resource Conservation and Recovery Acts were implemented in the mid-1980s, the cleanup goals for contaminants in ground water often defaulted to concentration-based standards for drinking water (maximum contaminants levels or MCLs). These standards were designed for public water supplies. Because water supply was seen as the important contribution of ground water, the application of these standards seemed to be relevant and appropriate. There was little awareness of the contribution of ground water to the function of the landscape. The impact of contaminants that discharged from ground water to sensitive receptor ecosystems received less attention.

Stringent drinking water standards were selected with the expectation that they could be met with existing pump-and-treat technology. Pump-and-treat was naively thought to be a quick, viable fix to ground-water contamination. To budget for the first authorization of Superfund, Congress estimated a unit cost for remediation that included application of pump-and-treat, then multiplied this estimate by the number of sites (1).

The Failure To Meet Cleanup Goals for Ground Water

In the mid-1990s, a National Research Council committee reviewed the performance of conventional pump-and-treat methods at 77 sites. At 69 of the sites, the cleanup goal had not been reached. Based on a body of science and empirical experience developed from the mid-1980s to the mid-1990s, the committee identified five reasons that pump-and-treat had failed to perform as expected (2):

- The physical heterogeneity of the subsurface makes contaminant migration pathways extremely difficult to detect.
- Contaminants are often present as nonaqueous-phase liquids (NAPLs) that are not efficiently removed by pumping ground water.
- Contaminants migrate to inaccessible regions so that their recovery is controlled by the rate of diffusion back out of the inaccessible regions, not by the rate of ground-water extraction.
- Sorption of contaminants to subsurface materials results in an underestimate of the total contaminant mass in the aquifer.
- Difficulties in characterizing the subsurface make it difficult to extrapolate between sampling points and produce uncertainty in engineering remedial designs.

The Ground-Water Remediation Treadmill

The default remedy selected to clean up ground water contamination was not working at most sites. Concentrations of contaminants in pumped wells often reached an asymptote that was above the cleanup goal. In the instances in which major reductions in contaminant concentrations were achieved, the concentrations of contaminants would often rebound after the pumps were turned off. As a result, major funds were being expended to operate and maintain systems that were not meeting cleanup objectives.

The NRC committee (2) evaluated alternative technologies and found that a substantial amount of performance data existed for three alternative technologies: soil vapor extraction, R.L. Raymond's process using hydrogen peroxide for in situ bioremediation of hydrocarbons, and bioventing. The Raymond process does not work for most chlorinated solvents; in particular, it does not work for tetrachloroethylene and trichloroethylene. Bioventing and soil vapor extraction work only in the vadose zone, not in aquifers.

The committee also evaluated developing technologies that still required more controlled field studies

and implementation at large-scale sites to generate reliable performance data. They considered pulsed or variable pumping, in situ bioremediation designed for chlorinated solvents, air sparging, steam-enhanced extraction, in situ thermal desorption, soil flushing, and in situ chemical treatment.

It is difficult for technologies presently available or under development to consistently clean aquifers contaminated with chlorinated solvents to drinking water MCLs. Presently, we can be more effective preventing the spread of contamination and reducing exposure.

Containment Instead of Cleanup

In the period from the early 1980s to mid-1990s, while pump-and-treat was being implemented as a remedial technology, microbiologists, hydrologists, engineers, and chemists were working to develop a quantitative understanding of the fate of chemical contaminants in the subsurface. The pump-and-treat systems were being monitored, and many of the ground-water contaminants were recognized to be transformation products of the chlorinated solvents that were originally spilled. For example, cis-dichloroethylene and vinyl chloride were often produced from reductive dechlorination of tetrachloroethylene and trichloroethylene.

By the mid-1990s, 10 years of monitoring data existed on many chlorinated solvent plumes. At many sites, there was clear evidence that the plumes were not expanding; some natural activity was preventing the spread of contamination. At other plumes, containment was not achieved, and contamination spread with the flow of ground water. The effectiveness of pump-and-treat containment should thus be compared to the containment provided by the processes that naturally attenuate contaminants in ground water. These processes include biodegradation, abiotic transformation, sorption, and dilution.

Contribution of Natural Attenuation to Containment

If natural attenuation can contain the spread of contamination, it is the philosophical equivalent of pump-and-treat, a cap on the source, a slurry wall, or an in situ reactive barrier.

Some regulators have dismissed natural attenuation as a "do nothing" approach. If site managers do nothing but compile monitoring data on the contaminants of concern, the characterization is accurate. All they know is the distribution of contaminants at their site. If site managers carry out careful and well-planned studies of the hydrology, geochemistry, and microbiology at their site and use this information to understand in detail the behavior of contaminants, they in turn can use this understanding to make rigorous and defensible predictions about the prospects for the spread of contaminants.

A good characterization study to predict containment by natural attenuation is the equivalent of reliable performance data on a proactive technology for containment. Because site characterizations often require sophisticated sampling techniques, new analytical approaches, and state-of-the-art ground-water modeling, natural attenuation becomes very much a "high-tech" approach (3).

The emerging approach to risk management uses ground-water science to predict the behavior of plumes, then takes advantage of natural attenuation in a comprehensive risk management strategy. These comprehensive strategies usually have some element of source removal or source control at the hot spots, with natural attenuation reserved for the diffuse contamination some distance from the source.

Impacts of Ground Water on Surface-Water Ecosystems

Many plumes of chlorinated solvents discharge to surface water. Discharge from chlorinated solvent plumes has been evaluated at the U.S. Army's Picatinny Arsenal, at the St. Joseph, Michigan, national priority list site, and at the fire training site at Plattsburgh Air Force Base in New York. Case studies on these plumes appear elsewhere in this volume.

When a plume discharges to surface water, the risk management emphasis shifts. The concentration of contaminants is much less important than the mass flux of contaminants to the receptor ecosystem. To manage risk associated with ground-water discharge, the loading of contaminants to the receptor ecosystem must be compared with the loading that can be accepted without damage to the receptor ecosystem. Chlorinated solvents do not bioaccumulate, and they rapidly volatilize to the atmosphere. As a consequence, there is little anecdotal evidence that discharge of chlorinated solvents from ground water has damaged surface-water ecosystems; nonetheless, these issues deserve systematic evaluation.

The discipline of toxicological assessment of ecosystems has made extensive progress in the last decade. No established and widely accepted protocol for making these assessments exists, however. As a result, much of the science is not readily available to regulators. This makes it difficult for the regulators to participate as intellectual partners in the risk assessment and risk management process. A protocol should be developed to evaluate the transfer of contaminants from ground-water to surface-water ecosystems. By documenting appropriate sampling methods, analytical procedures, procedures for interpreting the data, and mathematical models to collate and integrate data, such

a protocol would greatly facilitate the task of determining the loadings that surface-water ecosystems can receive without being damaged.

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Introductory Talk: Where Are We Now With Public and Regulatory Acceptance? (Resource Conservation and Recovery Act [RCRA] and Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA])

Kenneth Lovelace
U.S. Environmental Protection Agency, Washington, DC

(Paper unavailable at press time.)

Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water

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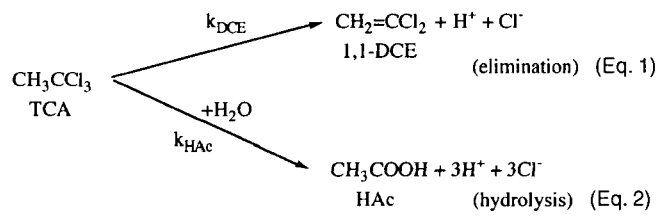
Introduction

Chlorinated solvents and their natural transformation products represent the most prevalent organic groundwater contaminants in the country. These solvents, consisting primarily of chlorinated aliphatic hydrocarbons (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 natural attenuation or intrinsic biotransformation (2).

The major chlorinated solvents are carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (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 (cis-DCE, t-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1-dichloroethane (DCA), and chloroethane (CA). Abiotic or chemical transformations of some CAHs can occur within the time frame of interest in ground water. CAHs can also be transformed through the action of aerobic or anaerobic microorganisms. In some cases, such transformations may be co-metabolic, that is, fortuitous transformation brought about by enzymes that microorganisms are using for other purposes. In such cases, the transforming microorganisms must be actively growing, which requires the presence of primary substrates. In other cases, the microorganisms may be using the CAHs in energy metabolism, a condition now being commonly found under anaerobic conditions. These are unique reactions, because the microorganisms use CAHs as electron acceptors just as aerobic organisms use oxygen. This in turn requires a suitable electron donor such as hydrogen or organic compounds. Transformations that are likely to occur in ground water 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 likely conditions 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:

$$C = C_o e^{-kt} \qquad \text{(Eq. 3)}$$

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 (k_{TCA}) is equal to the sum of the individual rate constants ($k_{DCE} + k_{HAc}$). The transformation rate constants are functions of temperature:

$$k = Ae^{-E/0.008314K} \qquad \text{(Eq. 4)}$$

where A and E are constants and K is the temperature in degrees Kelvin. Table 1 lists A and E values for TCA abiotic transformation reported by various investigators, as well as 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	3
6.31 $(10)^{20}$	119.3	0.060	0.145	0.34	4
1.56 $(10)^{20}$	116.1	0.058	0.137	0.31	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 is of great significance, however, because 1,1-DCE is considered more toxic than TCA, with an MCL of 7 micrograms per liter (µg/L) compared with TCA's MCL of 200 µg/L. 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.

CA, 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 harmless products (6).

Biological Transformation

CAHs can be oxidized or reduced, generally through co-metabolism, as noted in Table 2. In ground water, 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. Co-metabolic aerobic transformation of TCE is also possible, although if it did occur the intermediate products formed are unstable and more difficult, analytically, to measure. Thus, convincing evidence for the latter is more 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 not likely to occur often, natural attenuation by aerobic co-metabolism of TCE is probably of little significance.

Ample evidence suggests that anaerobic reductive transformation of CAHs occurs frequently, however, and this process is of importance 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 is often the case in aquifers. Indeed, the extent to which reductive dehalogenation occurs may be limited by the amount of these co-contaminants present. Theoretically, it would require only a 0.4-gram chemical oxygen demand (COD) equivalent of primary substrate to convert 1 gram of PCE to ethene (7), but many times more than this is actually required because of competition by other microorganisms for the electron donors present.

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 complete reduction to ethane. Table 3

Table 2. Conditions for Biotic and Abiotic Transformations of Chlorinated Solvents

	Carbon Tetrachloride (CTC)	Trichloroethene (PCE)	Tetrachloroethene (TCE)	1,1,1-Trichloroethane (TCA)
Biotic—Aerobic				
Primary substrate	No	No	No	No
Co-metabolism	No	No	Yes	Perhaps
Biotic—Anaerobic				
Primary substrate[a]	Perhaps	Yes	Yes	Perhaps
Co-metabolism	Yes	Yes	Yes	Yes
Hazardous intermediates	Yes	Yes	Yes	Yes
Abiotic	Perhaps	No	No	Yes

[a] Can be used as electron acceptor in energy metabolism.

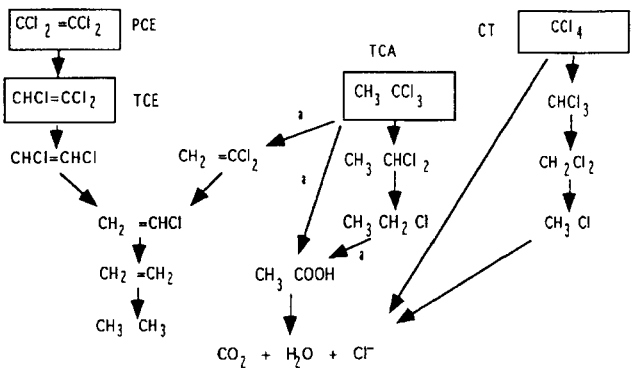


Figure 1. Anaerobic chemical and biological transformation pathways for chlorinated solvents.

indicates that while some transformations, such as that of CT to CF and carbon dioxide, may take place under mildly 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 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 all of the oxygen, nitrate, nitrite, and sulfate present. Some organics will be required to reduce the CAHs, and perhaps iron(II) as well, if present in significant amounts. If the potential for natural biological attenuation of CAHs is to be evaluated, then the concentrations of nitrate, nitrite, sulfate, iron(II), and methane, as well as organics as indicated by COD or total organic carbon (TOC), should be determined. Unfortunately, such analyses are not considered essential in remedial investigations—they should be.

Several pure cultures of microorganisms are now available that can also reduce PCE to cis-DCE (10-14). Only one has been reported that can convert PCE completely to ethene (15). Most of the isolates are strict anaerobes and use hydrogen as an electron donor, with CAHs being used as electron acceptors in energy metabolism. One isolate, however, is a facultative aerobe (14) that can use many organics, such as acetate, as the electron donor and oxygen, nitrate, PCE, or TCE as electron acceptors, which it does in that order of preference. It is now believed that the CAH reducers compete for the hydrogen they use, which is formed as an intermediate in anaerobic organic oxidation, with sulfate reducers, methanogens, and holoacetogens (16). This may explain the excessive donor requirements for CAH reduction.

Concerns are frequently expressed over the VC formed as an intermediate in reductive dehalogenation of PCE, TCE, and DCE in ground water, because VC is a known human carcinogen. It is possible to oxidize VC aerobically, however, with oxygen as an electron acceptor or even under anoxic conditions with iron(III) (17). In addition, VC is readily and very efficiently co-metabolized aerobically by methane, phenol, or toluene oxidizers (18, 19). Here, transformation yields of over 1 gram of VC per gram of methane have been obtained. Thus, at the aerobic fringes of plumes with methane and VC present, or where sufficient iron(III) is present, natural attenuation of VC through oxidation can occur.

Case Studies

Major et al. (20) reported field evidence for intrinsic bioremediation of PCE to ethene and ethane at a chemical transfer facility in North Toronto. In addition to high concentrations of PCE (4.4 milligrams per liter [mg/L]), high concentrations of methanol (810 mg/L) and acetate (430 mg/L) were found as co-contaminants in the ground water and served as electron donors for the transforming organisms. Where high concentrations of PCE were 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). At one downgradient well, however, no PCE or TCE were 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. Microcosm studies also suggested 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 the presence of suitable redox conditions for the transformation.

Fiorenza et al. (21) reported on PCE, TCE, TCA, and dichloromethane (DCM) contamination of ground water at a carpet backing manufacturing plant in Hawkesbury, Ontario. The ground water contained 492 mg/L of volatile

Table 3. Environmental Conditions for 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^-
Tetrachloroethene			PCE → 1,2-DCE	PCE → ethene
Trichloroethene			TCE → 1,2-DCE	TCE → ethene

fatty acids and 4.2 mg/L of methanol, organics that appeared to serve as electron donors for dehalogenation. Sulfate 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 above the upgradient concentration of 2.1 mg/L. Methane was present. This supports conditions suitable for natural biodegradation of the chlorinated solvents. While some chemical transformation of TCA to 1,1-DCE was indicated (0.4 mg/L) biotransformation was 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 because the cis-DCE, VC, and ethene concentrations were 56, 4.2, and 0.076 mg/L, respectively. Only traces of ethane were found. 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 natural attenuation exists for this site, the ethene and ethane concentrations were low compared with the 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 fermentation exists. A summary by McCarty and Reinhard (22) of data from Charnley et al. (23) reported average gaseous concentrations in parts per million by volume from eight refuse landfills as 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 high VC concentration 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, 24-27). Ground-water concentrations of TCE as high as 100 mg/L were found, 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 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 (25). Through more extensive analysis of ground water further downgradient from the contaminating source, Wilson et al. (26) found a 24-fold reduction in CAHs across the site. The great extent of aerobic co-metabolic VC transformation in the methane present suggests that aerobic oxidation at the plume fringes is likely to be occurring (18). 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.

Since the above early reports, many others have reported on the natural biological attenuation of CAHs in ground water, all showing conversion of PCE, TCE, or TCA to nonchlorinated end points (28-31). Whether complete dehalogenation is likely to occur over time at these sites is still not clear. Review of this literature by the reader interested in these processes is recommended.

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AEROBIC { O_2

ANAEROBIC { NO_3^- DENITRIFICATION
SO_4^{2-} SULFATE REDUCTION
CO_2 METHANOGENISIS

Microbiological Aspects Relevant to Natural Attenuation of Chlorinated Ethenes

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Introduction

Chlorinated ethenes are widely employed as solvents in civilian and military applications. They are excellent degreasing agents, nearly inflammable, and noncorrosive, and in most applications they do not pose an acute toxicological hazard. Not surprisingly, tetrachloroethene (PCE) and the less-chlorinated ethenes produced from it via reductive dehalogenation—trichloroethene (TCE), dichloroethene (DCE) isomers, and vinyl chloride (VC)—have become common ground-water pollutants, often present as co-contaminants with fuel-derived pollutants such as benzene, toluene, ethylbenzene, and xylenes (BTEX).

Results from many field and laboratory studies have shown that chlorinated ethenes can be sequentially, reductively dechlorinated under anaerobic conditions, ultimately yielding ethene, which is environmentally acceptable (1, 2). The process requires some form of electron donor (shown in Figure 1 as 2[H] per step), with the chlorinated ethene serving as electron acceptor. Since most significantly contaminated subsurface environments are indeed anaerobic, reductive dechlorination to ethene offers promise that natural attenuation may be exploited in many instances of contamination by chlorinated ethenes. The completeness of the conversion to ethene is highly variable from site to site, however, with the responsible factors for this variation not well understood.

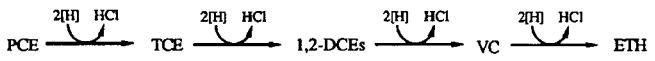

Figure 1. Reductive dechlorination of chlorinated ethenes (under anaerobic conditions).

This paper presents some of the microbiological factors that the authors believe influence the natural attenuation of chlorinated ethenes.

Co-metabolic Versus Direct Dechlorination

Many of the early observations of reductive dechlorination of PCE and TCE were studies in which the mediating microorganisms were either obviously methanogens (e.g., the pure-culture studies of Fathepure et al. [3-5]) or likely so. Many classes of anaerobic organisms (e.g., methanogens, acetogens, and sulfate reducers) have been found to possess metal-porphyrin-containing cofactors that can mediate the slow, incomplete reductive dechlorination of PCE and TCE to (usually) DCE isomers (6). This process is co-metabolic in that it happens more or less accidentally or incidentally as the organisms carry out their normal metabolic functions; the organisms apparently derive no growth-linked or energy-conserving benefit from the reductive dechlorination. Such co-metabolic dechlorinations undoubtedly are responsible for the incomplete, relatively slow transformations of chloroethenes observed at many field sites. The organisms that can mediate such processes are ubiquitous, but the process is sufficiently slow and incomplete that a successful natural attenuation strategy cannot completely rely upon it.

On the other hand, more recent studies have demonstrated the existence of direct dechlorinators—microorganisms derived from contaminated subsurface environments and treatment systems—that utilize chlorinated ethenes as electron acceptors in an energy-conserving, growth-coupled metabolism termed *dehalorespiration* (7). Several species that carry out direct dechlorination of chlorinated ethenes are described below.

To a large extent, then, success or failure of natural attenuation can be linked to the specific type of dechlorinator present (i.e., co-metabolic or direct), as well as to the relative supply of H_2 precursors compared with the supply of chlorinated ethene that must be reduced.

Competitive Aspects of Dechlorination

Unfortunately, many users compete for H_2 in anaerobic microbial environments. For example, direct dechlorinators must compete for available H_2 with hydrogenotrophic methanogens and sulfate reducers. Thus, in any comprehensive, meaningful assessment of prospects for natural attenuation, assessing only the nature of the dechlorinators and the quantities of available donors and chlorinated ethenes is insufficient; one must also take into account competing demands for H_2.

Because of the relatively high energy available from reductive dechlorination, it is reasonable to suspect that dechlorinators may out-compete methanogens for H_2 at very low H_2 levels. Experimental evidence for this comes from studies in which lactate was the administered electron donor, supplying H_2 as it was rapidly fermented to acetate. During the period of high H_2 levels, methane production co-existed with dechlorination. As lactate was depleted, H_2 production waned, and H_2 levels dropped to low levels; beyond this point, methane production was negligible while dechlorination continued slowly. In fact, kinetic analysis of mixed cultures of *Dehalococcus ethenogenes* and hydrogenotrophic methanogens showed that this dechlorinator has an affinity for H_2 10 times greater than that of the methanogens in the culture (8). We do not know whether this high affinity for H_2 is typical of dechlorinators, but thermodynamic arguments would suggest it. We also do not yet know the differences in relative affinity for H_2 between dechlorinators and sulfate-reducers, important competitors in many subsurface environments.

Competition for H_2 is thus important, and the partitioning of H_2 flows among the various competitors is a function of the H_2 concentration, which itself depends on the rates of H_2 production and utilization. Compounds such as lactate or ethanol that can be rapidly fermented to acetate, producing high, short-lived peaks of H_2, do not favor dechlorination as well as would more persistent, slowly fermented substrates such as benzoate or propionate (and by extension, probably BTEX components). The *quality* of the donor needs to be considered as much as does its quantity. Comprehensive assessment are best performed with microcosm studies, along with microbiological analyses of in situ relative populations of competing organisms and data on subsurface chemistry (particularly of potentially competing electron acceptors).

Microbiology of Direct Dechlorinators

As summarized in Table 1, several organisms have recently been isolated that can carry out direct respiratory reductive dechlorination of chloroethenes. All of these organisms have been isolated since 1993, and several more will likely be added to the list in the next few years. A few tentative conclusions may be drawn from this table. First, organisms that reduce PCE as far as *cis*-DCE are relatively abundant and easier to culture. This ability seems to have evolved in several different phylogenetic groups in the eubacteria, as determined by 16S rRNA sequence analysis. Many direct dechlorinators seem to be related to either the gram-negative sulfate-reducing bacteria (epsilon proteobacteria) or the gram-positive group, including *Desulfotomaculum*. Sulfate reducers

Table 1. Properties of Some Direct PCE Dechlorinators

Organism	Dechlorination Reactions	Electron Donors	Other Electron Acceptors	Morphology	Phylogenetic Position	References
Dehalobacter restrictus	PCE, TCE → *cis*-DCE	H_2	None	Rod	Gram + *Desulfotomaculum* group	9-11
Dehalospirillum multivorans	PCE, TCE → *cis*-DCE	H_2, formate, pyruvate, etc.	Thiosulfate, nitrate, fumarate, etc.	Spirillum	Epsilon proteobacteria	12
Strain TT4B	PCE, TCE → *cis*-DCE	Acetate	None	Rod	?	13
Enterobacter agglomerans	PCE, TCE → *cis*-DCE	Nonfermentable substrates	O_2, nitrate, etc.	Rod	Gamma proteobacteria	14
Desulfitobacterium sp. strain PCE1	PCE, TCE → (*cis*-DCE) o-chlorophenols	Lactate, pyruvate, butyrate, ethanol, etc.	Sulfite, thiosulfate, fumarate	Curved rod	Gram + *Desulfotomaculum* group	15
Dehalococcus ethenogenes strain 195	PCE, others → ethene	H_2	None	Irregular coccus	Novel eubacterium	16[a]

[a] Maymó-Gatell, X., Y.-T. Chien, J.M. Gossett, and S.H. Zinder. 1996. Isolation of a novel bacterium capable of reductively dechlorinating tetrachloroethene to ethene. Unpublished data.

tend to be versatile at using electron acceptors for anaerobic respiration. We know much less about organisms capable of reducing chloroethenes past DCE. These organisms play a crucial role in either producing VC, which is degradable aerobically and under ferric iron-reducing conditions, or ethene, which is nontoxic.

Some PCE-dechlorinating organisms appear versatile at using electron donors and acceptors, while others, most notably "*Dehalobacter restrictus*." "*D. ethenogenes*," and strain TT4B apparently can only use a single electron donor and only chlorinated aliphatic hydrocarbons as electron acceptors. These findings raise questions about what these organisms used as electron acceptors before widespread chlorinated ethene contamination. The organisms possibly use electron acceptors not yet tested, or may once have been more versatile but lost the ability to use other electron acceptors in chlorinated ethene-contaminated environments or when cultured on PCE as the sole electron acceptor.

Another important aspect of the PCE direct dechlorinators that Table 1 does not address is their nutrition. Some PCE dechlorinators, such as *Dehalospirillum multivorans*, require only acetate and carbon dioxide as a carbon source (PCE and its daughter products are not carbon sources), while others have a complex nutrition, such as *D. ethenogenes*, which requires acetate, vitamin B_{12}, unidentified factors in sewage sludge (16), and perhaps other factors. Indeed, this organism's requirement for vitamin B_{12} allowed a plausible explanation for methanol's being the best H_2-source for PCE dechlorination by the original mixed dechlorinating culture (17), since methanol-utilizing methanogens and acetogens are rich in vitamin B_{12} and related corrinoid compounds. A butyrate-fed bioreactor faltered until it was amended with vitamin B_{12} (18), which is not present in yeast extract and apparently is in low concentrations in the butyrate-oxidizing consortium present in that bioreactor.

The Importance of Assessing the Big Picture

This paper has attempted to address some of the microbial complexities of assessing natural attenuation potential. It is important to keep in mind the competitive aspects of electron donor flow. In essence, dechlorination is in a "foot race" with competing donor uses. If too little donor is initially present, the pattern of its conversion to H_2 is too unfavorable, or there is too much competition for it, dechlorination may not proceed adequately to completion. As other papers in this volume suggest, relying on reductive dechlorination to achieve complete conversion to ethene may not be necessary in all cases; for example, some aerobic and iron-reducing microbial processes can oxidize/mineralize VC. Therefore, conversion of PCE and TCE to VC by the time a plume reaches an aerobic or iron-reducing zone may be sufficient in many instances.

More problematic are situations in which degradation proceeds only as far as DCEs. At some sites, there may not be enough electron donor present. At other sites, a sufficient amount of potential electron donors appear to be present, and it is unclear whether further dechlorination is limited by physical/chemical factors, nutrients, or lack of the appropriate dechlorinating organisms. Particularly troubling are sites in which PCE, TCE, and DCEs reach aerobic zones in which they are essentially nondegradable under natural conditions. Unfortunately, our present understanding of the diversity and properties of organisms dechlorinating chlorinated ethenes past DCEs is rudimentary.

In summary, the goal of assessment should be to evaluate the potential for *sustained* conversion to at least VC in anaerobic zones. Comprehensive assessment thus requires knowledge of both the quantity and quality of the electron donor, of competing, alternative electron acceptors (e.g., sulfates, ferric iron), and of relative population levels of dechlorinating organisms and potentially competing microbial activities.

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Microbial Ecology of Adaptation and Response in the Subsurface

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Introduction

The release of bio-oxidizable organic contaminants into the subsurface and ground water quickly drives the local environment anoxic and initiates a series of complex and poorly understood responses by subsurface microorganisms. Field and laboratory research suggests that multiple, physiologically defined communities develop that are spatially and chronologically separate. These communities are most likely ecologically defined by the flux of biologically available electron donors and acceptors. Under anaerobic conditions most organics continue to degrade although the apparent rate may be slower. Some contaminants may not be oxidatively catabolized, however, due to thermodynamic limitations, lack of genomic potential, or physical/chemical properties.

The parent chloroethenes—tetrachloroethene (PCE) and trichloroethene (TCE)—are all too common examples of this type of ground-water contaminant. While PCE and TCE do not seem to serve as carbon/energy sources for subsurface bacteria, they can be reductively biotransformed. These microbially mediated, naturally occurring transformations (both oxidative and reductive) of subsurface and ground-water contaminants have been observed at many sites and hold significant potential for use as in situ remediation methods as the basis for active or passive biotreatment technologies. While these processes are observable and in some cases have been demonstrated as remedial technologies, however, our ability to predict the onset, extent, and rates of transformation is limited. This lack of predictive ability is more pronounced under anaerobic or intrinsic conditions, and is extremely limited when reductive transformations are the target processes. Little is known about the environmental parameters, microbial interactions, and metabolic responses that control these degradation processes in the subsurface.

A more complete understanding of the ecological and physiological factors is needed for accurate and appropriate predictions and evaluations, particularly for in situ transformation processes under intrinsic (native) conditions, where engineered approaches are not available to influence or dominate in situ hydrogeochemical conditions. Under "native" conditions, the heterogeneity of the site may also have a profound effect on the fate of the contaminants. An understanding of the three-dimensional distribution of geochemical and hydraulic conditions is important for evaluating the contaminant interactions with the subsurface microbial ecology. To evaluate the likelihood of contaminant transformation, it is necessary to have some understanding of the physiology of microorganisms in the subsurface and of the ecological constraints that effect biological processes in that environment.

Metabolic Principles

Heterotrophic organisms (like humans and most bacteria) oxidize organic compounds to obtain energy. In this process electrons, or reducing equivalents, from the oxidizable organic compound (substrate) are transferred to and ultimately reduce an electron acceptor. The electron acceptor may be an organic or inorganic compound. During this electron transfer process, usable energy is recovered through a complex series of oxidation-reduction (redox) reactions by the formation of energy storage compounds or electrochemical gradients. The oxidation of organic compounds coupled with the reduction of molecular oxygen is termed aerobic heterotrophic respiration and has been the basis of most applications of bioremediation.

When oxygen is unavailable, biotransformations can still occur. In anaerobic respiration, the oxidation of organic matter can be coupled with a number of other organic or inorganic electron acceptors. Some microorganisms carry out a process known as fermentation. Fermenting microorganisms utilize substrates as both an electron donor and an electron acceptor. In this process, an organic compound is metabolized, with a portion of molecule becoming a reduced end product(s) and another becoming an oxidized end product(s). A common example of this process is the alcoholic fermentation of starch to carbon dioxide (CO_2) (oxidized product) and ethanol (reduced product). Fermentative organisms play a critical role in anaerobic consortia by transforming organic substrates into simple products which can then be used by other members of the community, such as dehalgenators, for further oxidation.

The potential energy available from the oxidation of a particular substrate when coupled with the reduction of different electron acceptors varies considerably. A higher energy-yielding process will tend to predominate if the required electron acceptor is available at biologically significant concentrations (i.e., oxygen utilized before nitrate). Under anaerobic conditions, microorganisms may enter into very tightly linked metabolic consortia. That is, the catalytic entity responsible for the destruction of a contaminant is often not a single type of microorganism. Such consortia can develop regardless of the nature of the terminal electron acceptor.

As a class, the chloroethenes offer a diverse array of metabolic fates. The parent compounds PCE and TCE have been shown to undergo reductive transformations in subsurface systems under the appropriate environmental conditions. This reductive transformation process, referred to as reductive dechlorination or biodehalogenation, is a sequential removal of chlorine moieties from the ethene core during a biologically mediated two-electron transfer. Microorganisms in the subsurface and other environments use the chloroethenes as terminal electron acceptors and gain useable metabolic energy by linking the oxidation of electron donors such as molecular hydrogen or organic compounds to the reduction of chloroethenes. The exact mechanism of this type of anaerobic respiration and the enzymes and co-factors involved have yet to be identified. It is important to note that the reductive dechlorination process only supplies useable metabolic energy if coupled to the oxidation of an appropriate electron donor.

TCE, dichloroethenes (DCEs), and vinyl chloride have been shown to undergo co-metabolic oxidative transformations. By definition, co-metabolic process do not directly benefit the organisms buy supplying energy or material for cellular synthesis. The mono-oxygenase systems that transform chloroethenes may be inactivated during the process (competitive inhibitor). For the co-metabolic process to occur, the true parent substrate for the mono-oxygenase system and chloroethenes must be present, as well as molecular oxygen. This activity has been demonstrated as an active biotreatment process, but it is of limited significant under native or intrinsic conditions because of the anticompetitive effects on the microorganisms involved and the environmental conditions needed for significant transformation to occur.

The lesser-chlorinated DCEs can be reductively transformed, and a growing body of evidence suggests that they may be oxidatively catabolized with oxygen or other electron acceptors. Vinyl chloride (monochloroethene) is regarded as the most hazardous of the chloroethene series. A known carcinogen, vinyl chloride is more mobile than the parent compounds and is extremely volatile. Due to its toxicity, when vinyl chloride is detected in the subsurface environment with the other chloroethenes, it is usually the focus of risk-based evaluations and drives the cleanup process. Vinyl chloride can be reductively modified to the nonchlorinated and environmentally acceptable end product ethene. It can also be oxidatively catabolized to CO_2 and Cl^- under aerobic and iron-reducing conditions.

Ecological Principles

The subsurface environment is a unique and underappreciated ecosystem. The appropriate application of intrinsic remediation at a site requires an understanding of the ecological processes under site-specific conditions. Subsurface microorganisms will respond to take advantage of all available resources (i.e., energy, nutrients, space) that allow them to survive and reproduce. This response is bounded by evolutionary, physical, and thermodynamic constraints, but in general we see that microorganisms (and life in general) rapidly take advantage of resources and conditions. This concept is referred to as filling all available ecological niches. The converse statement is also true, however: subsurface microorganism do not respond in ways that are counterproductive to this competition for resources and survival. This beguilingly simple concept is often overlooked in the design and implementation of bioremediation.

The nature of the subsurface environment (i.e., its lack of primary production) makes it useful to view subsurface (microbial) ecology in terms of energy transformation and transfer. Under intrinsic conditions, bioavailable energy is the ecological resource that induces the observed biodegradation process. As noted earlier, the transfer or harvesting of this resource by subsurface microorganisms involves oxidation/reduction couples available to subsurface microorganisms. Under pristine conditions, energy transduction in ground-water environments is limited by the availability of carbon/energy sources (electron donors). Energy transduction in contaminated

subsurface systems is usually limited by the availability of the electron acceptor. When readily degradable organic matter enters the subsurface in sufficient quantities, it produces a series of zones defined by the terminal electron accepting process (TEAP). These zones are not necessarily mutually exclusive and depend on the availability of electron acceptors (O_2, NO_3=, SO_4=, Fe^{3+}, CO_2). There is no reason to assume a similarity between the biodegradation potential in different metabolic zones. This potential will be based on the energetics associated with the dominant redox processes, the metabolic diversity of the microbial communities, the immediate geochemical conditions, and the chemical nature of the contaminant of concern.

The reductive dehalogenation process may be thought of as another TEAP, and the microorganisms involved compete for the available flow of energy (reducing equivalents). As noted above, however, PCE or TCE, in the absence of sufficient electron donors such as an oxidizable co-contaminant or native organic matter, does not represent a resource to the indigenous microorganisms. This is why PCE and TCE plumes with detectable levels of dissolved oxygen do not show evidence of active biodegradation. The presence of dissolved oxygen indicates no significant quantities of oxidizable electron donor are present. Vinyl chloride (and perhaps DCEs) under the same conditions may undergo further transformation, however, if appropriate electron acceptors such as O_2 or Fe^{3+} are present. Under these conditions, the oxidation of vinyl chloride represents a resource (energy) to the subsurface microbial populations.

Mechanisms of Adaptation

While an understanding of the ecological processes is useful in predicting whether a transformation is likely to occur, an understanding of the adaptation processes' mechanisms is needed to predict the onset of the degradation activity. Possible mechanisms of adaptation include expression of catabolic potential (induction), selection of novel capabilities (mutation), growth of degradative populations, formation of degradative consortia, and formation of metabolic intermediate pools. Laboratory research results indicate that the formation of catabolically competent consortia could be a limiting step in the observed lag before the onset of degradation. Historical exposure and total microbial mass did not significantly affect the observed lag but did affect transformation rates. Environmental parameters that support anaerobic microbial transformation processes (both oxidative and reductive) positively affected the observed adaptation response. While more work is needed, these preliminary observations offer some explanations for varying field observations and suggest that clearer understanding of the mechanisms involved may lead to greater predictive capabilities.

Conclusion

Biotransformations that serve as major mass removal mechanisms for the intrinsic remediation of chloroethenes and other ground-water contaminants have been demonstrated in the laboratory and the field. The use of these processes as remedial technologies, however, is difficult to evaluate at field scale, which limits our ability to predict the rate and extent of the degradation of contaminants in complex, heterogeneous subsurface environments. An understanding of the physiology and ecology of subsurface microorganisms is one of the few tools regulators and scientists have to evaluate the appropriate implementation of intrinsic remediation for chloroethene sites. A greater understanding of the mechanisms of adaptation in subsurface microbial communities could also prove to be useful in the appropriate application of in situ bioremediation under active or intrinsic conditions.

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Identifying Redox Conditions That Favor the Natural Attenuation of Chlorinated Ethenes in Contaminated Ground-Water Systems

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Introduction

Over the last several years, it has been demonstrated that petroleum hydrocarbons biodegrade in virtually all ground-water systems (1), and that natural attenuation can greatly reduce the transport of contaminants away from particular hydrocarbon spills (2, 3). These results have raised the prospect that chlorinated ethenes—perchloroethene (PCE), trichloroethene (TCE), dichloroethenes (DCEs), and vinyl chloride (VC)—will prove similarly amenable to natural attenuation processes. The microbial processes leading to biodegradation of chlorinated ethenes, however, can be much different from those that degrade petroleum hydrocarbons. Petroleum hydrocarbons universally serve as *electron donors* (i.e., as an energy source) in microbial metabolism. In contrast, chlorinated ethenes, in addition to serving as electron donors, can function as *electron acceptors* (i.e., they are reduced via reductive dechlorination) or can be fortuitously degraded by various co-metabolic processes. Because of this diversity, it is not surprising that the efficiency with which chlorinated ethenes are naturally attenuated varies widely among ground-water systems.

Under anoxic conditions, chlorinated ethenes are subject to reductive dechlorination according to the sequence PCE $\rightarrow$ TCE + Cl $\rightarrow$ DCE + 2Cl $\rightarrow$ VC + 3Cl $\rightarrow$ ethylene + 4Cl (1). The *efficiency* of dechlorination, however, appears to differ under methanogenic, sulfate-reducing, iron(III)-reducing, and nitrate-reducing con- ditions. Dechlorination of PCE and TCE to DCE is favored under mildly reducing conditions such as nitrate or iron(III) reduction (4), whereas the transformations of DCE to VC or of VC to ethylene seems to require the more strongly reducing conditions of methanogenesis (5-7). Further complicating this picture, lightly chlorinated ethenes such as VC can be oxidized under oxic (8) or iron(III)-reducing conditions (9), and by various co-metabolic degradation processes (10).

Clearly, an accurate delineation of redox conditions is central to evaluating the potential for the natural attenuation of chlorinated ethenes in ground-water systems. This paper summarizes a methodology for identifying the zonation of redox conditions in the field. This methodology can serve as an a priori screening tool for identifying ground-water systems in which redox conditions will favor natural attenuation of chlorinated ethenes. Conversely, this methodology can identify systems for which natural attenuation of chlorinated ethenes is not favored and other remediation technologies should be considered.

Methodology for Determining Redox Processes in Ground-Water Systems

Platinum electrode redox potential measurement historically has been the most widely used method for determining redox conditions in ground-water systems. While redox potential measurements can accurately distinguish oxic from anoxic ground water, they cannot distinguish between different anoxic processes such as nitrate reduction, iron(III) reduction, sulfate reduction, or methanogenesis. One reason is that many redox species, such as hydrogen sulfide (H_2S) or methane (CH_4), are not electroactive on platinum electrode surfaces (11). Because distinguishing between these processes is critical to evaluate the natural attenuation of chlorinated ethenes, redox potential measurements alone cannot provide the needed information.

A different methodology, which is based on microbial physiology, has recently been introduced for delineating redox processes (12-14). This method relies on three lines of evidence: the consumption of electron acceptors, the production of metabolic end products, and the measurement of concentrations of transient intermediate

products. Molecular hydrogen (H_2), the most ubiquitous intermediate product of anaerobic microbial metabolism, has proven to be especially useful in this context. Different electron-accepting processes have characteristic H_2-utilizing efficiencies. Nitrate reduction, the most energetically favorable anoxic process, maintains H_2 concentrations below 0.1 nanomoles (nM) per liter. Iron(III) reduction maintains H_2 concentrations between 0.2 and 0.8 nM, whereas for sulfate reduction the characteristic range is between 1 and 4 nM. Methanogenesis, the least energetically favorable anoxic process, is characterized by H_2 in the 5 to 15 nM range.

Patterns of electron-acceptor consumption, final product accumulation, and H_2 concentrations can be combined to logically identify redox processes (13). For example, if sulfate concentrations are observed to decrease along an aquifer flowpath, if sulfide concentrations are observed to increase, and if H_2 concentrations are in the 1 to 4 nM range characteristic of sulfate reduction, it may be concluded with a high level of confidence that sulfate reduction is the predominant redox process. If all three possible indicators (electron acceptor consumption, end-product production, and H_2 concentrations) indicate the same redox process, a high degree of confidence in the delineation is warranted. Conversely, if only one indicator is available, or if lines of evidence conflict, proportionally less confidence in the redox delineation is warranted.

Measuring Hydrogen Concentrations in Ground Water

With the exception of dissolved hydrogen (H_2), all of the redox-sensitive parameters (dissolved oxygen, nitrate, nitrite, ferrous iron [Fe^{2+}], H_2S, sulfate, and methane) needed to assess redox processes are routinely examined in ground-water chemistry investigations. Hydrogen concentrations in ground water can be made using a gas-stripping procedure (13). A standard gas-sampling bulb is attached to a stream of water produced from a well and purged for several minutes (at approximately 500 milliliters/minute) to eliminate all gas bubbles. Next, 20 milliliters of nitrogen, made H_2-free by passage through a hopcalite column, is introduced to the bulb through a septum. As water continues to purge the bulb, H_2 and other slightly soluble gases partition to the headspace and asymptotically approach equilibrium with the dissolved phase. After 20 to 25 minutes, equilibrium is achieved, and the gas bubble is sampled using a syringe. A duplicate sample is taken 5 minutes later. H_2 is then measured by gas chromatography with reduction gas detection. Concentrations of aqueous H_2 are then calculated from H_2 solubility data. For fresh water in equilibrium with a gas phase at 1 atmosphere pressure, 1.0 parts per million H_2 in the gas phase corresponds to 0.8 nM of dissolved H_2.

An Example of Redox Zone Delineation Related to the Natural Attenuation of Chlorinated Ethenes—Cecil Field, Florida

An example of how redox processes can be delineated, and how this delineation affects assessment of natural attenuation of chlorinated ethenes, is a study performed by the U.S. Geological Survey in cooperation with the U.S. Navy at Site 8, Naval Air Station (NAS) Cecil Field. Site 8 was a fire-training area used to train Navy personnel in firefighting procedures (Figure 1). Over the operational life of Site 8, a variety of petroleum products and chlorinated solvents seeped into the underlying ground-water system.

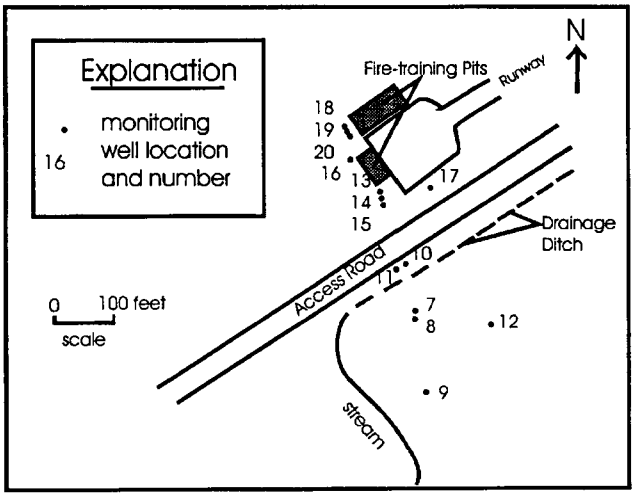

Figure 1. Map showing location of fire-training pits and monitoring wells, Site 8, NAS Cecil Field, Florida.

Changes in the concentrations of redox-sensitive constituents along the flowpath of the shallow aquifer system are shown in Figure 2. Ground water at the site is oxic upgradient of the fire pits but becomes anoxic downgradient of the fire pits (Figure 2A). Once the water becomes anoxic, concentrations of methane begin to rise, peaking at about 7 milligrams per liter 200 feet downgradient (Figure 2A) and indicating methanogenic conditions. Between 170 and 400 feet downgradient, concentrations of sulfate decrease and concentrations of H2S increase (Figure 2B), indicating active sulfate reduction. Concentrations of dissolved Fe2+ remain below 1 mg/L until about 400 feet along the flowpath, then increase to about 2.5 mg/L, indicating active iron(III) reduction. The H2 concentrations are consistent with the redox zonation indicated by the other redox-sensitive parameters (Figure 2C). H2 concentrations in the range characteristic of methanogenesis are observed in ground water near the fire-training pits where high methane concentrations are present.

Between 200 and 170 feet downgradient, where sulfate concentrations decline and sulfide concentrations in-

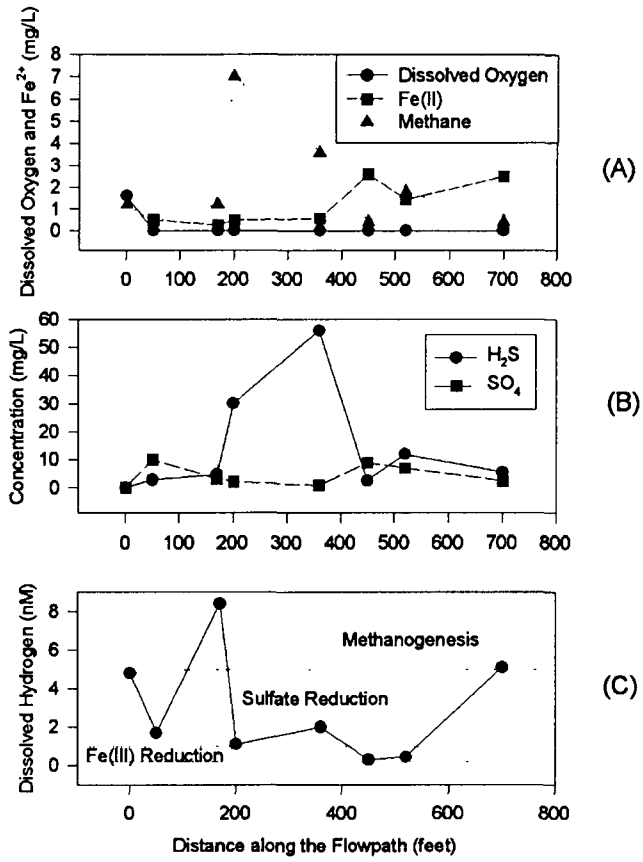

Figure 2. Concentration changes of redox-sensitive parameters along ground-water flowpaths in the shallow aquifer, Site 8, NAS Cecil Field, Florida.

crease, H_2 concentrations are in the 1 to 4 nM range characteristic of sulfate reduction. Finally, between 400 and 500 feet downgradient, where concentrations of Fe^{2+} increase, H_2 concentrations are in the 0.2 to 0.8 nM range characteristic of iron(III) reduction.

A cross section showing the interpretation of these data and including wells screened deeper in the flow system is given in Figure 3. A methanogenic zone is present near the contaminant source, surrounded by sulfate-reducing and iron(III)-reducing zones further downgradient. This redox zonation suggests that the natural attenuation of chlorinated ethenes will be rapid and efficient at this site. Near the contaminant source, methanogenic and sulfate-reducing zones favor dechlorination of PCE, TCE, and DCE. In the downgradient iron(III)-reducing zone, anoxic oxidation of VC to carbon dioxide (CO_2) can occur (Figure 3).

These biodegradation processes, which can be postulated solely on the basis of the observed redox zonation, are consistent with the observed behavior of chlorinated ethenes at this site (Figure 4A). PCE, TCE, and VC are present in ground water near the fire-training pits but drop below detectable levels along the flowpath. In fact, natural attenuation of chlorinated ethenes at this site has

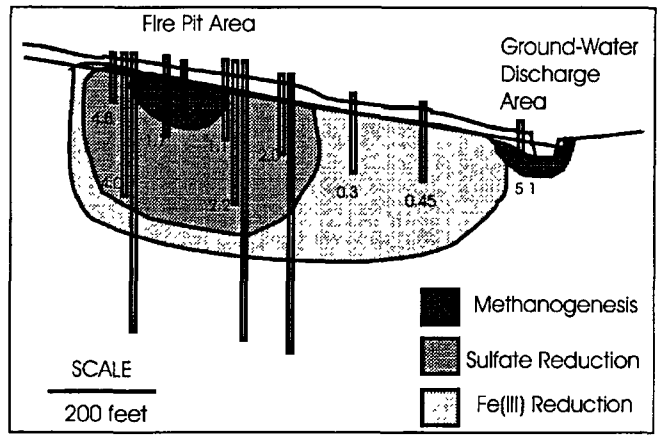

Figure 3. Concentrations of dissolved hydrogen (nM) and the zonation of predominant redox processes, Site 8, NAS Cecil Field, Florida.

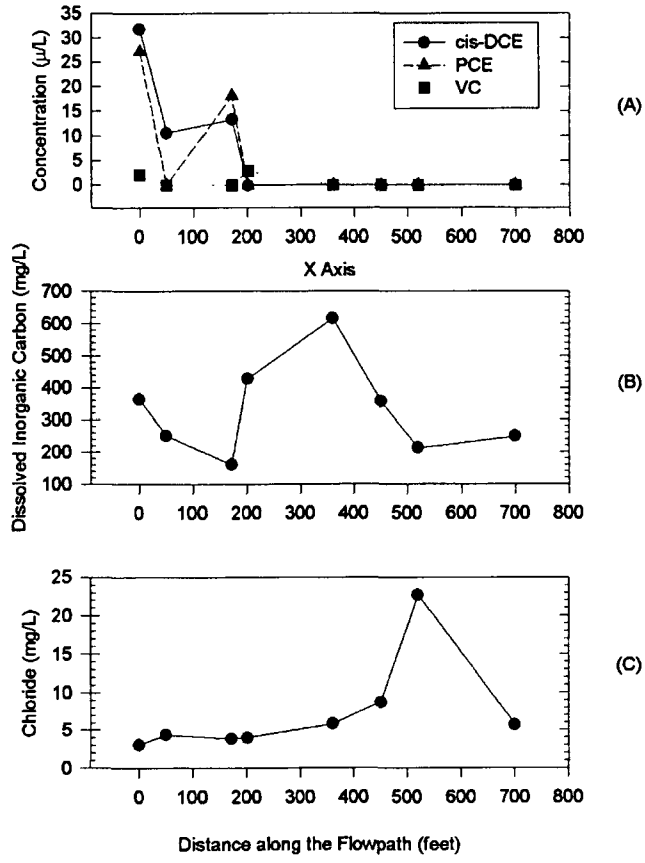

Figure 4. Concentration changes of chloride, dissolved inorganic carbon, and chlorinated ethenes along ground-water flowpaths.

been so efficient that the best water-chemistry record of the original contamination is probably the elevated concentrations of dissolved inorganic carbon (Figure 4B) and dissolved chloride (Figure 4C) observed in downgradient ground water that currently lacks measurable chlorinated ethene contamination. These patterns suggest that most of the chlorinated ethenes have been completely transformed to CO_2 and chloride by the cumula-

tive effects of reductive dehalogenation in the methanogenic and sulfate-reducing zones and oxidative processes in the downgradient iron(III)-reducing and oxic zones.

Conclusion

An understanding of ambient redox conditions is a powerful tool for assessing the efficiency of natural attenuation of chlorinated ethenes. The methodology for assessing redox conditions involves tracking the disappearance of electron acceptors, the appearance of end products, and concentrations of H_2. Using this information, it is possible to logically deduce redox zonation at particular sites, and assess the confidence that is appropriate for the delineation. This methodology was demonstrated at a site at NAS Cecil Field, Florida. The progression from methanogenic → sulfate reduction → Iron(III) reduction → oxygen reduction has efficiently decreased concentrations of chlorinated ethenes, indicating that natural attenuation is a viable remedial option at this site.

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Design and Interpretation of Microcosm Studies for Chlorinated Compounds

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Introduction

Three lines of evidence are used to support natural attenuation as a remedy for chlorinated solvent contamination in ground water: documented loss of contaminant at field scale, geochemical analytical data, and direct microbiological evidence. The first line of evidence (documented loss) involves using statistically significant historical trends in contaminant concentration in conjunction with aquifer hydrogeological 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 (geochemical data) involves the use of chemical analytical data in mass balance calculations to show that decreases in contaminant concentrations can be directly correlated to increases in metabolic byproduct concentrations. This evidence can be used to show that concentrations of electron donors or acceptors in ground water are sufficient to facilitate degradation of the dissolved contaminants (i.e., there is sufficient capacity). Solute fate and transport models can be used to aid the mass balance calculations and to collate information on degradation.

Microcosm studies are often used to provide a third line of evidence. The potential for biodegradation of the contaminants of interest can be confirmed using of microcosms through comparison of removals in the living treatments with removals in the controls. Microcosm studies also permit an absolute mass balance determination based on biodegradation of the contaminants of interest. Further, the appearance of daughter products in the microcosms can be used to confirm biodegradation of the parent compound.

When To Use Microcosms

Microcosms have two fundamentally different applications. First, they are frequently used in a qualitative way to illustrate the important processes that control the fate of organic contaminants. Second, they are used to estimate rate constants for biotransformation of contaminants that can be used in a site-specific transport-and-fate model of a contaminated ground-water plume. This paper discusses the second application.

Microcosms should be used when there is no other way to obtain a rate constant for attenuation of contaminants, particularly when estimating the rate of attenuation from monitoring well data in the plume of concern is impossible. In some situations, there are legal or physical impediments to the comparison of concentrations in monitoring wells along a flow path. In many landscapes, the direction of ground-water flow (and water-table elevations in monitoring wells) can vary over short periods due to tidal influences or changes in barometric pressure. Changes in the stage of a nearby river or pumping wells in the vicinity can also affect the direction of ground-water flow. These changes in ground-water flow direction do not allow simple "snapshot" comparisons of concentrations in monitoring wells because of uncertainties in identifying the flow path. Rate constants from microcosms can be used with average flow conditions to estimate attenuation at some point of discharge or point of compliance.

Application of Microcosms

The primary objective of microcosm studies is to obtain rate constants applicable to average flow conditions. These average conditions can be determined by continuous monitoring of water-table elevations in the aquifer being evaluated. The product of the microcosm study, and the continuous monitoring of water-table elevations, will be a yearly or seasonal estimate of the extent of attenuation along average flow paths. Removals seen at field scale can be attributed to biological

activity. If removals in the microcosms duplicate removal at field scale, the rate constant can be used for risk assessment purposes.

Selecting Material for Study

Prior to choosing material for microcosm studies, the location of major conduits of ground-water flow should be identified, and the geochemical regions along the flow path should be determined. The important geochemical regions for natural attenuation of chlorinated aliphatic hydrocarbons are regions that are actively methanogenic, exhibit sulfate reduction and iron reduction concomitantly, or exhibit iron reduction alone. The pattern of chlorinated solvent biodegradation varies in different regions. Vinyl chloride tends to accumulate during reductive dechlorination of trichloroethylene (TCE) or tetrachloroethylene (PCE) in methanogenic regions (1, 2); it does not accumulate to the same extent in regions exhibiting iron reduction and sulfate reduction (3). In regions showing iron reduction alone, vinyl chloride is consumed but dechlorination of PCE, TCE, or dichloroethylene (DCE) may not occur (4). Core material must be acquired from each geochemical region in major flow paths represented by the plume, and the hydraulic conductivity of each depth at which core material is acquired must be measured. If possible, the microcosms should be constructed with the most transmissive material in the flow path.

Several characteristics of ground water from the same interval used to collect the core material should be determined, including temperature, redox potential, pH, and concentrations of oxygen, sulfate, sulfide, nitrate, ferrous iron, chloride, methane, ethane, ethene, total organic carbon, and alkalinity. The concentrations of compounds of regulatory concern and any breakdown products for each site must be determined. The ground water should be analyzed for methane to determine whether methanogenic conditions exist and for daughter products ethane and ethene. A comparison of the ground-water chemistry from the interval in which the cores were acquired with that in neighboring monitoring wells will demonstrate whether the collected cores are representative of that section of the contaminant plume.

Reductive dechlorination of chlorinated solvents requires an electron donor for the process to proceed. The electron donor could be soil organic matter, low molecular weight organic compounds (e.g., lactate, acetate, methanol, glucose), H_2, or a co-contaminant such as landfill leachate or petroleum compounds (5-7). In many instances, the actual electron donor(s) may not be identified.

Several characteristics of the core material should also be evaluated. The initial concentration of the contaminated material (in micrograms per kilogram) should be identified before constructing the microcosms. It is also necessary to determine whether the contamination is present as a nonaqueous-phase liquid (NAPL) or in solution. A total petroleum hydrocarbon (TPH) analysis will reveal the presence of any hydrocarbon-based oily materials. The water-filled porosity, a parameter generally used to extrapolate rates to the field, can be calculated by comparing wet and dry weights of the aquifer material.

To ensure sample integrity and stability during acquisition, it is important to quickly transfer the aquifer material into a jar, exclude air by adding ground water, and seal the jar without headspace. The material should be cooled during transportation to the laboratory, then incubated at the ambient ground-water temperature in the dark before the construction of microcosms.

At least one microcosm study per geochemical region should be completed. If the plume is greater than 1 kilometer in length, several microcosm studies per geochemical region may need to be constructed.

Geochemical Characterization of the Site

The geochemistry of the subsurface affects the behavior of organic and inorganic contaminants, inorganic minerals, and microbial populations. Major geochemical parameters that characterize the subsurface include alkalinity, pH, redox potential, dissolved constituents (including electron acceptors), temperature, the physical and chemical characterization of the solids, and microbial processes. The most important of these in relation to biological processes are alkalinity, redox potential, the concentration of electron acceptors, and the chemical nature of the solids.

Alkalinity

Biologically active portions of a plume may be identified in the field by their increased alkalinity (compared with background wells), caused by the carbon dioxide resulting from biodegradation of the pollutants. Increases in both alkalinity and pH have been measured in portions of an aquifer contaminated by gasoline undergoing active utilization of the gasoline components (8). Alkalinity can be one of the parameters used to identify where to collect biologically active core material.

pH

Bacteria generally prefer a neutral or slightly alkaline pH level, with an optimum pH range for most microorganisms between 6.0 and 8.0; many microorganisms, however, can tolerate a pH range of 5.0 to 9.0. Most ground waters in uncontaminated aquifers are within these ranges. Natural pH values may be as low as 4.0 or 5.0 in aquifers with active oxidation of sulfides, and pH values as high as 9.0 may be found in carbonate-buffered systems (9). pH values as low as 3.0 have been measured for ground waters contaminated with municipal

waste leachates, however, which often contain elevated concentrations of organic acids (10). In ground waters contaminated with sludges from cement manufacturing, pH values as high as 11.0 have been measured (9).

Redox Potential

The oxidation/reduction (redox) potential of ground water is a measure of electron activity that indicates the relative ability of a solution to accept or transfer electrons. Most redox reactions in the subsurface are microbially catalyzed during metabolism of native organic matter or contaminants. The only elements that are predominant participants in aquatic redox processes are carbon, nitrogen, oxygen, sulfur, iron, and manganese (11). The principal oxidizing agents in ground water are oxygen, nitrate, sulfate, manganese(IV), and iron(III).

Biological reactions in the subsurface both influence and are affected by the redox potential and the available electron acceptors. The redox potential changes with the predominant electron acceptor, with reducing conditions increasing through the sequence oxygen, nitrate, iron, sulfate, and carbonate. The redox potential decreases in each sequence, with methanogenic (carbonate as the electron acceptor) conditions being most reducing. The interpretation of redox potentials in ground water is difficult (12). The potential obtained in ground water is a mixed potential that reflects the potential of many reactions and cannot be used for quantitative interpretation (11). The approximate location of the contaminant plume can be identified in the field by measuring the redox potential of the ground water.

To overcome the limitations imposed by traditional redox measurements, recent work has focused on measuring molecular hydrogen to accurately describe the predominant in situ redox reactions (13-15). The evidence suggests that concentrations of H_2 in ground water can be correlated with specific microbial processes, and these concentrations can be used to identify zones of methanogenesis, sulfate reduction, and iron reduction in the subsurface (3).

Electron Acceptors

Measuring the available electron acceptors is a critical step in identifying the predominant microbial and geochemical processes occurring in situ at the time of sample collection. Nitrate and sulfate are found naturally in most ground waters and will subsequently be used as electron acceptors once oxygen is consumed. Oxidized forms of iron and manganese can be used as electron acceptors before sulfate reduction commences. Iron and manganese minerals solubilize coincidently with sulfate reduction, and their reduced forms scavenge oxygen to the extent that strict anaerobes (some sulfate reducers and all methanogens) can develop. Sulfate is found in many depositional environments, and sulfate reduction may be very common in many contaminated ground waters. In environments where sulfate is depleted, carbonate becomes the electron acceptor, with methane gas produced as an end product.

Temperature

The temperature at all monitoring wells should be measured to determine when the pumped water has stabilized and is ready for collection. Below approximately 30 feet, the temperature in the subsurface is fairly consistent on an annual basis. Microcosms should be stored at the average in situ temperature. Biological growth can occur over a wide range of temperatures, although most microorganisms are active primarily between 10°C and 35°C (50°F to 95°F).

Chloride

Reductive dechlorination results in the accumulation of inorganic chloride. In aquifers with a low background of inorganic chloride, the concentration of inorganic chloride should increase as the chlorinated solvents degrade. The sum of the inorganic chloride plus the contaminant being degraded should remain relatively consistent along the ground-water flow path.

Tables 1 and 2 list the geochemical parameters, contaminants, and daughter products that should be measured during site characterization for natural attenuation. The tables include the analyses that should be performed, the optimum range for natural attenuation of chlorinated solvents, and the interpretation of the value in relation to biological processes.

Table 1. Geochemical Parameters

Analysis	Range	Interpretation
Redox potential	< 50 mV against Ag/AgCl	Reductive pathway possible
Sulfate	< 20 mg/L	Competes at higher concentrations with reductive pathway
Nitrate	< 1 mg/L	Competes at higher concentrations with reductive pathway
Oxygen	< 0.5 mg/L	Tolerated; toxic to reductive pathway at higher concentrations
Oxygen	> 1 mg/L	Vinyl chloride oxidized
Iron(II)	> 1 mg/L	Reductive pathway possible
Sulfide	> 1 mg/L	Reductive pathway possible
Hydrogen	> 1 nM	Reductive pathway possible; vinyl chloride may accumulate
Hydrogen	< 1 nM	Vinyl chloride oxidized
pH	5 < pH < 9	Tolerated range

Table 2. Contaminants and Daughter Products

Analysis	Interpretation
PCE	Material spilled
TCE	Material spilled or daughter product of perchloroethylene
1,1,1-Trichloroethane	Material spilled
cis-DCE	Daughter product of trichloroethylene
trans-DCE	Daughter product of trichloroethylene
Vinyl chloride	Daughter product of dichloroethylene
Ethene	Daughter product of vinyl chloride
Ethane	Daughter product of ethene
Methane	Ultimate reductive daughter product
Chloride	Daughter product of organic chlorine
Carbon dioxide	Ultimate oxidative daughter product
Alkalinity	Results from interaction of carbon dioxide with aquifer minerals

Microcosm Construction

During construction of the microcosms, manipulations should take place in an anaerobic glovebox. These gloveboxes exclude oxygen and provide an environment in which the integrity of the core material may be maintained, since many strict anaerobic bacteria are sensitive to oxygen. Stringent aseptic precautions are not necessary for microcosm construction; maintaining the anaerobic conditions of the aquifer material and solutions added to the microcosm bottles is more important.

The microcosms should have approximately the same ratio of solids to water as the in situ aquifer material, with minimal or negligible headspace. Most bacteria in the subsurface are attached to the aquifer solids. If a microcosm has too much water and the contaminant is primarily in the dissolved phase, the bacteria must consume or transform a great deal more contaminant to produce the same relative change in the contaminant concentration. As a result, the kinetics of removal at field scale will be underestimated in the microcosms.

A minimum of three replicate microcosms for both living and control treatments should be constructed for each sampling event. Microcosms sacrificed at each sampling interval are preferable to microcosms that are repetitively sampled. The compounds of regulatory interest should be added at concentrations representative of the higher concentrations found in the geochemical region of the plume being evaluated, and should be added as concentrated aqueous solutions. If an aqueous solution is not feasible, dioxane or acetonitrile may be used as solvents. Carriers that can be metabolized anaerobically should be avoided, particularly alcohols. If possible, ground water from the site should be used to prepare dosing solutions and to restore water lost from the core barrel during sample collection.

Although no method is perfect, autoclaving is the preferred sterilization method for long-term microcosm studies, and mercuric chloride is excellent for short-term studies (weeks or months). Mercuric chloride complexes to clays, however, and control may be lost as it is sorbed over time. Sodium azide is effective in repressing metabolism of bacteria that have cytochromes but is not effective on strict anaerobes.

The microcosms should be incubated in the dark at the ambient temperature of the aquifer. Preferably, the microcosms should be inverted in an anaerobic glovebox as they incubate; anaerobic jars are also available that maintain an oxygen-free environment. Dry redox indicator strips can be placed in the jars to ensure that anoxic conditions are maintained. If no anaerobic storage is available, the inverted microcosms can be immersed in approximately 2 inches of water during incubation. Teflon-lined butyl rubber septa are excellent for excluding oxygen and should be used if the microcosms must be stored outside an anaerobic environment.

The studies should last from 12 to 18 months. The residence time of a plume may be several years to tens of years at field scale. Rates of transformation that are slow in terms of laboratory experimentation may have a considerable environmental significance, and a microcosm study lasting only a few weeks to months may not have the resolution to detect slow changes that are of environmental significance. Additionally, microcosm studies often distinguish a pattern of sequential biodegradation of the contaminants of interest and their daughter products.

Microcosm Interpretation

As a practical matter, batch microcosms with an optimal solids/water ratio that are sampled every 2 months in triplicate for up to 18 months, can resolve biodegradation from abiotic losses with a detection limit of 0.001 to 0.0005 per day. Rates determined from replicated batch microcosms are found to more accurately duplicate field rates of natural attenuation than column studies. Many plumes show significant attenuation of contamination at field-calibrated rates that are slower than the detection limit of microcosms constructed with that aquifer material. Although rate constants for modeling purposes are more appropriately acquired from field-scale studies, agreement between rates in the field and rates in the laboratory is reassuring.

The rates measured in the microcosm study may be faster than the estimated field rate. This may not be due to an error in the laboratory study, particularly if estimation of the field-scale rate of attenuation did not account for regions of preferential flow in the aquifer. The regions

of preferential flow may be determined using a down-hole flow meter or a geoprobe method for determining hydraulic conductivity in 1- to 2-foot sections of the aquifer.

Statistical comparisons can determine whether removals of contaminants of concern in the living treatments are significantly different from zero or significantly different from any sorption that is occurring. Comparisons are made on the first-order rate of removal, that is, the slope of a linear regression of the natural logarithm of the concentration remaining against time of incubation for both the living and control microcosm. These slopes (removal rates) are compared to determine whether they are different and, if so, the extent of the difference that can be detected at a given level of confidence

The Tibbetts Road Case Study

The Tibbetts Road Superfund site in Barrington, New Hampshire, a former private home, was used to store drums of various chemicals from 1944 to 1984. The primary ground-water contaminants in the overburden and bedrock aquifers were TCE and benzene, with respective concentrations of 7,800 µg/L and 1,100 µg/L. High concentrations of arsenic, chromium, nickel, and lead were also found.

Material collected at the site was used to construct a microcosm study evaluating the removal of benzene, toluene, and TCE. This material was acquired from the waste pile near the origin of Segment A (Figure 1), the most contaminated source at the site. Microcosms were incubated for 9 months. The aquifer material was added to 20-milliliter headspace vials; dosed with 1 milliliter of spiking solution; capped with a Teflon-lined, gray butyl rubber septa; and sealed with an aluminum crimp cap. Controls were prepared by autoclaving the material used to construct the microcosms overnight. Initial concentrations for benzene, toluene, and TCE were 380 µg/L, 450 µg/L, and 330 µg/L, respectively. The microcosms were thoroughly mixed by vortexing, then stored inverted in the dark at the ambient temperature of 10°C.

The results (Figures 2 through 4 and Table 3) show that significant biodegradation of both petroleum aromatic hydrocarbons and the chlorinated solvent had occurred. Significant removal in the control microcosms also occurred for all compounds. The data exhibited more variability

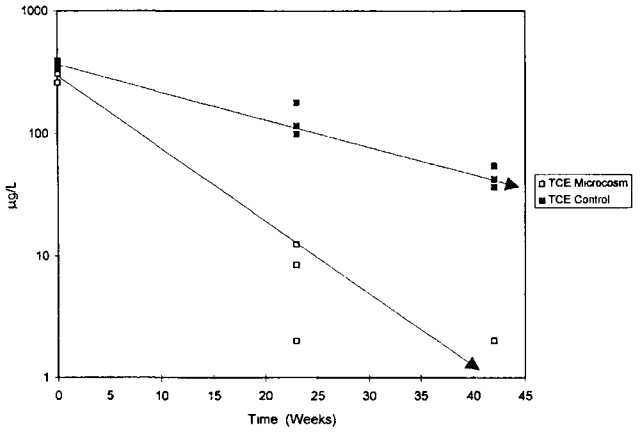

Figure 1. TCE concentrations in the Tibbetts Road microcosm study.

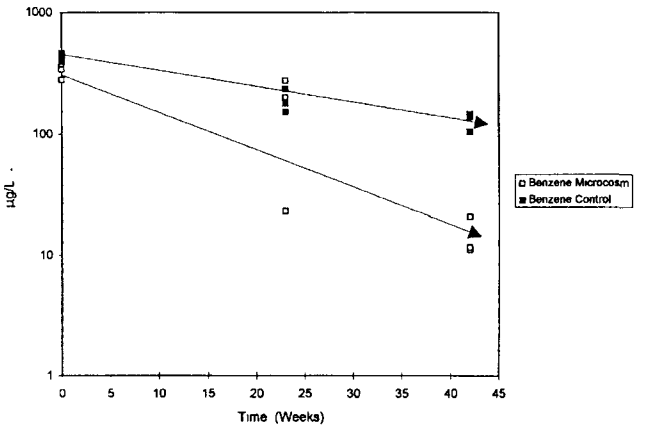

Figure 2. Benzene concentrations in the Tibbetts Road microcosm study.

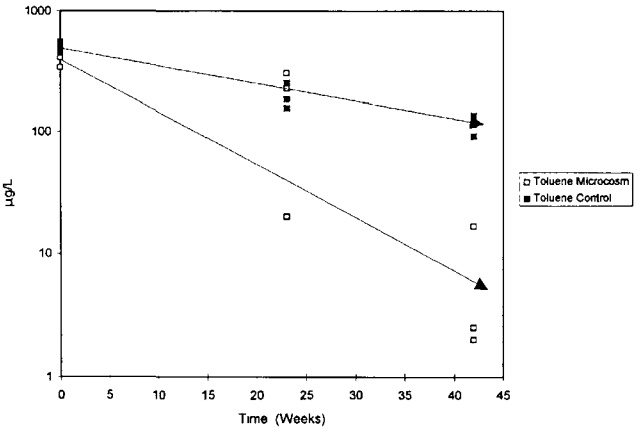

Figure 3. Toluene concentrations in the Tibbetts Road microcosm study.

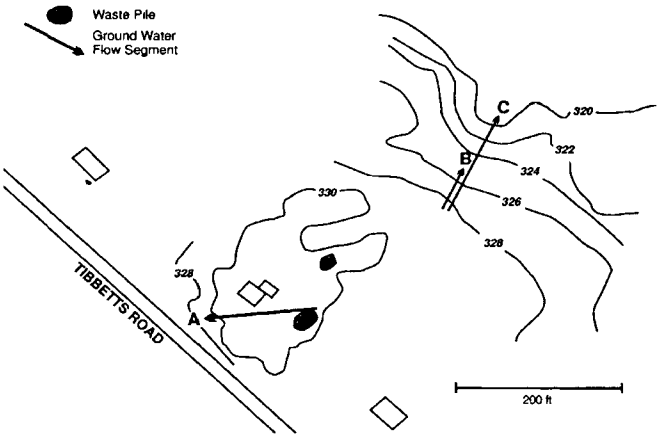

Figure 4. Location of waste piles and flow path segments at the Tibbetts Road Superfund site.

Table 3. Concentrations of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms

Compound	Time Zero Microcosms	Time Zero Controls	Week 23 Microcosms	Week 23 Controls	Week 42 Microcosms	Week 42 Controls
TCE	328	337	1	180	2	36.3
	261	394	12.5	116	2	54.5
	309	367	8.46	99.9	2	42.3
Mean ± standard deviation	299 ± 34.5	366 ± 28.5	7.32 ± 5.83	132 ± 42.4	2.0 ± 0.0	44.4 ± 9.27
Benzene	366	396	201	236	11.1	146
	280	462	276	180	20.5	105
	340	433	22.8	152	11.6	139
Mean ± standard deviation	329 ± 44.1	430 ± 33.1	167 ± 130	189 ± 42.8	14.4 ± 5.29	130 ± 21.9
Toluene	443	460	228	254	2	136
	342	557	304	185	2.5	92
	411	502	19.9	157	16.6	115
Mean ± standard deviation	399 ± 51.6	506 ± 48.6	184 ± 147	199 ± 49.9	7.03 ± 8.29	114 ± 22.0

in the living microcosms than in the control treatment, a pattern that has been observed in other microcosm studies. The removals observed in the controls are probably due to sorption; however, this study exhibited more sorption than typically seen.

The rate constants determined from the microcosm study for the three compounds are shown in Table 4. The appropriate rate constant to be used in a model or a risk assessment would be the first-order removal in the living treatment minus the first-order removal in the control, in other words, the removal that is in excess of the removal in the controls.

The first-order removal in the living and control microcosms was estimated as the linear regression of the natural logarithm of concentration remaining in each microcosm in each treatment against time of incubation. Student's t distribution with n - 2 degrees of freedom was used to estimate the 95 percent confidence interval. The standard error of the difference of the rates of removal in living and control microcosms was estimated as the square root of the sum of the squares of the standard errors of the living and control microcosms, with n - 4 degrees of freedom (16).

Table 5 presents the concentrations of organic compounds and their metabolic products in monitoring wells used to define line segments in the aquifer for estimation of field-scale rate constants. Wells in this aquifer showed little accumulation of *trans*-DCE, 1,1-DCE, vinyl chloride, or ethene, although removals of TCE and *cis*-DCE were extensive. This can be explained by the observation that iron-reducing bacteria can rapidly oxidize vinyl chloride to carbon dioxide (4). Filterable iron accumulated in ground water in this aquifer.

The extent of attenuation from well to well (Table 5) and the travel time between wells in a segment (Figure 4) were used to calculate first-order rate constants for each segment (Table 6). Travel time between monitoring wells was calculated from site-specific estimates of hydraulic conductivity and from the hydraulic gradient. In the area sampled for the microcosm study, the estimated Darcy

Table 4. First-Order Rate Constants for Removal of TCE, Benzene, and Toluene in the Tibbetts Road Microcosms

Parameter	Living Microcosms	Autoclaved Controls	Removal Above Controls
	First-Order Rate of Removal (per year)		
TCE	6.31	2.62	3.69
95% confidence interval	± 2.50	± 0.50	± 2.31
Minimum rate significant at 95% confidence			1.38
Benzene	3.87	1.51	2.36
95% confidence interval	± 1.96	± 0.44	± 1.83
Minimum rate significant at 95% confidence			0.53
Toluene	5.49	1.86	3.63
95% confidence interval	± 2.87	± 0.45	± 2.64
Minimum rate significant at 95% confidence			0.99

Table 5. Concentration of Contaminants and Metabolic Byproducts in Monitoring Wells Along Segments in the Plume Used To Estimate Field-Scale Rate Constants

Parameter	Segment A		Segment B		Segment C	
Monitoring well	80S	79S	70S	52S	70S	53S
	Upgradient g/L	Downgradient g/L	Upgradient g/L	Downgradient g/L	Upgradient g/L	Downgradient g/L
TCE	200	13.7	710	67	710	3.1
cis-DCE	740	10.9	220	270	220	2.9
trans-DCE	0.41	< 1	0.8	0.3	0.8	< 1
1, 1-DCE	0.99	< 1	< 1	1.6	< 1	< 1
Vinyl Chloride	< 1	< 1	< 1	< 1	< 1	< 1
Ethene	< 4	< 4	7	< 4	7	< 4
Benzene	510	2.5	493	420	493	< 1
Toluene	10,000	< 1	3,850	900	3,850	< 1
o-Xylene	1,400	8.4	240	71	240	< 1
m-Xylene	2,500	< 1	360	59	360	< 1
p-Xylene	1,400	22	1,100	320	1,100	< 1
Ethylbenzene	1,300	0.7	760	310	760	< 1
Methane	353	77	8	3	8	< 2
Iron						27,000

Table 6. First-Order Rate Constants in Segments of the Tibbetts Road Plume

Compound	Flow Path Segments in Length and Time of Ground-Water Travel		
	Segment A 130 feet = 6.4 years	Segment B 80 feet = 2.4 years	Segment C 200 feet = 10 years
	First-Order Rate Constants in Segments (per year)		
TCE	0.41	0.59	0.54
cis-DCE	0.65	Produced	0.43
Benzene	0.82	0.04	> 0.62
Toluene	> 1.42	0.36	> 0.83
o-Xylene	0.79	0.30	> 0.55
m-Xylene	> 1.20	0.45	> 0.59
p-Xylene	0.64	0.31	> 0.70
Ethylbenzene	1.16	0.22	> 0.66

flow was 2.0 feet per year. With an estimated porosity in this particular glacial till of 0.1, this corresponds to a plume velocity of 20 feet per year.

Summary

Table 7 compares the first-order rate constants estimated from the microcosm studies with the rate constants estimated at field scale. The agreement between the independent estimates of rate is good, indicating that the rates can appropriately be used in a risk assessment. The rates of biodegradation documented in the microcosm study could easily account for the disappearance of TCE, trichloroethylene, benzene, and toluene observed at field scale. The rates estimated from the microcosm study are several-fold higher than the rates estimated at field scale, which may reflect an underestimation of the true rate in the field. The estimates of plume velocity assumed that the aquifer was homogeneous. No attempt was made in this study to correct the estimate of plume velocity for

Table 7. Comparison of First-Order Rate Constants in a Microcosm Study and in the Field at the Tibbetts Road NPL Site

Parameter	Microcosms Corrected for Controls		Field Scale		
	Average Rate	Minimum Rate Significant at 95% Confidence	Segment A	Segment B	Segment C
	First-Order Rate (per year)				
Trichloroethylene	3.69	1.38	0.41	0.59	0.54
Benzene	2.36	0.53	0.82	0.04	> 0.62
Toluene	3.63	0.99	> 1.42	0.36	> 0.83

the influence of preferential flow paths. Preferential flow paths with a higher hydraulic conductivity than average would result in a faster velocity of the plume, thus a lower residence time and faster rate of removal at field scale.

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Conceptual Models for Chlorinated Solvent Plumes and Their Relevance to Intrinsic Remediation

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Introduction

Plumes in which chlorinated solvents are the primary contaminants of concern are common in aquifers in North America and Europe. Most of these plumes have existed for two decades or longer, but only a few were delineated before the mid-1980s. In general, solvent plumes are deeper and more extensive than other types of plumes. Many unremediated solvent plumes have shown little change in peak concentrations or shape since monitoring began more than a decade ago. Plumes subjected to pump-and-treat often have shown an initial decline in solvent concentrations but thereafter have nearly constant concentrations in the source zones. Permanent restoration of these ground-water systems has not yet been accomplished at significant solvent contamination sites.

Conceptual Models for Dense Nonaqueous-Phase Liquid Sites

The conceptual models that best explain chlorinated solvent plumes have considerable immobile immiscible-phase solvent mass (dense nonaqueous-phase liquid [DNAPL]) situated below the water table that continually contributes dissolved solvents to the plume. Within the subsurface zone causing plume development in fractured porous media, the original DNAPL mass may have undergone phase transfer so that the mass now resides totally or partly as dissolved and sorbed mass in the low-permeability matrix blocks between fractures. The subsurface zone of plume origin is referred to as the subsurface source zone or simply the source zone, whether it has DNAPL residual or free product or has phased-transferred DNAPL in low-permeability zones. Significant solvent mass may also reside above the water table, but this mass is typically not a major contributor to the ground-water plume relative to the deeper solvent mass.

Although many indirect lines of evidence indicate that the solvent mass in the subsurface source zone is the long-term cause of the plumes, reliable estimates of the mass in this zone are very rare. The monitoring data necessary for such estimates are usually not achievable because of the excessive time and cost involved. At nearly all solvent contamination sites, disposals, leakages, or spills have ceased; therefore, the solvent mass in the source zone is now slowly diminishing and eventually the source zone will be depleted. This depletion, however, is expected to take many decades or even centuries.

Many solvent plumes have traveled sufficiently far to encounter natural hydrologic boundaries such as streams, lakes, or wetlands or induced boundaries such as water wells. The fronts of some solvent plumes have not yet encountered boundaries, and questions arise as to how much farther these fronts will travel while maintaining hazardous concentration levels. These questions are linked to possibilities for the plume front to achieve an effective steady-state position. If the frontal zone of a plume achieves this steady-state or near steady-state position, then in the context of downgradient receptors the plume can be viewed as having achieved intrinsic remediation. It is unlikely that depletion of the source zones contributes to intrinsic remediation of chlorinated solvent plumes; therefore, intrinsic remediation must depend on attenuation processes operating within the plume.

Intrinsic Remediation

Intrinsic remediation occurrences are well known at petroleum contamination sites, but little is known about the actual applicability of this concept to chlorinated solvent plumes. Use of the term "intrinsic remediation" implies nothing about the specific subsurface processes that cause the remediation other than that the various processes somehow combine to cause the plume front to achieve steady state or near steady state or perhaps cause plume shrinkage.

The three processes that can drive the plume front towards the steady-state condition are mechanical dispersion, molecular diffusion, and degradation. Sorption can contribute to the appearance of a quasi-steady state for some interval of time, but it does not cause permanent mass removal from or dilution of the plume. In the context of chlorinated solvent plumes, biotic or abiotic processes commonly cause transformations of the parent contaminant, such as trichloroethene (TCE) or tetrachloroethene (PCE), to hazardous transformation products such as trans- or cis-dichloroethene (DCE) and vinyl chloride. Unfortunately, this often renders the plume more hazardous. The term "intrinsic remediation" for chlorinated solvent sites should be reserved for plumes in which the degree of hazard has diminished sufficiently within the plume front to achieve a drinking-water standard or some other state of acceptably low risk. Thus, intrinsic remediation requires the degradation to be sufficiently complete to attenuate the hazard of the plume front or the dispersion to cause sufficient dilution to reduce concentrations to acceptable levels.

It is not feasible using laboratory studies to draw conclusions on the propensity for chlorinated solvent plumes to achieve intrinsic remediation. Conclusions about propensity must come from comprehensive observations of the nature and fate of actual plumes. Whether or not a set of observations can be regarded as comprehensive depends on the conceptual model or models deemed to be most applicable.

The Fringe and Core Hypothesis

This paper presents a conceptual model for the anatomy of chlorinated solvent plumes. Emphasis is on plumes in sandy or gravelly aquifers. Based primarily on field observations, it argues the merits of a conceptual model in which solvent plumes typically have two components: a low-concentration fringe that surrounds a high-concentration core. Multiple cores can exist in some plumes due to the complexity of the source zone. The fringe, which has concentrations in the range of one to a thousand micrograms per liter, is commonly large relative to the volume of the core, which commonly has concentrations between one and a few tens of milligrams per liter. Although concentrations in most of the core are orders of magnitude larger than those in most of the fringe, the peak concentrations in the core are much less than DNAPL solubility, except close to the source zone. To achieve intrinsic remediation, plume concentrations in the core must decline orders of magnitude to attain maximum contaminant levels (MCLs) for drinking water. Thus, the attenuation processes must act much more strongly on the core than the fringe to reach MCLs. Such strong attenuation is unlikely to occur in many plumes.

Delineation of chlorinated solvent plumes in the United States began in the early to mid-1980s as a result of Superfund and the Resource Conservation and Recovery Act. During the past 15 years, millions of conventional monitoring wells have been used at many thousands of solvent sites in the United States and several other countries. Solvent plumes present an exceptionally difficult monitoring challenge because the spatial distribution of contamination is often complex due to the variability of the subsurface source zones and to geologic heterogeneity within the plumes. Conventional monitoring networks using monitoring wells usually indicate the presence of the fringe, which is commonly taken to represent the plume as a whole. Due to the sparseness of data points, conventional networks only rarely establish the existence of cores, except perhaps close to the source zones. Thus, such plumes with no observed cores are perceived to have relatively low concentrations and therefore small total contaminant mass.

Detailed monitoring of experimental solvent plumes produced at the Borden field site (an unconfined sand aquifer located 60 kilometers northwest of Toronto, Canada [1]) using unconventional techniques, as well as similar monitoring of several plumes at actual industrial sites, provides exceptional spatial resolution of the distribution of contaminants and confirms the presence of cores as well as fringes. Many if not most plumes in which cores have not been identified based on conventional monitoring may actually have cores that have gone undetected because of the sparseness of the monitoring networks.

Conclusion

Information on the concentration distribution in solvent plumes is limited, particularly at and near the plume fronts. Conventional approaches to monitoring result in data that are too sparse to identify cores. Cores extending far from the subsurface source zones are likely a common feature of solvent plumes in sand or gravel aquifers. Although thousands of solvent plumes have been monitored for many years, the sparseness of data severely limits possibilities for determining the number of occurrences of intrinsic remediation. More detailed data sets that can be obtained using new methods of monitoring, primarily direct push methods for spatial rather than temporal resolution, offer the best possibilities for examining the fringe-and-core conceptual model and intrinsic remediation of solvent plumes.

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Site Characterization Tools: Using a Borehole Flowmeter To Locate and Characterize the Transmissive Zones of an Aquifer

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Introduction

A study in which both direct and indirect techniques for developing hydraulic conductivity (*K*) logs of screened wells and/or boreholes were examined concluded that techniques relying on direct hydraulic measurements, such as transient pressure changes or flow rates, offer the most promising methodology for determining accurate logs of horizontal *K* versus elevation in aquifers (1). The borehole flowmeter, which can be used to measure the vertical flow distribution in pumped wells, offers one of the most direct techniques available for measuring a *K* log. These conclusions have been supported by more recent studies (2-7).

Inadequate performance of many pump-and-treat systems has been attributed to improper design (8, 9). In far too many cases, underestimation of aquifer heterogeneity plays a significant role in these design failures. Bioremediation design is also sensitive to aquifer heterogeneity. For example, if rate constants for attenuation of chlorinated contaminants are to be used for exposure assessments, it is necessary to estimate the residence time of the contaminant in the aquifer as accurately as possible. Conventional estimates of plume velocity use the average hydraulic conductivity as determined by an aquifer test. These average hydraulic conductivities can underestimate the local hydraulic conductivity of the geological interval carrying a plume of contamination by a factor of ten or more. Proper characterization of aquifer hydraulic properties, especially the spatial variations, is currently limited by the methods for measuring those properties. The borehole flowmeter enables one to determine two basic things: the natural (ambient) vertical flow that exists in most wells, and, through a small pumping test, the flow distribution entering the well from the surrounding formation. If certain conditions are met, the distributions provide sufficient information to determine the hydraulic conductivity of the aquifer zones selected as measurement intervals (4, 10).

Interest in borehole flowmeters as a means to directly measure the variation of hydraulic conductivity became apparent in the 1980s through the publication of a number of papers (11-13). By the late 1980s, the electromagnetic (EM) flowmeter had been designed, developed, and tested by the Tennessee Valley Authority. This unique flowmeter has several practical advantages. This paper presents the results of EM flowmeter studies and explains the capabilities of the instrument. It is now recognized that the application of such instruments to the characterization of aquifer properties will greatly enhance the understanding of heterogeneity and its effect on contaminant migration (3, 6).

Conducting a Flowmeter Test

A flowmeter test may be viewed as a natural generalization of a standard, fully penetrating pumping test. In the latter application, only the steady pumping rate, *QP*, is measured, whereas during a flowmeter test the vertical flow rate distribution within the borehole or well screen, *Q*(z), is recorded as well as *QP* (Figure 1).

Shown in Figure 2 are the discharge rates that are provided directly by the instrument. "Ambient flow" refers to the natural flow in a test well due to small hydraulic head differences in the vertical direction that are detectable in most aquifers. "Pumping induced flow" represents the flow distribution in a test well caused by a small pump, which is also illustrated in Figure 1. The flow data that ultimately go into a hydraulic

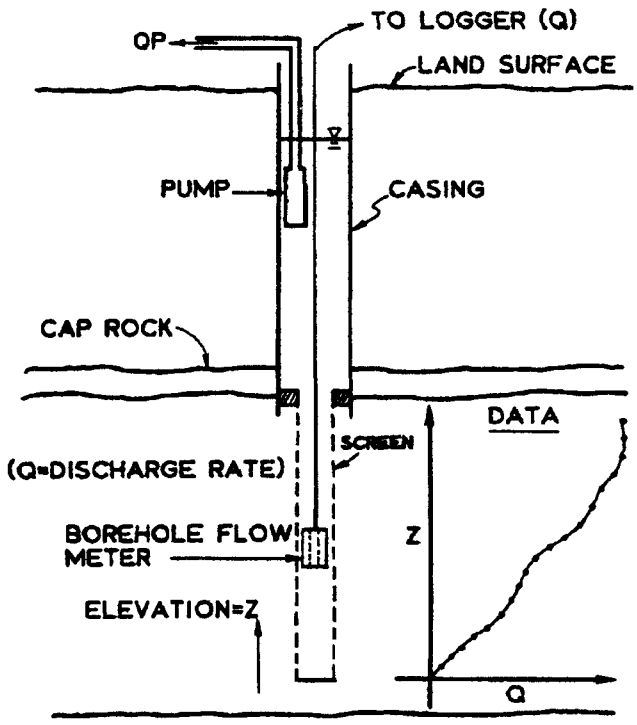

Figure 1. Apparatus and geometry associated with a borehole flowmeter test. The flowmeter measures the vertical discharge distribution in the well caused by the pump. A hypothetical data set (Q(z) versus z) is shown at the bottom of the figure.

conductivity computation are represented by the "net pumping flow," which is the difference between pumping induced flow and ambient flow (4).

To convert flow distributions in a well into flow to or from aquifer layers, the discharge data are differenced (i.e., value at lower elevation subtracted from value at upper elevation) to produce the "differential ambient flow" and the "differential net flow." The result of doing this to the hypothetical data in Figure 2 is shown in Figure 3. Once the flow to the well has stabilized, the differential net flow (DNF) is proportional to the horizontal hydraulic conductivity distribution, $K(z)$. The process of converting a DNF curve into $K(z)$ involves only algebra and a small amount of additional data (4).

Flowmeter technology is very cost effective. It may be viewed as an extension of a standard pumping test, since flow distribution in the pumping well is measured in addition to pumping rate and drawdown, but the cost is less. Only a few hundred gallons of water are produced per test versus thousands or tens of thousands for conventional pumping tests. Thus, potential treatment and disposal costs are minimal. A typical flowmeter test can be completed in an hour or two. Cost per data point is less than standard pumping tests by a factor of 100 or more, and the quantity of hydraulic conductivity information produced is increased dramatically.

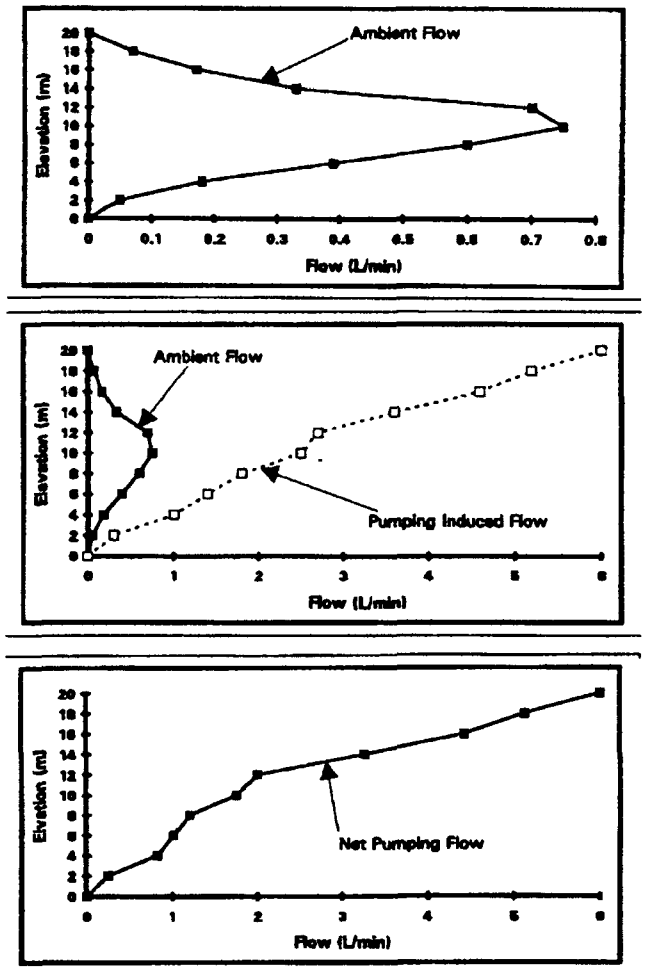

Figure 2. The data actually recorded by a flowmeter are ambient flow and pumping-induced flow. In both cases, positive values indicate upward flow. Net pumping flow is pumping-induced flow minus ambient flow.

Measured $K(z)$ Distributions

A commercial version of the EM borehole flowmeter is now available, and it has been applied recently at several sites, including the Savannah River site, the Louisiana Army Ammunition Plant, and George Air Force Base (AFB), California. The Savannah River application was in a 14-meter thick confined aquifer in an alluvial basin composed of sand, silt, and clay strata of variable composition. The K distribution obtained in well P26-M1 is shown in Figure 4. Heterogeneity is evident, with K varying by an order of magnitude at various locations in the aquifer (3).

A particularly illuminating EM flowmeter application at George AFB was reported by Wilson et al. (Figure 5) (6). The concentration data were obtained from core samples, while the K data are based on EM flowmeter measurements in Well MW-27, which was located nearby. The transmissive layer identified by the flowmeter is likely the main stratum where the benzene is migrating. This inference is supported by additional flowmeter tests in neighboring wells (6).

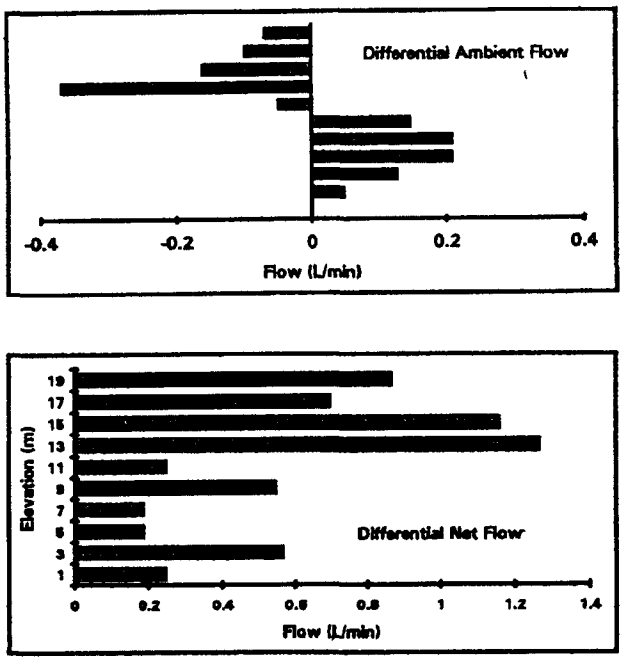

Figure 3. Plots of the differences of neighboring values of ambient flow (differential ambient flow) and net flow (differential net flow). These values represent the flow entering (positive) or leaving (negative) the well from/to the various layers of the aquifer.

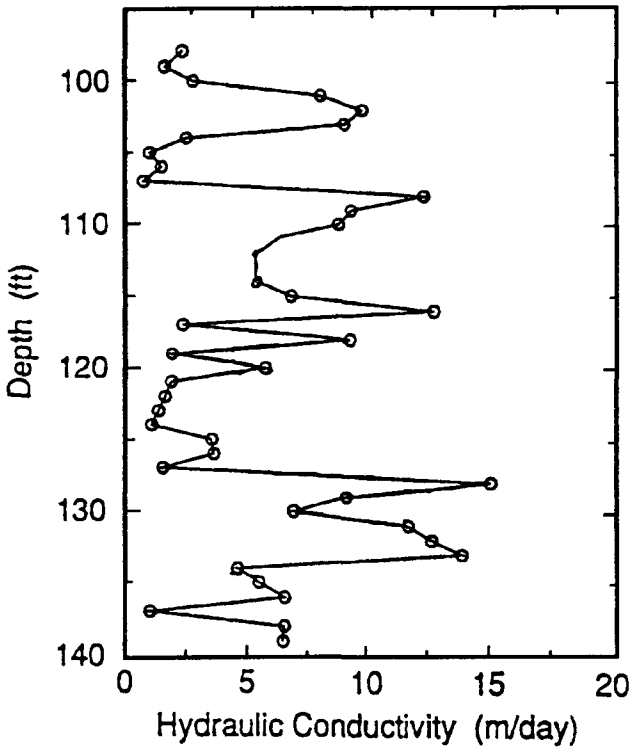

Figure 4. Hydraulic conductivity as a function of depth in Well P26-M1 at the Savannah River site. The measurement interval (layer thickness) was 1 foot.

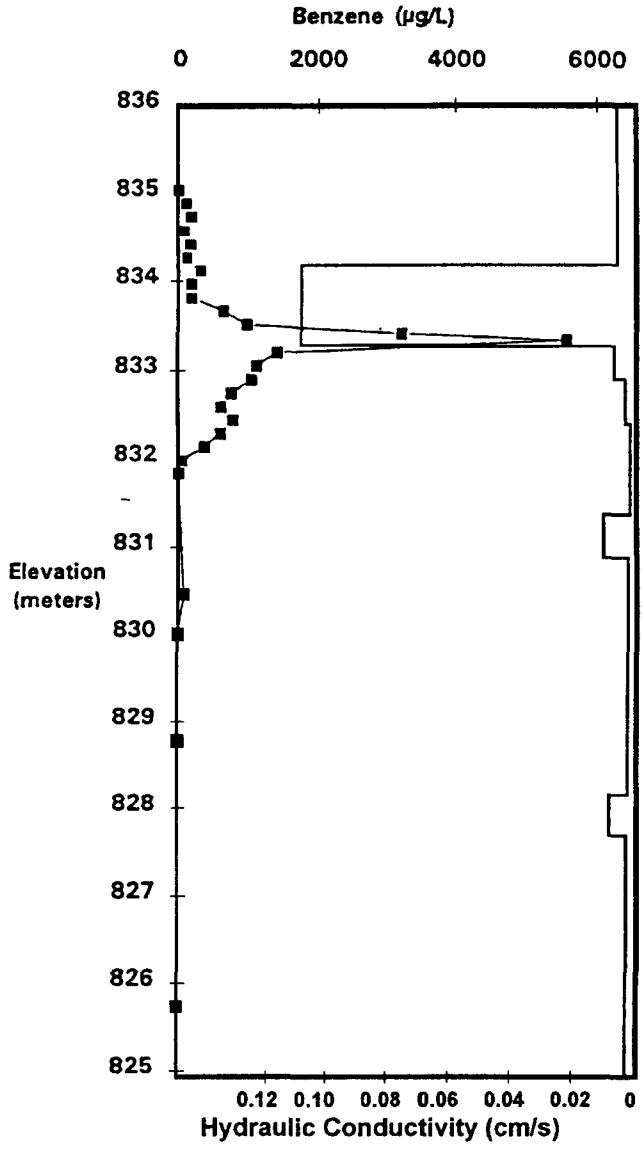

Figure 5. Benzene concentration and hydraulic conductivity as functions of elevation at George Air Force Base. The benzene appears to be migrating in the high transmissivity layer defined by a flowmeter analysis (6).

Conclusion

Flowmeter tests have now been conducted at sites in many regions of the United States. Results document that the EM flowmeter is capable of supplying a new level of detail concerning *K* distributions in granular aquifers (2-4, 6, 7, 11, 13) and flowpath delineation in fractured-rock aquifers (5, 12, 14). The resulting information concerning hydraulic heterogeneity is unprecedented and promises to serve as valuable input to monitoring well screen location and remediation design. Because basic data input has been the "weak link" in the chain of activities constituting subsurface remediation, the potential impact of flowmeters on site

characterization and modeling is dramatic. Simultaneously, the effort required to perform flowmeter tests is practical and economical.

While we view the technology represented by the EM flowmeter as a definite step forward, the instrument in its present prototype form is rather awkward to use on a routine basis (3). The flowmeter probe hangs from stiff electrical (not logging) cable and requires a packer inflation gas line to be attached. One must raise and lower the instrument by hand, usually using the cable, the inflation line, and a measuring tape bound together with ties. The cable is difficult to clean, and stretching leads to depth placement errors with increasing cable length. These shortcomings may be removed by a redesign effort that we are attempting to initiate. None of the existing shortcomings, however, prevent effective use of the EM borehole flowmeter, and the resulting data provide hydraulic conductivity information far superior to that derived from standard pumping tests.

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Overview of the Technical Protocol for Natural Attenuation of Chlorinated Aliphatic Hydrocarbons in Ground Water Under Development for the U.S. Air Force Center for Environmental Excellence

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Introduction

Over the past several years, natural attenuation has become increasingly accepted as a remedial alternative for organic compounds dissolved in ground water. The U.S. Environmental Protection Agency's (EPA) Office of Research and Development and Office of Solid Waste and Emergency Response define natural attenuation as:

> The biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem.

In practice, natural attenuation has several other names, such as intrinsic remediation, intrinsic bioremediation, or passive bioremediation. The goal of any site characterization effort is to understand the fate and transport of the contaminants of concern over time in order to assess any current or potential threat to human health or the environment. Natural attenuation processes, such as biodegradation, can often be dominant factors in the fate and transport of contaminants. Thus, consideration and quantification of natural attenuation is essential to more thoroughly understand contaminant fate and transport.

This paper presents a technical protocol for data collection and analysis in support of remediation by natural attenuation to restore ground water contaminated with chlorinated aliphatic hydrocarbons and ground water contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons. In some cases, the information collected using this protocol will show that natural attenuation processes, with or without source removal, will reduce the concentrations of these contaminants to below risk-based corrective action criteria or regulatory standards before potential receptor exposure pathways are completed. The evaluation should include consideration of existing exposure pathways as well as exposure pathways arising from potential future use of the ground water.

This protocol is intended to be used within the established regulatory framework. It is not the intent of this document to replace existing EPA or state-specific guidance on conducting remedial investigations.

Overview of the Technical Protocol

Natural attenuation in ground-water systems results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization. The natural attenuation of fuel hydrocarbons is described in the *Technical Protocol for Implementing Intrinsic Remediation With Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater,* recently published by the U.S. Air Force Center for Environmental

Excellence (AFCEE) (1). This document differs from the technical protocol for intrinsic remediation of fuel hydrocarbons because the individual processes of chlorinated aliphatic hydrocarbon biodegradation are fundamentally different from the processes involved in the biodegradation of fuel hydrocarbons.

For example, biodegradation of fuel hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and biodegradation of these compounds generally will proceed until all of the contaminants are destroyed. In the experience of the authors, there appears to be an inexhaustible supply of electron acceptors in most, if not all, hydrogeologic environments. On the other hand, the more highly chlorinated solvents (e.g., perchloroethene and trichloroethene) typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the chlorinated aliphatic hydrocarbons) and an adequate supply of electron donors. Electron donors include fuel hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate, BTEX, or natural organic carbon). If the subsurface environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are removed, reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. This is the most significant difference between the processes of fuel hydrocarbon and chlorinated aliphatic hydrocarbon biodegradation.

For this reason, it is more difficult to predict the long-term behavior of chlorinated aliphatic hydrocarbon plumes than fuel hydrocarbon plumes. Thus, it is important to have a thorough understanding of the operant natural attenuation mechanisms. In addition to having a better understanding of the processes of advection, dispersion, dilution from recharge, and sorption, it is necessary to better quantify biodegradation. This requires a thorough understanding of the interactions between chlorinated aliphatic hydrocarbons, anthropogenic/natural carbon, and inorganic electron acceptors at the site. Detailed site characterization is required to adequately understand these processes.

Chlorinated solvents are released into the subsurface under two possible scenarios: 1) as relatively pure solvent mixtures that are more dense than water, or 2) as mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons which, depending on the relative proportion of each, may be more or less dense than water. These products commonly are referred to as "nonaqueous-phase liquids," or NAPLs. If the NAPL is more dense than water, the material is referred to as a "dense nonaqueous-phase liquid," or DNAPL. If the NAPL is less dense than water, the material is referred to as a "light nonaqueous-phase liquid," or LNAPL. In general, the greatest mass of contaminant is associated with these NAPL source areas, not with the aqueous phase.

As ground water moves through or past the NAPL source areas, soluble constituents partition into the moving ground water to generate a plume of dissolved contamination. After further releases have been stopped, these NAPL source areas tend to slowly weather away as the soluble components, such as BTEX or trichloroethene, are depleted. In cases where source removal or reduction is feasible, it is desirable to remove product and decrease the time required for complete remediation of the site. At many sites, however, mobile NAPL removal is not feasible with available technology. In fact, the quantity of NAPL recovered by commonly used recovery techniques is a trivial fraction of the total NAPL available to contaminate ground water. Mobile NAPL recovery typically recovers less than 10 percent of the total NAPL mass in a spill.

Compared with conventional engineered remediation technologies, natural attenuation has the following advantages:

- During natural attenuation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide, ethene, and water), not just transferred to another phase or location in the environment.
- Natural attenuation is nonintrusive and allows continuing use of infrastructure during remediation.
- Engineered remedial technologies can pose greater risk to potential receptors than natural attenuation because contaminants may be transferred into the atmosphere during remediation activities.
- Natural attenuation is less costly than currently available remedial technologies, such as pump-and-treat.
- Natural attenuation is not subject to the limitations of mechanized remediation equipment (e.g., no equipment downtime).
- Those compounds that are the most mobile and toxic are generally the most susceptible to biodegradation.

Natural attenuation has the following limitations:

- Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in ground-water gradients and velocity, pH, electron acceptor concentrations, electron donor concentrations, and/or potential future contaminant releases.
- Aquifer heterogeneity may complicate site characterization and quantification of natural attenuation.
- Time frames for complete remediation may be relatively long.

- Intermediate products of biodegradation (e.g., vinyl chloride) can be more toxic than the original contaminant.

This document describes those processes that bring about natural attenuation, the site characterization activities that may be performed to support a feasibility study to include an evaluation of natural attenuation, natural attenuation modeling using analytical or numerical solute fate-and-transport models, and the post-modeling activities that should be completed to ensure successful support and verification of natural attenuation. The objective of the work described herein is to quantify and provide defensible data in support of natural attenuation at sites where naturally occurring subsurface attenuation processes are capable of reducing dissolved chlorinated aliphatic hydrocarbon and/or fuel hydrocarbon concentrations to acceptable levels. A comment made by a member of the regulatory community (2) summarizes what is required to successfully implement natural attenuation:

> A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense the use of biological treatment systems calls for the same level of investigation, demonstration of effectiveness, and monitoring as any conventional [remediation] system.

To support remediation by natural attenuation, the proponent 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 natural attenuation of chlorinated aliphatic hydrocarbons, including:

- Observed reduction in contaminant concentrations along the flow path downgradient from the source of contamination.
- Documented loss of contaminant mass at the field scale using:
  - Chemical and geochemical analytical data (e.g., decreasing parent compound concentrations, increasing daughter compound concentrations, depletion of electron acceptors and donors, and increasing metabolic byproduct concentrations).
  - A conservative tracer and a rigorous estimate of residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale.
- Microbiological laboratory data that support the occurrence of biodegradation and give rates of biodegradation.

At a minimum, the investigator must obtain the first two lines of evidence or the first and third lines of evidence. The second and third lines of evidence are crucial to the natural attenuation demonstration because they provide biodegradation rate constants. These rate constants are used in conjunction with the other fate-and-transport parameters to predict contaminant concentrations and to assess risk at downgradient points of compliance.

The first line of evidence is simply an observed reduction in the concentration of released contaminants downgradient from the NAPL source area along the groundwater flow path. This line of evidence does not prove that contaminants are being destroyed because the reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization with no loss of contaminant mass (i.e., the majority of apparent contaminant loss could be due to dilution). Conversely, an increase in the concentrations of some contaminants, most notably degradation products such as vinyl chloride, could be indicative of natural attenuation.

To support remediation by natural attenuation at most sites, the investigator will have to show that contaminant mass is being destroyed via biodegradation. This is done using either or both of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed via biodegradation, not just diluted. The second line of evidence is divided into two components:

- Using chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor and donor concentrations can be directly correlated to increases in metabolic end products and daughter compounds. This evidence can be used to show that electron acceptor and donor concentrations in ground water are sufficient to facilitate degradation of dissolved contaminants. Solute fate-and-transport models can be used to aid mass balance calculations and to collate information on degradation.
- Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters, such as seepage velocity and dilution, to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The third line of evidence, microbiological laboratory data, can be used to provide additional evidence that indigenous biota are capable of degrading site contaminants at a particular rate. Because it is necessary to show that biodegradation is occurring and to obtain biodegradation rate constants, the most useful type of microbiological laboratory data is the microcosm study.

This paper presents a technical course of action that allows converging lines of evidence to be used to scientifically document the occurrence and quantify the rates of natural attenuation. Ideally, the first two lines of evidence

should be used in the natural attenuation demonstration. To further document natural attenuation, or at sites with complex hydrogeology, obtaining a field-scale biodegradation rate may not be possible; in this case, microbiological laboratory data can be used. Such a "weight-of-evidence" approach will greatly increase the likelihood of successfully implementing natural attenuation at sites where natural processes are restoring the environmental quality of ground water.

Collection of an adequate database during the iterative site characterization process is an important step in the documentation of natural attenuation. Site characterization should provide data on the location, nature, and extent of contaminant sources. Contaminant sources generally consist of hydrocarbons present as mobile NAPL (i.e., NAPL occurring at sufficiently high saturations to drain under the influence of gravity into a well) and residual NAPL (i.e., NAPL occurring at immobile, residual saturation that is unable to drain into a well by gravity). Site characterization also should provide information on the location, extent, and concentrations of dissolved contamination; ground-water geochemical data; geologic information 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 receptor exposure points.

The data collected during site characterization can be used to simulate the fate and transport of contaminants in the subsurface. Such simulation allows prediction of the future extent and concentrations of the dissolved contaminant plume. Several models can be used to simulate dissolved contaminant transport and attenuation. The natural attenuation modeling effort has three primary objectives: 1) to predict the future extent and concentration of a dissolved contaminant plume by simulating the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory or risk-based levels intended to be protective of human health and the environment; and 3) to provide technical support for the natural attenuation remedial option at postmodeling regulatory negotiations to help design a more accurate verification and monitoring strategy and to help identify early source removal strategies.

Upon completion of the fate-and-transport modeling effort, model predictions can be used in an exposure pathways analysis. If natural attenuation is sufficient to mitigate risks to potential receptors, the proponent of natural attenuation has a reasonable basis for negotiating this option with regulators. The exposure pathways analysis allows the proponent to show that potential exposure pathways to receptors will not be completed.

The material presented herein was prepared through the joint effort of the AFCEE Technology Transfer Division; the Bioremediation Research Team at EPA's National Risk Management Research Laboratory in Ada, Oklahoma (NRMRL), Subsurface Protection and Remediation Division; and Parsons Engineering Science, Inc. (Parsons ES). This compilation is designed to facilitate implementation of natural attenuation at chlorinated aliphatic hydrocarbon-contaminated sites owned by the U.S. Air Force and other U.S. Department of Defense agencies, the U.S. Department of Energy, and public interests.

Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation

Because biodegradation is the most important process acting to remove contaminants from ground water, an accurate estimate of the potential for natural biodegradation is important to obtain when determining whether ground-water contamination presents a substantial threat to human health and the environment. This information also will be useful when selecting the remedial alternative that will be most cost-effective in eliminating or abating these threats should natural attenuation alone not prove to be sufficient.

Over the past two decades, numerous laboratory and field studies have demonstrated that subsurface microorganisms can degrade a variety of hydrocarbons and chlorinated solvents (3-23). Whereas fuel hydrocarbons are biodegraded through use as a primary substrate (electron donor), chlorinated aliphatic hydrocarbons may undergo biodegradation through three different pathways: through use as an electron acceptor, through use as an electron donor, or through co-metabolism, where degradation of the chlorinated organic is fortuitous and there is no benefit to the microorganism. At a given site, one or all of these processes may be operating, although at many sites the use of chlorinated aliphatic hydrocarbons as electron acceptors appears to be most important under natural conditions. In general, but in this case especially, biodegradation of chlorinated aliphatic hydrocarbons will be an electron-donor-limited process. Conversely, biodegradation of fuel hydrocarbons is an electron-acceptor-limited process.

In a pristine aquifer, native organic carbon is used as an electron donor, and dissolved oxygen (DO) is used first as the prime electron acceptor. Where anthropogenic carbon (e.g., fuel hydrocarbon) is present, it also will be used as an electron donor. After the DO is consumed, anaerobic microorganisms typically use additional electron acceptors (as available) in the following order of preference: nitrate, ferric iron oxyhydroxide, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron acceptors can provide evidence of where and how chlorinated aliphatic hydrocarbon biodegradation

is occurring. In addition, because chlorinated aliphatic hydrocarbons may be used as electron acceptors or electron donors (in competition with other acceptors or donors), isopleth maps showing the distribution of these compounds can provide evidence of the mechanisms of biodegradation working at a site. As with BTEX, the driving force behind oxidation-reduction reactions resulting in chlorinated aliphatic hydrocarbon degradation is electron transfer. Although thermodynamically favorable, most of the reactions involved in chlorinated aliphatic hydrocarbon reduction and oxidation do not proceed abiotically. Microorganisms are capable of carrying out the reactions, but they will facilitate only those oxidation-reduction reactions that have a net yield of energy.

Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation

Electron Acceptor Reactions (Reductive Dechlorination)

The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination. During this process, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. In general, reductive dechlorination occurs by sequential dechlorination from perchloroethene to trichloroethene to dichloroethene to vinyl chloride to ethene. Depending on environmental conditions, this sequence may be interrupted, with other processes then acting on the products. During reductive dechlorination, all three isomers of dichloroethene can theoretically be produced; however, Bouwer (24) reports that under the influence of biodegradation, *cis*-1,2-dichloroethene is a more common intermediate than *trans*-1,2-dichloroethene, and that 1,1-dichloroethene is the least prevalent intermediate of the three dichloroethene isomers. Reductive dechlorination of chlorinated solvent compounds is associated with all accumulation of daughter products and an increase in the concentration of chloride ions.

Reductive dechlorination affects each of the chlorinated ethenes differently. Of these compounds, perchloroethene is the most susceptible to reductive dechlorination because it is the most oxidized. Conversely, vinyl chloride is the least susceptible to reductive dechlorination because it is the least oxidized of these compounds. The rate of reductive dechlorination also has been observed to decrease as the degree of chlorination decreases (24, 25). Murray and Richardson (26) have postulated that this rate decrease may explain the accumulation of vinyl chloride in perchloroethene and trichloroethene plumes that are undergoing reductive dechlorination.

Reductive dechlorination has been demonstrated under nitrate- and sulfate-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under methanogenic conditions (24). Because chlorinated aliphatic hydrocarbon compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon in order for microbial growth to occur (24). Potential carbon sources include natural organic matter, fuel hydrocarbons, or other organic compounds such as those found in landfill leachate.

Electron Donor Reactions

Murray and Richardson (26) write that microorganisms are generally believed to be incapable of growth using trichloroethene and perchloroethene as a primary substrate (i.e., electron donor). Under aerobic and some anaerobic conditions, the less-oxidized chlorinated aliphatic hydrocarbons (e.g., vinyl chloride) can be used as the primary substrate in biologically mediated redox reactions (22). In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. This is the process by which fuel hydrocarbons are biodegraded.

In contrast to reactions in which the chlorinated aliphatic hydrocarbon is used as an electron acceptor, only the least oxidized chlorinated aliphatic hydrocarbons can be used as electron donors in biologically mediated redox reactions. McCarty and Semprini (22) describe investigations in which vinyl chloride and 1,2-dichloroethane were shown to serve as primary substrates under aerobic conditions. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. In addition, Bradley and Chapelle (27) show evidence of mineralization of vinyl chloride under iron-reducing conditions so long as there is sufficient bioavailable iron(III). Aerobic metabolism of vinyl chloride may be characterized by a loss of vinyl chloride mass and a decreasing molar ratio of vinyl chloride to other chlorinated aliphatic hydrocarbon compounds.

Co-metabolism

When a chlorinated aliphatic hydrocarbon is biodegraded via co-metabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated aliphatic hydrocarbon; in fact, the co-metabolic degradation of the chlorinated aliphatic hydrocarbon may be harmful to the microorganism responsible for the production of the enzyme or cofactor (22).

Co-metabolism is best documented in aerobic environments, although it could occur under anaerobic conditions. It has been reported that under aerobic conditions

chlorinated ethenes, with the exception of perchloroethene, are susceptible to co-metabolic degradation (22, 23, 26). Vogel (23) further elaborates that the co-metabolism rate increases as the degree of dechlorination decreases. During co-metabolism, trichloroethene is indirectly transformed by bacteria as they use BTEX or another substrate to meet their energy requirements. Therefore, trichloroethene does not enhance the degradation of BTEX or other carbon sources, nor will its co-metabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources.

Behavior of Chlorinated Solvent Plumes

Chlorinated solvent plumes can exhibit three types of behavior depending on the amount of solvent, the amount of biologically available organic carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors being used. Individual plumes may exhibit all three types of behavior in different portions of the plume. The different types of plume behavior are summarized below.

Type 1 Behavior

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and this anthropogenic carbon drives reductive dechlorination. When evaluating natural attenuation of a plume exhibiting Type 1, behavior the following questions must be answered:

1. Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms "strangle" before they "starve"—will they run out of chlorinated aliphatic hydrocarbons (electron acceptors) before they run out of electron donors?
2. What is the role of competing electron acceptors (e.g., DO, nitrate, iron(III), and sulfate)?
3. Is vinyl chloride oxidized, or is it reduced?

Type 1 behavior results in the rapid and extensive degradation of the highly chlorinated solvents such as perchloroethene, trichloroethene, and dichloroethene.

Type 2 Behavior

Type 2 behavior dominates in areas that are characterized by relatively high concentrations of biologically available native organic carbon. This natural carbon source drives reductive dechlorination (i.e., is the primary substrate for microorganism growth). When evaluating natural attenuation of a Type 2 chlorinated solvent plume, the same questions as those posed for Type 1 behavior must be answered. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon contents) this type of behavior also can result in rapid degradation of these compounds.

Type 3 Behavior

Type 3 behavior dominates in areas that are characterized by low concentrations of native and/or anthropogenic carbon and by DO concentrations greater than 1.0 milligrams per liter. Under these aerobic conditions, reductive dechlorination will not occur; thus, there is no removal of perchloroethene, trichloroethene, and dichloroethene. The most significant natural attenuation mechanisms for these compounds is advection, dispersion, and sorption. However, vinyl chloride can be rapidly oxidized under these conditions.

Mixed Behavior

A single chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated aliphatic hydrocarbon plumes. For example, Wiedemeier et al. (28) describe a plume at Plattsburgh Air Force Base, New York, that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. The most fortuitous scenario involves a plume in which perchloroethene, trichloroethene, and dichloroethene are reductively dechlorinated (Type 1 or 2 behavior), then vinyl chloride is oxidized (Type 3 behavior) either aerobically or via iron reduction. Vinyl chloride is oxidized to carbon dioxide in this type of plume and does not accumulate. The following sequence of reactions occurs in a plume that exhibits this type of mixed behavior:

Perchloroethene → Trichloroethene →
Dichloroethene → Vinyl chloride → Carbon dioxide

The trichloroethene, dichloroethene, and vinyl chloride may attenuate at approximately the same rate, and thus these reactions may be confused with simple dilution. Note that no ethene is produced during this reaction. Vinyl chloride is removed from the system much faster under these conditions than it is under vinyl chloride-reducing conditions.

A less desirable scenario—but one in which all contaminants may be entirely biodegraded— involves a plume in which all chlorinated aliphatic hydrocarbons are reductively dechlorinated via Type 1 or Type 2 behavior. Vinyl chloride is reduced to ethene, which may be further reduced to ethane or methane. The following sequence of reactions occurs in this type of plume:

Perchloroethene → Trichloroethene →
Dichloroethene → Vinyl chloride → Ethene → Ethane

This sequence has been investigated by Freedman and Gossett (13). In this type of plume, vinyl chloride degrades more slowly than trichloroethene and thus tends to accumulate.

Protocol for Quantifying Natural Attenuation During the Remedial Investigation Process

The primary objective of the natural attenuation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations in ground water to below risk-based corrective action or regulatory levels before potential receptor exposure pathways are completed. This requires a projection of the potential extent and concentration of the contaminant plume in time and space. The projection should be based on historic variations in, and the current extent and concentrations of, the contaminant plume, as well as the measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, the investigator must provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of conservative solute fate-and-transport model 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 contaminant plume.

Figure 1 outlines the steps involved in the natural attenuation demonstration. This figure also shows the important regulatory decision points in the process of implementing natural attenuation. Predicting the fate of a contaminant plume requires the quantification of solute transport and transformation processes. Quantification of contaminant migration and attenuation rates and successful implementation of the natural attenuation remedial option requires completion of the following steps:

1. Review available site data, and develop a preliminary conceptual model.
2. Screen the site, and assess the potential for natural attenuation.
3. Collect additional site characterization data to support natural attenuation, as required.
4. Refine the conceptual model, complete premodeling calculations, and document indicators of natural attenuation.
5. Simulate natural attenuation using analytical or numerical solute fate-and-transport models that allow incorporation of a biodegradation term, as necessary.
6. Identify potential receptors, and conduct an exposure-pathway analysis.
7. Evaluate the practicability and potential efficiency of supplemental source removal options.
8. If natural attenuation with or without source removal is acceptable, prepare a long-term monitoring plan.
9. Present findings to regulatory agencies, and obtain approval for remediation by natural attenuation.

Review Available Site Data, and Develop a Preliminary Conceptual Model

Existing site characterization data should be reviewed and used to develop a conceptual model for the site. The preliminary conceptual model will help identify any shortcomings in the data and will allow placement of additional data collection points in the most scientifically advantageous and cost-effective manner. A conceptual model is a three-dimensional representation of the ground-water flow and solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site. This type of conceptual model differs from the conceptual site models that risk assessors commonly use that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. The ground-water system conceptual model, however, facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual model can be used to help determine optimal placement of additional data collection points (as necessary) to aid in the natural attenuation investigation and to develop the solute fate-and-transport model.

Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort. In cases where few or no site-specific data are available, all future site characterization activities should be designed to collect the data necessary to screen the site to determine the potential for remediation by natural attenuation. The additional costs incurred by such data collection are greatly outweighed by the cost savings that will be realized if natural attenuation is selected. Moreover, most of the data collected in support of natural attenuation can be used to design and support other remedial measures.

Table 1 contains the soil and ground-water analytical protocol for natural attenuation of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Table 1A lists a standard set of methods, while Table 1B lists methods that are under development and/or consideration. Any plan to collect additional ground-water and soil quality data should include targeting the analytes listed in Table 1A, and possibly Table 1B.

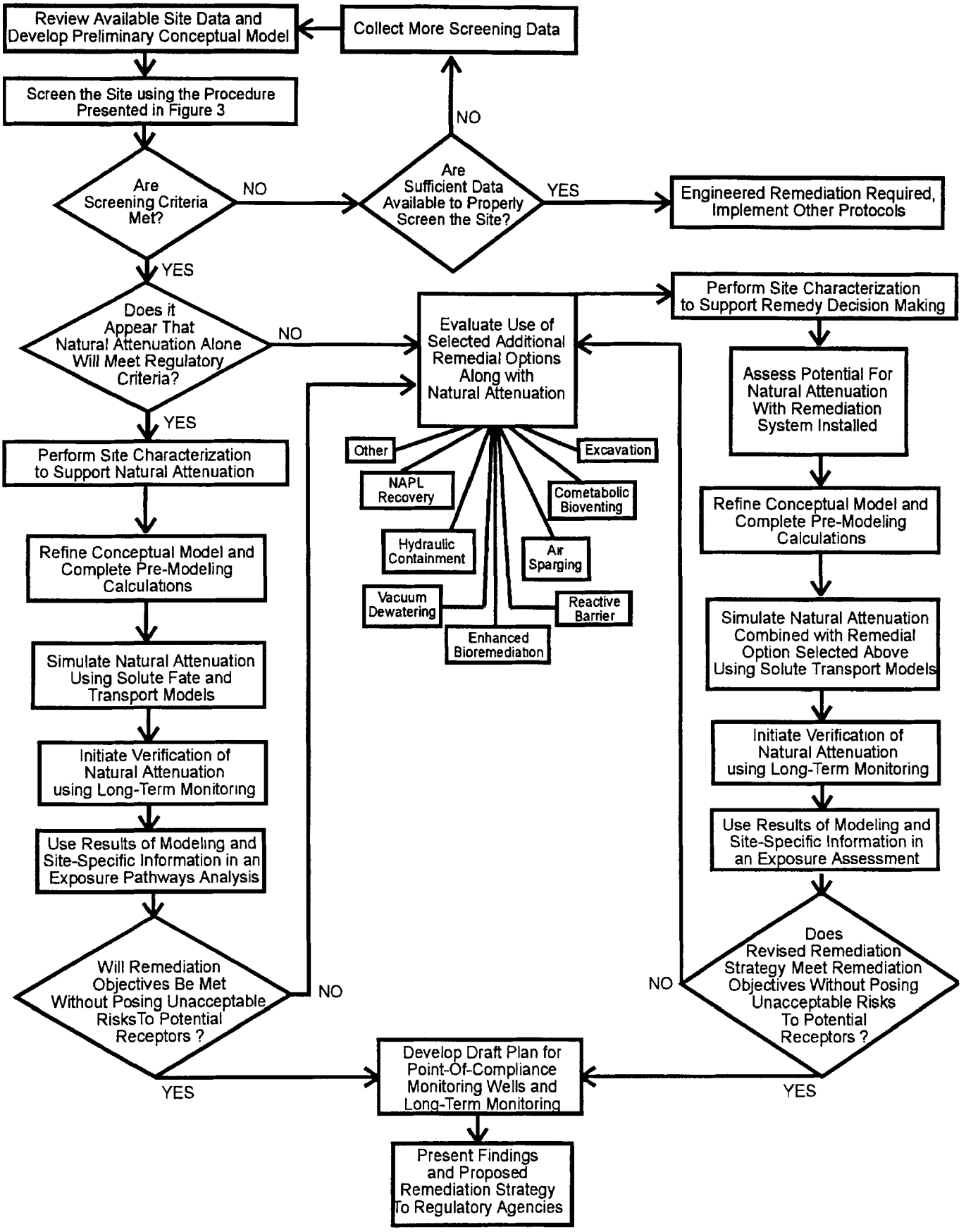


Figure 1. Natural attenuation of chlorinated solvents flow chart.

Table 1A. Soil and Ground-Water Analytical Protocol[a]

Matrix	Analysis	Method/Reference[b-e]	Comments[f,g]	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Volatile organic compounds	SW8260A	Handbook method modified for field extraction of soil using methanol	Useful for determining the extent of soil contamination, the contaminant mass present, and the need for source removal	Each soil sampling round	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil	Total organic carbon (TOC)	SW9060, modified for soil samples	Procedure must be accurate over the range of 0.5 to 15% TOC	The amount of TOC in the aquifer matrix influences contaminant migration and biodegradation	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Soil gas	O_2, CO_2	Field soil gas analyzer		Useful for determining bioactivity in the vadose zone	At initial sampling and respiration testing	Reuseable 3-L Tedlar bags	Field
Soil gas	Fuel and chlorinated volatile organic compounds	EPA Method TO-14		Useful for determining the distribution of chlorinated and BTEX compounds in soil	At initial sampling	1-L Summa canister	Fixed-base
Water	Volatile organic compounds	SW8260A	Handbook method; analysis may be extended to higher molecular-weight alkyl benzenes	Method of analysis for BTEX and chlorinated solvents/byproducts	Each sampling round	Collect water samples in a 40-mL volatile organic analysis vial; cool to 4°C; add hydrochloric acid to pH 2	Fixed-base
Water	Polycyclic aromatic hydro-carbons (PAHs) (optional; intended for diesel and other heavy oils)	Gas chromatography/ mass spectroscopy Method SW8270B; high-performance liquid chromatography Method SW8310	Analysis needed only when required for regulatory compliance	PAHs are components of fuel and are typically analyzed for regulatory compliance	As required by regulations	Collect 1 L of water in a glass container; cool to 4°C	Fixed-base
Water	Oxygen	DO meter	Refer to Method A4500 for a comparable laboratory procedure	Concentrations less than 1 mg/L generally indicate an anaerobic pathway	Each sampling round	Measure DO on site using a flow-through cell	Field
Water	Nitrate	Iron chromatography Method E300; anion method	Method E300 is a handbook method; also provides chloride data	Substrate for microbial respiration if oxygen is depleted	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; add H_2SO_4 to pH less than 2; cool to 4°C	Fixed-base
Water	Iron(II) (Fe^{+2})	Colorimetric HACH Method 8146	Filter if turbid	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	Each sampling round	Collect 100 mL of water in a glass container	Field

Table 1A. Soil and Ground-Water Analytical Protocol[a] (Continued)

Matrix	Analysis	Method/Reference[b-e]	Comments[f,g]	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Sulfate (SO_4-2)	Iron chromatography Method E300 or HACH Method 8051	Method E300 is a handbook method, HACH Method 8051 is a colorimetric method; use one or the other	Substrate for anaerobic microbial respiration	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C	E300 = Fixed-base HACH Method 8051 = Field
Water	Methane, ethane, and ethene	Kampbell et al. (35) or SW3810, modified	Method published by EPA researchers	The presence of CH_4 suggests biodegradation of organic carbon via methanogensis; ethane and ethane are produced during reductive dechlorination	Each sampling round	Collect water samples in 50 mL glass serum bottles with butyl gray/Teflon-lined caps; add H_2SO_4 to pH less than 2; cool to 4°C	Fixed-base
Water	Alkalinity	HACH alkalinity test kit Model AL AP MG-L	Phenolphtalein method	Water quality parameter used to measure the buffering capacity of ground water; can be used to estimate the amount of CO_2 produced during biodegradation	Each sampling round	Collect 100 mL of water in glass container	Field
Water	Oxidation-reduction potential	A2580B	Measurements made with electrodes, results are displayed on a meter, protect samples from exposure to oxygen; report results against a silver/silver chloride reference electrode	The oxidation-reduction potential of ground water influences and is influenced by the nature of the biologically mediated degradation of contaminants; the oxidation-reduction potential of ground water may range from more than 800 mV to less than -400 mV	Each sampling round	Collect 100 to 250 mL of water in a glass container	Field
Water	pH	Field probe with direct reading meter	Field	Aerobic and anaerobic processes are pH-sensitive	Each sampling round	Collect 100 to 250 mL of water in a glass or plastic container; analyze immediately	Field
Water	Temperature	Field probe with direct reading meter	Field only	Well development	Each sampling round	Not applicable	Field
Water	Conductivity	E120.1/SW9050, direct reading meter	Protocols/ Handbook methods	Water quality parameter used as a marker to verify that site samples are obtained from the same ground-water system	Each sampling round	Collect 100 to 250 mL of water in a glass or plastic container	Field
Water	Chloride	Mercuric nitrate titration A4500-Cl^- C	Ion chromatography Method E300; Method SW9050 may also be used	Final product of chlorinated solvent reduction; can be used to estimate dilution in calculation of rate constant	Each sampling round	Collect 250 mL of water in a glass container	Fixed-base

Table 1A. Soil and Ground-Water Analytical Protocol[a] (Continued)

Matrix	Analysis	Method/Reference[b-e]	Comments[f,g]	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Chloride (optional; see data use)	HACH chloride test kit Model 8-P	Silver nitrate titration	As above, and to guide selection of additional data points in real time while in the field	Each sampling round	Collect 100 mL of water in a glass container	Field
Water	Total organic carbon	SW9060	Laboratory	Used to classify plumes and to determine whether anaerobic metabolism of chlorinated solvents is possible in the absence of anthropogenic carbon	Each sampling round	Collect 100 mL of water in a glass container; cool	Laboratory

[a] Analyses other than those listed in this table may be required for regulatory compliance.
[b] "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods* (29).
[c] "E" refers to *Methods for Chemical Analysis of Water and Wastes* (30).
[d] "HACH" refers to the Hach Company catalog (31).
[e] "A" refers to *Standard Methods for the Examination of Water and Wastewater* (32).
[f] "Handbook" refers to the AFCEE *Handbook to Support the Installation Restoration Program (IRP) Remedial Investigations and Feasibility Studies (RI/FS)* (33).
[g] "Protocols" refers to the AFCEE *Environmental Chemistry Function Installation Restoration Program Analytical Protocols* (34).

Table 1B. Soil and Ground-Water Analytical Protocol: Special Analyses Under Development and/or Consideration[a,b]

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Container, Preservation	Field or Fixed-Base Laboratory
Soil	Biologically available iron(III)	Under development	HCl extraction followed by quantification of released iron(III)	To predict the possible extent of iron reduction in an aquifer	One round of sampling in five borings, five cores from each boring	Collect minimum 1-inch diameter core samples into a plastic liner; cap and prevent aeration	Laboratory
Water	Nutritional quality of native organic matter	Under development	Spectro-photometric method	To determine the extent of reductive dechlorination allowed by the supply of electron donor	One round of sampling in two to five wells	Collect 1,000 mL in an amber glass container	Laboratory
Water	Hydrogen (H_2)	Equilibration with gas in the field; determined with a reducing gas detector	Specialized analysis	To determine the terminal electron accepting process, predicts the possibility for reductive dechlorination	One round of sampling	Sampling at well head requires the production of 100 mL per minute of water for 30 minutes	Field
Water	Oxygenates (including methyl-*tert*-butyl ether, ethers, acetic acid, methanol, and acetone)	SW8260/8015[c]	Laboratory	Contaminant or electron donors for dechlorination of solvents	At least one sampling round or as determined by regulators	Collect 1 L of water in a glass container; preserve with HCl	Laboratory

[a] Analyses other than those listed in this table may be required for regulatory compliance.
[b] Site characterization should not be delayed if these methods are unavailable.
[c] "SW" refers to *Test Methods for Evaluating Solid Waste, Physical and Chemical Methods* (29).

Screen the Site, and Assess the Potential for Natural Attenuation

After reviewing available site data and developing a preliminary conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful in determining whether natural attenuation will be sufficient to prevent a dissolved contaminant plume from completing exposure pathways, or from reaching a predetermined point of compliance, in concentrations above applicable regulatory or risk-based corrective action standards. Determining the likelihood of exposure pathway completion is an important component of the natural attenuation investigation. This is achieved by estimating the migration and future extent of the plume based on contaminant properties, including volatility, sorptive properties, and biodegradability; aquifer properties, including hydraulic gradient, hydraulic conductivity, porosity, and total organic carbon (TOC) content; and the location of the plume and contaminant source relative to potential receptors (i.e., the distance between the leading edge of the plume and the potential receptor exposure points). These parameters (estimated or actual) are used in this section to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

If, after completing the steps outlined in this section, it appears that natural attenuation will be a significant factor in contaminant removal, detailed site characterization activities in support of this remedial option should be performed. If exposure pathways have already been completed and contaminant concentrations exceed regulatory levels, or if such completion is likely, other remedial measures should be considered, possibly in conjunction with natural attenuation. Even so, the collection of data in support of the natural attenuation option can be integrated into a comprehensive remedial plan and may help reduce the cost and duration of other remedial measures, such as intensive source removal operations or pump-and-treat technologies. For example, dissolved iron concentrations can have a profound influence on the design of pump-and-treat systems.

Based on the experience of the authors, in an estimated 80 percent of fuel hydrocarbon spills at federal facilities, natural attenuation alone will be protective of human health and the environment. For spills of chlorinated aliphatic hydrocarbons at federal facilities, however, natural attenuation alone will be protective of human health and the environment in an estimated 20 percent of the cases. With this in mind, it is easy to understand why an accurate assessment of the potential for natural biodegradation of chlorinated compounds should be made before investing in a detailed study of natural attenuation. The screening process presented in this section is outlined in Figure 2. This approach should allow the investigator to determine whether natural attenuation is likely to be a viable remedial alternative before additional time and money are expended. The data required to make the preliminary assessment of natural attenuation can also be used to aid the design of an engineered remedial solution, should the screening process suggest that natural attenuation alone is not feasible.

The following information is required for the screening process:

- The chemical and geochemical data presented in Table 2 for a minimum of six samples. Figure 3 shows the approximate location of these data collection points. If other contaminants are suspected, then data on the concentration and distribution of these compounds also should be obtained.
- Locations of source(s) and receptor(s).
- An estimate of the contaminant transport velocity and direction of ground-water flow.

Once these data have been collected, the screening process can be undertaken. The following steps summarize the screening process:

1. Determine whether biodegradation is occurring using geochemical data. If biodegradation is occurring, proceed to Step 2. If it is not, assess the amount and types of data available. If data are insufficient to determine whether biodegradation is occurring, collect supplemental data.
2. Determine ground-water flow and solute transport parameters. Hydraulic conductivity and porosity may be estimated, but the ground-water gradient and flow direction may not. The investigator should use the highest hydraulic conductivity measured at the site during the preliminary screening because solute plumes tend to follow the path of least resistance (i.e., highest hydraulic conductivity). This will give the "worst case" estimate of solute migration over a given period.
3. Locate sources and receptor exposure points.
4. Estimate the biodegradation rate constant. Biodegradation rate constants can be estimated using a conservative tracer found commingled with the contaminant plume, as described by Wiedemeier et al. (36). When dealing with a plume that contains only chlorinated solvents, this procedure will have to be modified to use chloride as a tracer. Rate constants derived from microcosm studies can also be used. If it is not possible to estimate the biodegradation rate using these procedures, then use a range of accepted literature values for biodegradation of the contaminants of concern.

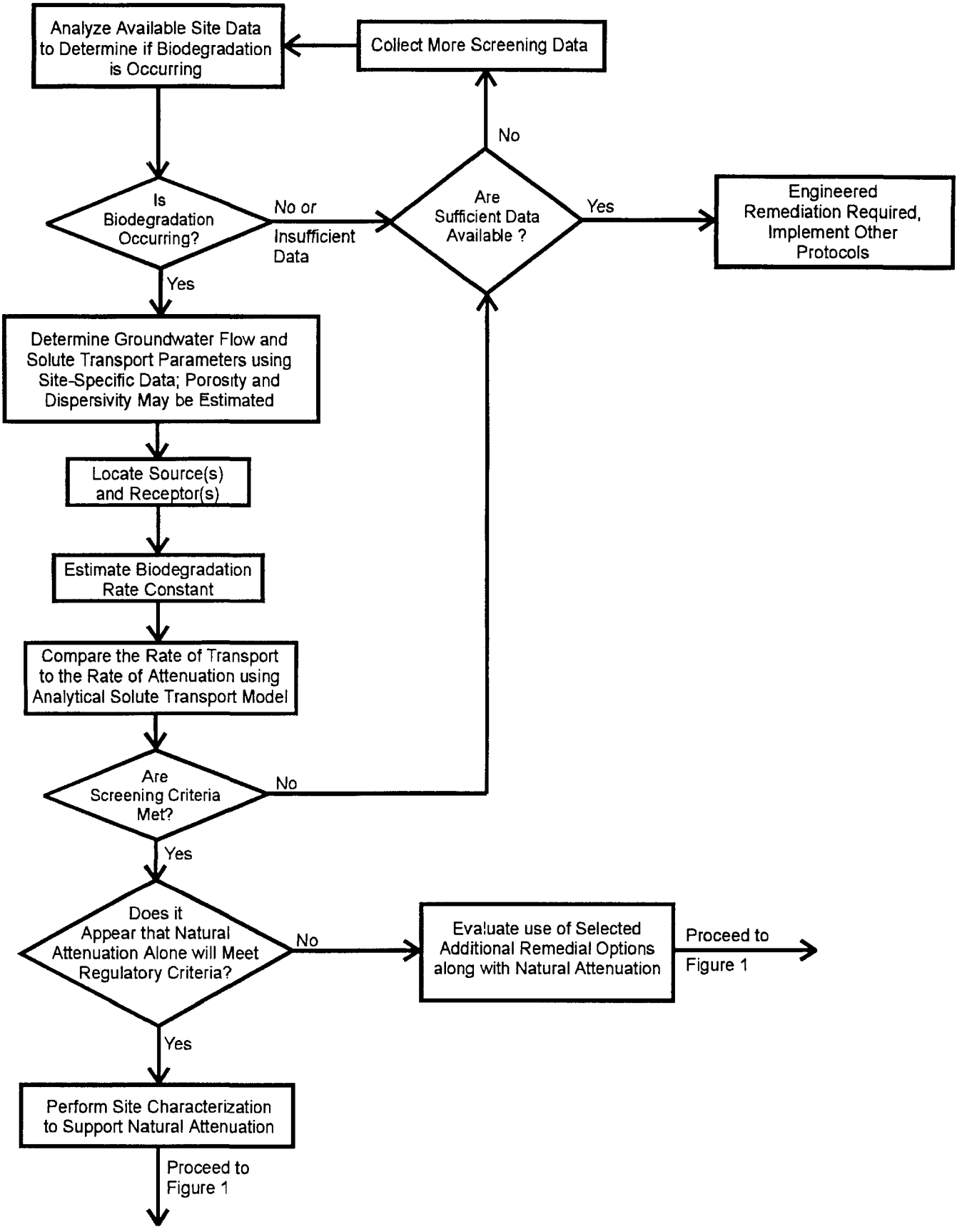


Figure 2. Initial screening process flow chart.

Table 2. Analytical Parameters and Weighting for Preliminary Screening

Analyte	Concentration in Most Contaminated Zone	Interpretation	Points Awarded
Oxygen[a]	< 0.5 mg/L	Tolerated; suppresses reductive dechlorination at higher concentrations	3
Oxygen[a]	> 1 mg/L	Vinyl chloride may be oxidized aerobically, but reductive dechlorination will not occur	-3
Nitrate[a]	< 1 mg/L	May compete with reductive pathway at higher concentrations	2
Iron (II)[a]	> 1 mg/L	Reductive pathway possible	3
Sulfate[a]	< 20 mg/L	May compete with reductive pathway at higher concentrations	2
Sulfide[a]	> 1 mg/L	Reductive pathway possible	3
Methane[a]	> 0.1 mg/L	Ultimate reductive daughter product	2
	> 1	Vinyl chloride accumulates	3
	< 1	Vinyl chloride oxidizes	
Oxidation reduction potential[a]	< 50 mV against Ag/AgCl	Reductive pathway possible	< 50 mV = 1 < -100 mV = 2
pH[a]	5 < pH < 9	Tolerated range for reductive pathway	
DOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature[a]	> 20°C	At T > 20ÉC, biochemical process is accelerated	1
Carbon dioxide	> 2x background	Ultimate oxidative daughter product	1
Alkalinity	> 2x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride[a]	> 2x background	Daughter product of organic chlorine; compare chloride in plume to background conditions	2
Hydrogen	> 1 nM	Reductive pathway possible; vinyl chloride may accumulate	3
Hydrogen	< 1 nM	Vinyl chloride oxidized	
Volatile fatty acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX[a]	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Perchloroethene[a]		Material released	
Trichloroethene[a]		Material released or daughter product of perchloroethene	2[b]
Dichloroethene[a]		Material released or daughter product of trichloroethene; if amount of *cis*-1,2-dichloroethene is greater than 80% of total dichloroethene, it is likely a daughter product of trichloroethene	2[b]
Vinyl chloride[a]		Material released or daughter product of dichloroethenes	2[b]
Ethene/Ethane	< 0.1 mg/L	Daughter product of vinyl chloride/ethene	> 0.01 mg/L= 2 > 0.1 = 3
Chloroethane[a]		Daughter product of vinyl chloride under reducing conditions	2
1,1,1-Trichloroethane[a]		Material released	
1,1-dichloroethene[a]		Daughter product of trichloroethene or chemical reaction of 1,1,1-trichloroethane	

[a] Required analysis.
[b] Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

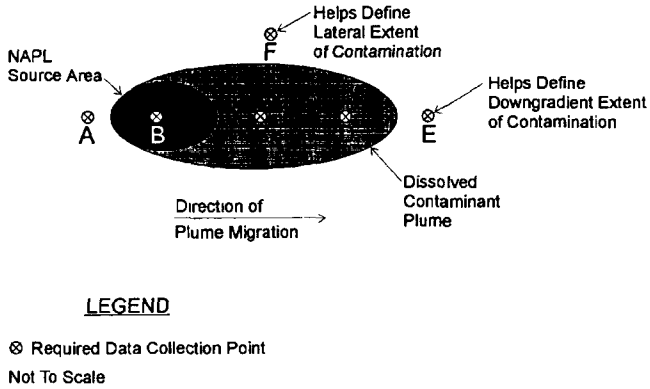


Figure 3. Data collection points required for screening.

5. Compare the rate of transport to the rate of attenuation, using analytical solutions or a screening model such as BIOSCREEN.
6. Determine whether the screening criteria are met.

Each of these steps is described in detail below.

Step 1: Determine Whether Biodegradation Is Occurring

The first step in the screening process is to sample at least six wells that are representative of the contaminant flow system and to analyze the samples for the parameters listed in Table 2. Samples should be taken 1) from the most contaminated portion of the aquifer (generally in the area where NAPL currently is present or was present in the past); 2) downgradient from the NAPL source area but still in the dissolved contaminant plume; 3) downgradient from the dissolved contaminant plume; and 4) from upgradient and lateral locations that are not affected by the plume.

Samples collected in the NAPL source area allow determination of the dominant terminal electron-accepting processes at the site. In conjunction with samples collected in the NAPL source zone, samples collected in the dissolved plume downgradient from the NAPL source zone allow the investigator to determine whether the plume is degrading with distance along the flow path and what the distribution of electron acceptors and donors and metabolic byproducts might be along the flow path. The sample collected downgradient from the dissolved plume aids in plume delineation and allows the investigator to determine whether metabolic byproducts are present in an area of ground water that has been remediated. The upgradient and lateral samples allow delineation of the plume and indicate background concentrations of the electron acceptors and donors.

After these samples have been analyzed for the parameters listed in Table 2, the investigator should analyze the data to determine whether biodegradation is occurring. The right-hand column of Table 2 contains scoring values that can be used for this task. For example, if the DO concentration in the area of the plume with the highest contaminant concentration is less than 0.5 milligrams per liter, this parameter is awarded 3 points. Table 3 summarizes the range of possible scores and gives an interpretation for each score. If the site scores a total of 15 or more points, biodegradation is probably occurring, and the investigator can proceed to Step 2. This method relies on the fact that biodegradation will cause predictable changes in ground-water chemistry.

Table 3. Interpretation of Points Awarded During Screening Step 1

Score	Interpretation
0 to 5	Inadequate evidence for biodegradation of chlorinated organics
6 to 14	Limited evidence for biodegradation of chlorinated organics
15 to 20	Adequate evidence for biodegradation of chlorinated organics
> 20	Strong evidence for biodegradation of chlorinated organics

Consider the following two examples. Example 1 contains data for a site with strong evidence that reductive dechlorination is occurring. Example 2 contains data for a site with strong evidence that reductive dechlorination is not occurring.

Example 1. Strong Evidence for Biodegradation of Chlorinated Organics

Analyte	Concentration in Most Contaminated Zone	Points Awarded
DO	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron(II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	5 mg/L	3
Oxidation-reduction potential	-190 mV	2
Chloride	3x background	2
Perchloroethene (released)	1,000 µg/L	0
Trichloroethene (none released)	1,200 µg/L	2
cis-1,2-Dichloroethene (none released)	500 µg/L	2
Vinyl chloride (none released)	50 µg/L	2
	Total points awarded	23

In this example, the investigator can infer that biodegradation is occurring and may proceed to Step 2.

Example 2. Biodegradation of Chlorinated Organics Unlikely

Analyte	Concentration in Most Contaminated Zone	Points Awarded
DO	3 mg/L	-3
Nitrate	0.3 mg/L	2
Iron(II)	Not detected	0
Sulfate	10 mg/L	2
Methane	ND	0
Oxidation-reduction potential	100 mV	0
Chloride	Background	0
Trichloroethene (released)	1,200 µg/L	0
cis-1,2-Dichloroethene	Not detected	0
Vinyl chloride	ND	0
	Total points awarded	1

In this example, the investigator can infer that biodegradation is probably not occurring or is occurring too slowly to be a viable remedial option. In this case, the investigator cannot proceed to Step 2 and will likely have to implement an engineered remediation system.

Step 2: Determine Ground-Water Flow and Solute Transport Parameters

After biodegradation has been shown to be occurring, it is important to quantify ground-water flow and solute transport parameters. This will make it possible to use a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. To use an analytical model, it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of the porosity and dispersivity. The coefficient of retardation also is helpful to know. Quantification of these parameters is discussed by Wiedemeier et al. (1).

To make modeling as accurate as possible, the investigator must have site-specific hydraulic gradient and hydraulic conductivity data. To determine the ground-water flow and solute transport direction, the site must have at least three accurately surveyed wells. The porosity and dispersivity are generally estimated using accepted literature values for the types of sediments found at the site. If the investigator does not have TOC data for soil, the coefficient of retardation can be estimated; however, assuming that the solute transport and ground-water velocities are the same may be more conservative.

Step 3: Locate Sources and Receptor Exposure Points

To determine the length of flow for the predictive modeling conducted in Step 5, it is important to know the distance between the source of contamination, the downgradient end of the dissolved plume, and any potential downgradient or cross-gradient receptors.

Step 4: Estimate the Biodegradation Rate Constant

Biodegradation is the most important process that degrades contaminants in the subsurface; therefore, the biodegradation rate is one of the most important model input parameters. Biodegradation of chlorinated aliphatic hydrocarbons can commonly be represented as a first-order rate constant. Site-specific biodegradation rates generally are best to use. Calculation of site-specific biodegradation rates is discussed by Wiedemeier et al. (1, 36, 37). If determining site-specific biodegradation rates is impossible, then literature values for the biodegradation rate of the contaminant of interest must be used. It is generally best to start with the average value and then to vary the model input to predict "best case" and "worst case" scenarios. Estimated biodegradation rates can be used only after biodegradation has been shown to be occurring (see Step 1).

Step 5: Compare the Rate of Transport to the Rate of Attenuation

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation is best accomplished using an analytical model. Several analytical models are available, but the BIOSCREEN model is probably the simplest to use. This model is nonproprietary and is available from the Robert S. Kerr Laboratory's home page on the Internet (www.epa.gov/ada/kerrlab.html). The BIOSCREEN model is based on Domenico's solution to the advection-dispersion equation (38), and allows use of either a first-order biodegradation rate or an instantaneous reaction between contaminants and electron acceptors to simulate the effects of biodegradation. To model transport of chlorinated aliphatic hydrocarbons using BIOSCREEN, only the first-order decay rate option should be used. BIOCHLOR, a similar model, is under development by the Technology Transfer Division of AFCEE. This model will likely use the same analytical solution as BIOSCREEN but will be geared towards evaluating transport of chlorinated compounds under the influence of biodegradation.

The primary purpose of comparing the rate of transport with the rate of attenuation is to determine whether the

residence time along the flow path is adequate to be protective of human health and the environment (i.e., to qualitatively estimate whether the contaminant is attenuating at a rate fast enough to allow degradation of the contaminant to acceptable concentrations before receptors are reached). It is important to perform a sensitivity analysis to help evaluate the confidence in the preliminary screening modeling effort. If modeling shows that receptors may not be exposed to contaminants at concentrations above risk-based corrective action criteria, then the screening criteria are met, and the investigator can proceed with the natural attenuation feasibility study.

Step 6: Determine Whether the Screening Criteria Are Met

Before proceeding with the full-scale natural attenuation feasibility study, the investigator should ensure that the answers to all of the following criteria are "yes":

- Has the plume moved a distance less than expected, based on the known (or estimated) time since the contaminant release and the contaminant velocity, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, as well as estimates of effective porosity and contaminant retardation?
- Is it likely that the contaminant mass is attenuating at rates sufficient to be protective of human health and the environment at a point of discharge to a sensitive environmental receptor?
- Is the plume going to attenuate to concentrations less than risk-based corrective action guidelines before reaching potential receptors?

Collect Additional Site Characterization Data To Support Natural Attenuation, As Required

Detailed site characterization is necessary to document the potential for natural attenuation. Review of existing site characterization data is particularly useful before initiating site characterization activities. Such review should allow identification of data gaps and guide the most effective placement of additional data collection points.

There are two goals during the site characterization phase of a natural attenuation investigation. The first is to collect the data needed to determine whether natural mechanisms of contaminant attenuation are occurring at rates sufficient to protect human health and the environment. The second is to provide sufficient site-specific data to allow prediction of the future extent and concentration of a contaminant plume through solute fate-and-transport modeling. Because the burden of proof for natural attenuation is on the proponent, detailed site characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of natural attenuation requires that the following site-specific parameters be determined:

- The extent and type of soil and ground-water contamination.
- The location and extent of contaminant source area(s) (i.e., areas containing mobile or residual NAPL).
- The potential for a continuing source due to leaking tanks or pipelines.
- Aquifer geochemical parameters.
- Regional hydrogeology, including drinking water aquifers and 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 (current and future); lithology; site stratigraphy, including identification of transmissive and nontransmissive units; grain-size distribution (sand versus silt versus clay); aquifer hydraulic conductivity; ground-water hydraulic information; preferential flow paths; locations and types of surface water bodies; and areas of local ground-water recharge and discharge.
- Identification of potential exposure pathways and receptors.

The following sections describe the methodologies that should be implemented to allow successful site characterization in support of natural attenuation. Additional information can be obtained from Wiedemeier et al. (1, 37).

Soil Characterization

To adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of mobile and residual NAPL that can act as a continuing source of ground-water contamination, extensive soil characterization must be completed. Depending on the status of the site, this work may have been completed during previous remedial investigation activities. The results of soils characterization will be used as input into a solute fate-and-transport model to help define a contaminant source term and to support the natural attenuation investigation.

The purpose of soil sampling is to determine the subsurface distribution of hydrostratigraphic units and the distribution of mobile and residual NAPL. These objectives can be achieved through the use of conventional soil borings or direct-push methods (e.g., Geoprobe or cone penetrometer testing). All soil samples should be collected, described, analyzed, and disposed of in accordance with local, state, and federal guidance. Wiedemeier et al. (1) present suggested procedures for soil sample collection. These procedures may require modification to comply with local, state, and federal regulations or to accommodate site-specific conditions.

The analytical protocol to be used for soil sample analysis is presented in Table 1. This analytical protocol

includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Knowledge of the location, distribution, concentration, and total mass of contaminants of regulatory concern sorbed to soils or present as residual and/or mobile NAPL is required to calculate contaminant partitioning from NAPL into ground water. Knowledge of the TOC content of the aquifer matrix is important for sorption and solute-retardation calculations. TOC samples should be collected from a background location in the stratigraphic horizon(s) where most contaminant transport is expected to occur. Oxygen and carbon dioxide measurements of soil gas can be used to find areas in the unsaturated zone where biodegradation is occurring. Knowledge of the distribution of contaminants in soil gas can be used as a cost-effective way to estimate the extent of soil contamination.

Ground-Water Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of natural attenuation, ground-water samples must be collected and analyzed. Biodegradation of organic compounds, whether natural or anthropogenic, brings about measurable changes in the chemistry of ground water in the affected area. By measuring these changes, documentation and quantitative evaluation of natural attenuation's importance at a site are possible.

Ground-water sampling is conducted to determine the concentrations and distribution of contaminants, daughter products, and ground-water geochemical parameters. Ground-water samples may be obtained from monitoring wells or with point-source sampling devices such as a Geoprobe, Hydropunch, or cone penetrometer. All ground-water samples should be collected in accordance with local, state, and federal guidelines. Wiedemeier et al. (1) suggest procedures for ground-water sample collection. These procedures may need to be modified to comply with local, state, and federal regulations or to accommodate site-specific conditions.

The analytical protocol for ground-water sample analysis is presented in Table 1. This analytical protocol includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Data obtained from the analysis of ground water for these analytes is used to scientifically document natural attenuation and can be used as input into a solute fate-and-transport model. The following paragraphs describe each ground-water analytical parameter and the use of each analyte in the natural attenuation demonstration.

Volatile organic compound analysis (by Method SW8260a) is used to determine the types, concentrations, and distributions of contaminants and daughter products in the aquifer. DO is the electron acceptor most thermodynamically favored by microbes for the biodegradation of organic carbon, whether natural or anthropogenic. Reductive dechlorination will not occur, however, if DO concentrations are above approximately 0.5 milligrams per liter. During aerobic biodegradation of a substrate, DO concentrations decrease because of the microbial oxygen demand. After DO depletion, anaerobic microbes will use nitrate as an electron acceptor, followed by iron(III), then sulfate, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the oxidation-reduction potential of the ground water further into the realm where reductive dechlorination can occur. The oxidation-reduction potential range of sulfate reduction and methanogenesis is optimal, but reductive dechlorination may occur under nitrate- and iron(III)-reducing conditions as well. Because reductive dechlorination works best in the sulfate-reduction and methanogenesis oxidation-reduction potential range, competitive exclusion between microbial sulfate reducers, methanogens, and reductive dechlorinators can occur.

After DO has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation via denitrification. In some cases iron(III) is used as an electron acceptor during anaerobic biodegradation of electron donors. During this process, iron(III) is reduced to iron(II), which may be soluble in water. Iron(II) concentrations can thus be used as an indicator of anaerobic degradation of fuel compounds. After DO, nitrate, and bioavailable iron(III) have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulfate reduction and results in the production of sulfide. During methanogenesis (an anaerobic biodegradation process), carbon dioxide (or acetate) is used as an electron acceptor, and methane is produced. Methanogenesis generally occurs after oxygen, nitrate, bioavailable iron(III), and sulfate have been depleted in the treatment zone. The presence of methane in ground water is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane in ground water above background concentrations in contact with fuels is indicative of microbial degradation of fuel hydrocarbons.

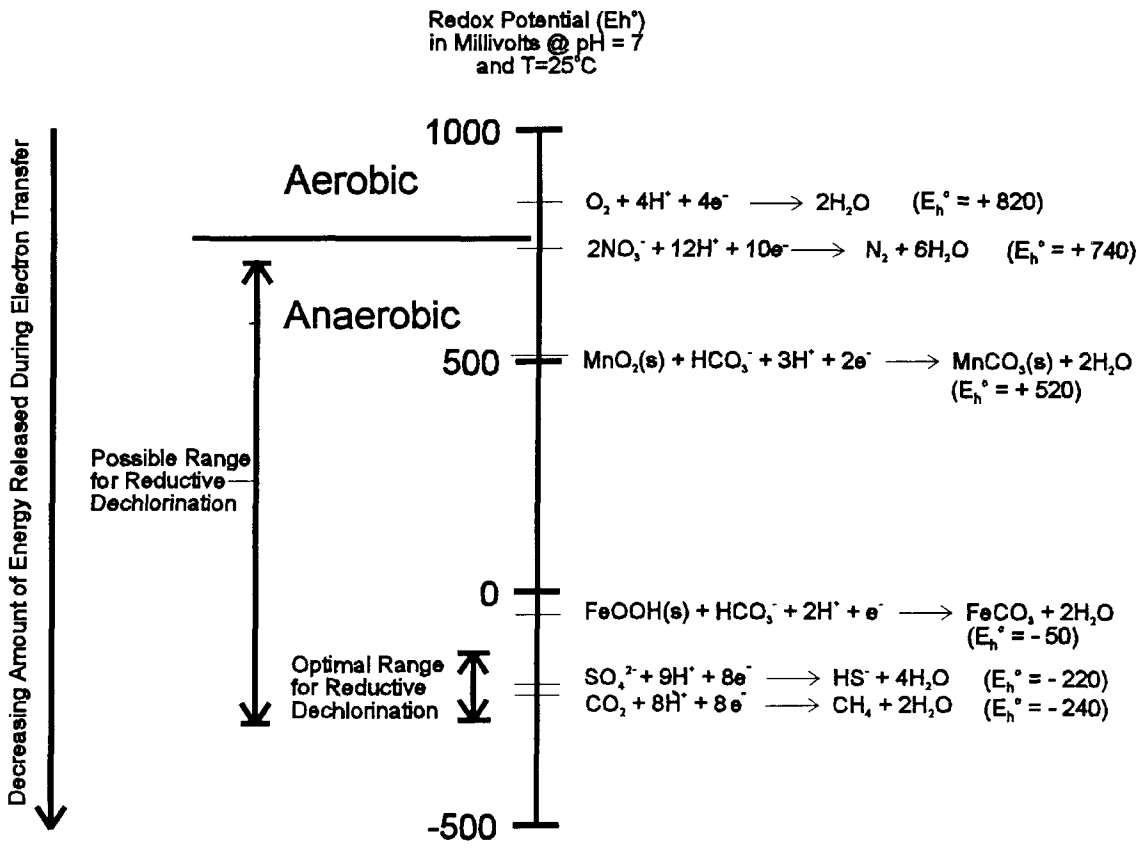
The total alkalinity of a ground-water system is indicative of a water's capacity to neutralize acid. Alkalinity is defined as "the net concentration of strong base in excess of strong acid with a pure CO_2-water system as the point of reference" (39). Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. These species result from the dissolution of rock (especially carbonate rocks), the transfer of carbon dioxide from the atmosphere, and the

respiration of microorganisms. Alkalinity is important in the maintenance of ground-water pH because it buffers the ground-water system against acids generated during both aerobic and anaerobic biodegradation.

In general, areas contaminated by fuel hydrocarbons exhibit a total alkalinity that is higher than that seen in background areas. This is expected because the microbially mediated reactions causing biodegradation of fuel hydrocarbons cause an increase in the total alkalinity in the system. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and are less pronounced during methanogenesis (40). In addition, Willey et al. (41) show that short-chain aliphatic acid ions produced during biodegradation of fuel hydrocarbons can contribute to alkalinity in ground water.

The oxidation-reduction potential of ground water is a measure of electron activity and an indicator of the relative tendency of a solution to accept or transfer electrons. Redox reactions in ground water containing organic compounds (natural or anthropogenic) are usually biologically mediated; therefore, the oxidation-reduction potential of a ground-water system depends on and influences rates of biodegradation. Knowledge of the oxidation-reduction potential of ground water also is important because some biological processes operate only within a prescribed range of redox conditions. The oxidation-reduction potential of ground water generally ranges from -400 to 800 millivolts (mV). Figure 4 shows the typical redox conditions for ground water when different electron acceptors are used.

Oxidation-reduction potential can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the oxidation-reduction potential of the ground water while in the field helps the field scientist to determine the approximate location of the contaminant plume. To perform this task, it is important to have at least one redox measurement (preferably more) from a well located upgradient from the plume. Oxidation-reduction potential measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected ground-water samples (which can affect oxidation-reduction



Modified From Bouwer (1994)

Figure 4. Redox potentials for various electron acceptors.

potential measurements), it is important to minimize potential aeration.

Dissolved hydrogen concentrations can be used to determine the dominant terminal electron-accepting process in an aquifer. Because of the difficulty in obtaining hydrogen analyses commercially, this parameter should be considered optional at this time. Table 4 presents the range of hydrogen concentrations for a given terminal electron-accepting process. Much research has been done on the topic of using hydrogen measurements to delineate terminal electron-accepting processes (42-44). Because the efficiency of reductive dechlorination differs for methanogenic, sulfate-reducing, iron(III)-reducing, or denitrifying conditions, it is helpful to have hydrogen concentrations to help delineate redox conditions when evaluating the potential for natural attenuation of chlorinated ethenes in ground-water systems. Collection and analysis of ground-water samples for dissolved hydrogen content is not yet commonplace or standardized, however, and requires a relatively expensive field laboratory setup.

Table 4. Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

Terminal Electron-Accepting Process	Hydrogen Concentration (nanomoles per liter)
Denitrification	< 0.1
Iron(III) reduction	0.2 to 0.8
Sulfate reduction	1 to 4
Methanogenesis	> 5

Because the pH, temperature, and conductivity of a ground-water sample can change significantly shortly following sample acquisition, these parameters must be measured in the field in unfiltered, unpreserved, "fresh" water collected by the same technique as the samples taken for DO and redox analyses. The measurements should be made in a clean glass container separate from those intended for laboratory analysis, and the measured values should be recorded in the ground-water sampling record.

The pH of ground water has an effect on the presence and activity of microbial populations in the ground water. This is especially true for methanogens. Microbes capable of degrading chlorinated aliphatic hydrocarbons and petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units. Ground-water temperature directly affects the solubility of oxygen and other geochemical species. The solubility of DO is temperature dependent, being more soluble in cold water than in warm water. Ground-water temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature ("Q"$_{10}$ rule) over the temperature range between 5°C and 25°C. Ground-water temperatures less than about 5°C tend to inhibit biodegradation, and slow rates of biodegradation are generally observed in such waters.

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases. Conductivity measurements are used to ensure that ground water samples collected at a site are representative of the water in the saturated zone containing the dissolved contamination. If the conductivities of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones.

Elemental chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl^- to Cl^{+7}, the chloride form (Cl^-) is the only form of major significance in natural waters (45). Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (45). The chemical behavior of chloride is neutral. Chloride ions generally do not enter into oxidation-reduction reactions, form no important solute complexes with other ions unless the chloride concentration is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (45). Thus, physical processes control the migration of chloride ions in the subsurface.

Kaufman and Orlob (46) conducted tracer experiments in ground water and found that chloride moved through most of the soils tested more conservatively (i.e., with less retardation and loss) than any of the other tracers tested. During biodegradation of chlorinated hydrocarbons dissolved in ground water, chloride is released into the ground water. This results in chloride concentrations in the ground water of the contaminant plume that are elevated relative to background concentrations. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates using methods similar to those discussed by Wiedemeier et al. (36).

Field Measurement of Aquifer Hydraulic Parameters

The properties of an aquifer that have the greatest impact on contaminant fate and transport include hydraulic conductivity, hydraulic gradient, porosity, and dispersivity. Estimating hydraulic conductivity and gradient in the field is fairly straightforward, but obtaining field-scale information on porosity and dispersivity can be difficult.

Therefore, most investigators rely on field data for hydraulic conductivity and hydraulic gradient and on literature values for porosity and dispersivity for the types of sediments present at the site. Methods for field measurement of aquifer hydraulic parameters are described by Wiedemeier et al. (1, 37).

Microbiological Laboratory Data

Microcosm studies are used to show that the microorganisms necessary for biodegradation are present and to help quantify rates of biodegradation. If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of biodegradation. Such studies are the only "line of evidence" that allows an unequivocal mass balance determination based on the biodegradation of environmental contaminants. The results of a well-designed microcosm study will be easy for decision-makers with nontechnical backgrounds to interpret. Results of such studies are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Because microcosm studies are time-consuming and expensive, they should be undertaken only at sites where there is considerable skepticism concerning the biodegradation of contaminants.

Biodegradation rate constants determined by microcosm studies often are much greater than rates achieved in the field. Microcosms are most appropriate as indicators of the potential for natural bioremediation and to prove that losses are biological, but it may be inappropriate to use them to generate rate constants. The preferable method of contaminant biodegradation rate-constant determination is in situ field measurement. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm, and the interpretation of the results of the microcosm study are presented by Wiedemeier et al. (1).

Refine the Conceptual Model, Complete Premodeling Calculations, and Document Indicators of Natural Attenuation

Site investigation data should first be used to refine the conceptual model and quantify ground-water flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to help simulate natural attenuation over time. Because the burden of proof is on the proponent, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that natural attenuation is occurring.

Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered site characterization data to refine the preliminary conceptual model that was developed based on previously existing site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This conceptual model can then be used for contaminant fate-and-transport modeling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant contour (isopleth) maps, and electron acceptor and metabolic byproduct contour (isopleth) maps. Refinement of the conceptual model is described by Wiedemeier et al. (1).

Premodeling Calculations

Several calculations must be made prior to implementation of the solute fate-and-transport model. These calculations include sorption and retardation calculations, NAPL/water-partitioning calculations, ground-water flow velocity calculations, and biodegradation rate-constant calculations. Each of these calculations is discussed in the following sections. Most of the specifics of each calculation are presented in the fuel hydrocarbon natural attenuation technical protocol by Wiedemeier et al. (1), and all will be presented in the protocol incorporating chlorinated aliphatic hydrocarbon attenuation (37).

Biodegradation Rate Constant Calculations

Biodegradation rate constants are necessary to simulate accurately the fate and transport of contaminants dissolved in ground water. In many cases, biodegradation of contaminants can be approximated using first-order kinetics. To calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution and volatilization. Two methods for determining first-order rate constants are described by Wiedemeier et al. (36). One method involves the use of a biologically recalcitrant compound found in the dissolved contaminant plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (47) involves interpretation of a steady-state contaminant plume and is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (48). The first-order biodegradation rate constants for chlorinated aliphatic hydrocarbons are also presented (J. Wilson et al., this volume).

Simulate Natural Attenuation Using Solute Fate-and-Transport Models

Simulating natural attenuation using a solute fate-and-transport model allows prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation modeling is a tool that allows site-specific

data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterization will improve the validity of the modeling results. In some cases, straightforward analytical models of contaminant attenuation are adequate to simulate natural attenuation.

Several well-documented and widely accepted solute fate-and-transport models are available for simulating the fate-and-transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation. The use of solute fate-and-transport modeling in the natural attenuation investigation is described by Wiedemeier et al. (1).

Identify Potential Receptors, and Conduct an Exposure-Pathway Analysis

After the rates of natural attenuation have been documented and predictions of the future extent and concentrations of the contaminant plume have been made using the appropriate solute fate-and-transport model, the proponent of natural attenuation should combine all available data and information to negotiate for implementation of this remedial option. Supporting the natural attenuation option generally will involve performing a receptor exposure-pathway analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and ground-water use scenarios. The results of solute fate-and-transport modeling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate-and-transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site can be estimated.

Evaluate Supplemental Source Removal Options

Source removal or reduction may be necessary to reduce plume expansion if the exposure-pathway analysis suggests that one or more exposure pathways may be completed before natural attenuation can reduce chemical concentrations below risk-based levels of concern. Further, some regulators may require source removal in conjunction with natural attenuation. Several technologies suitable for source reduction or removal are listed in Figure 1. Other technologies may also be used as dictated by site conditions and local regulatory requirements. The authors' experience indicates that source removal can be very effective at limiting plume migration and decreasing the remediation time frame, especially at sites where biodegradation is contributing to natural attenuation of a dissolved contaminant plume. The impact of source removal can readily be evaluated by modifying the contaminant source term if a solute fate-and-transport model has been prepared for a site; this will allow for a reevaluation of the exposure-pathway analysis.

Prepare a Long-Term Monitoring Plan

Ground-water flow rates at many Air Force sites studied to date are such that many years will be required before contaminated ground water could potentially reach Base property boundaries. Thus, there frequently is time and space for natural attenuation alone to reduce contaminant concentrations in ground water to acceptable levels. Experience at 40 Air Force sites contaminated with fuel hydrocarbons using the protocol presented by Wiedemeier et al. (1) suggests that many fuel hydrocarbon plumes are relatively stable or are moving very slowly with respect to ground-water flow. This information is complemented by data collected by Lawrence Livermore National Laboratories in a study of over 1,100 leaking underground fuel tank sites performed for the California State Water Resources Control Board (49). These examples demonstrate the efficacy of long-term monitoring to track plume migration and to validate or refine modeling results. There is not a large enough database available at this time to assess the stability of chlorinated solvent plumes, but in the authors' experience chlorinated solvent plumes are likely to migrate further downgradient than fuel hydrocarbon plumes before reaching steady-state equilibrium or before receding.

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 natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on site characterization data, the results of solute fate-and-transport modeling, and the results of the exposure-pathway analysis.

The long-term monitoring plan includes two types of monitoring wells: long-term monitoring wells are intended to determine whether the behavior of the plume is changing; point-of-compliance wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage the risk associated with such expansion. Figure 5 depicts 1) an upgradient well in unaffected ground water, 2) a well in the NAPL source area, 3) a well downgradient of the NAPL source area in a zone of anaerobic treatment, 4) a well in the zone of aerobic treatment, along the periphery of the plume, 5) a well

located downgradient from the plume where contaminant concentrations are below regulatory acceptance levels and soluble electron acceptors are depleted with respect to unaffected ground water, and 6) three point-of-compliance wells.

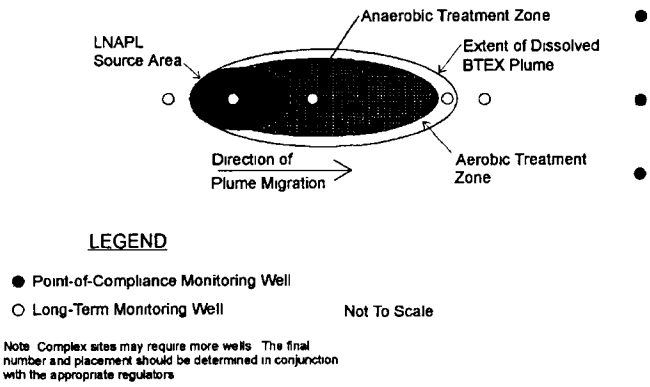


Figure 5. Hypothetical long-term monitoring strategy.

Although the final number and placement of long-term monitoring and point-of-compliance wells is determined through regulatory negotiation, the following guidance is recommended. Locations of long-term monitoring wells are based on the behavior of the plume as revealed during the initial site characterization and on regulatory considerations. Point-of-compliance wells are placed 500 feet downgradient from the leading edge of the plume or the distance traveled by the ground water in 2 years, whichever is greater. If the property line is less than 500 feet downgradient, the point-of-compliance wells are placed near and upgradient from the property line. The final number and location of point-of-compliance monitoring wells also depends on regulatory considerations.

The results of a solute fate-and-transport model can be used to help site the long-term monitoring and point-of-compliance wells. To provide a valid monitoring system, all monitoring wells must be screened in the same hydrogeologic unit as the contaminant plume. This generally requires detailed stratigraphic correlation. To facilitate accurate stratigraphic correlation, detailed visual descriptions of all subsurface materials encountered during borehole drilling should be prepared prior to monitoring-well installation.

A ground-water sampling and analysis plan should be prepared in conjunction with point-of-compliance and long-term monitoring well placement. For long-term monitoring wells, ground-water analyses should include volatile organic compounds, DO, nitrate, iron(II), sulfate, and methane. For point-of-compliance wells, ground-water analyses should be limited to determining volatile organic compound and DO concentrations. Any state-specific analytical requirements also should be addressed in the sampling and analysis plan to ensure that all data required for regulatory decision-making are collected. Water level and LNAPL thickness measurements must be made during each sampling event. Except at sites with very low hydraulic conductivity and gradients, quarterly sampling of long-term monitoring wells is recommended during the first year to help determine the direction of plume migration and to determine baseline data. Based on the results of the first year's sampling, the sampling frequency may be reduced to annual sampling in the quarter showing the greatest extent of the plume. Sampling frequency depends on the final placement of the point-of-compliance monitoring wells and ground-water flow velocity. The final sampling frequency should be determined in collaboration with regulators.

Present Findings to Regulatory Agencies, and Obtain Approval for Remediation by Natural Attenuation

The purpose of regulatory negotiations is to provide scientific documentation that supports natural attenuation as the most appropriate remedial option for a given site. All available site-specific data and information developed during the site characterization, conceptual model development, premodeling calculations, biodegradation rate calculation, ground-water modeling, model documentation, and long-term monitoring plan preparation phases of the natural attenuation investigation should be presented in a consistent and complementary manner at the regulatory negotiations. Of particular interest to the regulators will be proof that natural attenuation is occurring at rates sufficient to meet risk-based corrective action criteria at the point of compliance and to protect human health and the environment. The regulators must be presented with a "weight-of-evidence" argument in support of this remedial option. For this reason, all model assumptions should be conservative, and all available evidence in support of natural attenuation must be presented at the regulatory negotiations.

A comprehensive long-term monitoring and contingency plan also should be presented to demonstrate a commitment to proving the effectiveness of natural attenuation as a remedial option. Because long-term monitoring and contingency plans are very site specific, they should be addressed in the individual reports generated using this protocol.

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The BIOSCREEN Computer Tool

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Introduction

BIOSCREEN is an easy-to-use screening tool for simulating the natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. The software, programmed in the Microsoft Excel spreadsheet environment and based on the Domenico analytical solute transport model (1), has the ability to simulate advection, dispersion, adsorption, and aerobic decay, as well as anaerobic reactions that have been shown to be the dominant biodegradation processes at many petroleum release sites. BIOSCREEN includes three different model types: solute transport without decay, solute transport with biodegradation modeled as a first-order decay process (simple, lumped-parameter approach), and solute transport with biodegradation modeled as an "instantaneous" biodegradation reaction (the approach used by BIOPLUME models) (2).

Intended Uses for BIOSCREEN

BIOSCREEN attempts to answer two fundamental questions regarding intrinsic remediation (3):

- How far will the plume extend if no engineered control or source zone reduction is implemented?

  BIOSCREEN uses an analytical solute transport model with two options for simulating in situ biodegradation: first order decay and instantaneous reaction. The model predicts the maximum extent of plume migration, which may then be compared with the distance to potential points of exposure (e.g., drinking water wells, ground-water discharge areas, or property boundaries).

- How long will the plume persist until natural attenuation processes cause it to dissipate?

  BIOSCREEN uses a simple mass balance approach, based on the mass of dissolvable hydrocarbons in the source zone and the rate of hydrocarbons leaving the source zone, to estimate the source zone concentration versus time. Because an exponential decay in source zone concentration is assumed, the predicted plume lifetimes can be large, usually ranging from 5 to 500 years. Note that this is an unverified relationship (there are little data showing source concentrations versus long periods), and the results should be considered order-of-magnitude estimates of the time to dissipate the plume.

BIOSCREEN is intended to be used in two ways:

- As a screening model to determine whether intrinsic remediation is feasible at a given site. In this case, BIOSCREEN is used early in the remediation process and before site characterization activities are completed. Some data, such as electron acceptor concentrations, may not be available, so typical values are used. The BIOSCREEN results are used to determine whether an intrinsic remediation field program should be implemented to quantify the natural attenuation occurring at a site. In addition, BIOSCREEN is an excellent communication and teaching tool that can be used to present information in a graphical manner and help explain the concepts behind natural attenuation.

- As the primary intrinsic remediation ground-water model at smaller sites. The U.S. Air Force Intrinsic Remediation Protocol describes how intrinsic remediation models may be used to help verify that natural attenuation is occurring and to help predict how far plumes might extend under an intrinsic remediation scenario. At large, high-effort sites, such as Superfund and Resource Conservation and Recovery Act sites, a more sophisticated intrinsic remediation model is probably more appropriate. At smaller, lower-effort sites, such as service stations, BIOSCREEN

may be sufficient to complete the intrinsic remediation study.

BIOSCREEN Input and Output

To run BIOSCREEN, the user enters site data in the following categories: hydrogeologic, dispersion, adsorption, biodegradation, general information, source characteristics, and observed data. For several parameters (e.g., seepage velocity), the user can either enter the value directly or use supporting data (hydraulic conductivity, hydraulic gradient, and effective porosity) to calculate the value. Figure 1 shows the actual input screen. BIOSCREEN output includes plume centerline graphs, three-dimensional color plots of plume concentrations, and mass balance data showing the contaminant mass removal by each electron acceptor (instantaneous reaction option). Figures 2 and 3 show the two output screens. The input and output screens have on-line help built into the software. A detailed user's manual is also available (4).

BIOCHLOR: A BIOSCREEN for Chlorinated Solvents

While BIOSCREEN was originally designed to simulate intrinsic remediation at petroleum release sites, the system can be modified to simulate intrinsic remediation of chlorinated hydrocarbons. Current plans call for converting the BIOSCREEN model to BIOCHLOR. Key changes are:

- *Biodegradation using first-order decay only:* Microbial constraints on kinetics are much more important for chlorinated solvents than for petroleum compounds. Therefore, the first-order decay approach will be emphasized in both the BIOCHLOR software and manual. A detailed survey of solute decay data and source decay data from existing sites and the literature will be provided.
- *More detailed information on source terms:* Chlorinated solvents are associated with the presence of free-phase and residual dense nonaqueous phase liquids (DNAPLs) rather than residual light nonaqueous phase liquids (LNAPLs) such as gasoline and JP-4. The source terms will be discussed in more detail to ensure that model input data and preliminary calculations are representative of DNAPL sites.
- *Evaluation of biodegradation products:* The generation of products of chlorinated solvent biodegradation will be discussed. Simple analytical tools may be developed and incorporated into BIOCHLOR.

BIOSCREEN is available by contacting EPA's Center for Subsurface Modeling Support (CSMoS), NRMRL/SPRD, P.O. Box 1198, Ada, OK 74821-1198, telephone 405-436-8594, fax 405-436-8718, bulletin board 405-436-8506

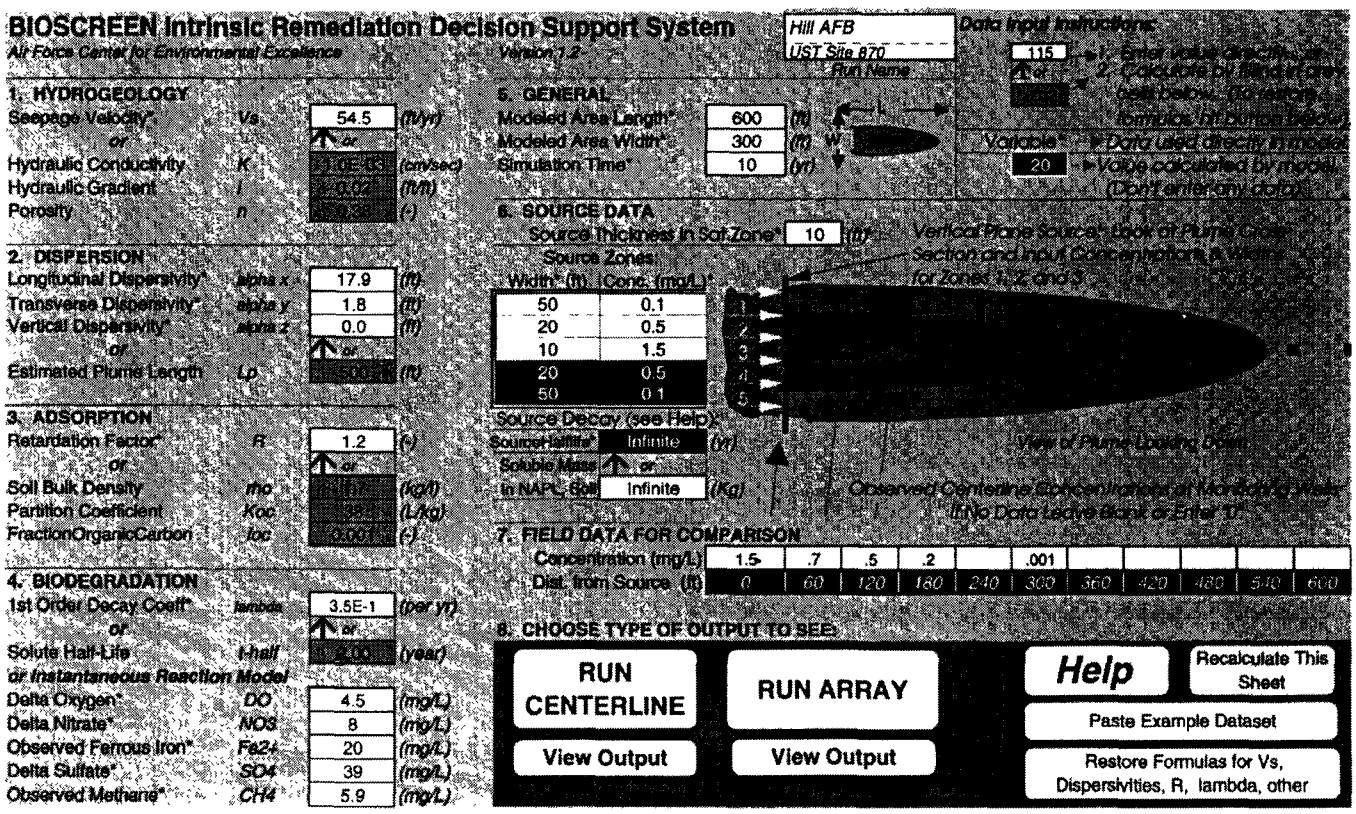

Figure 1. BIOSCREEN input screen.

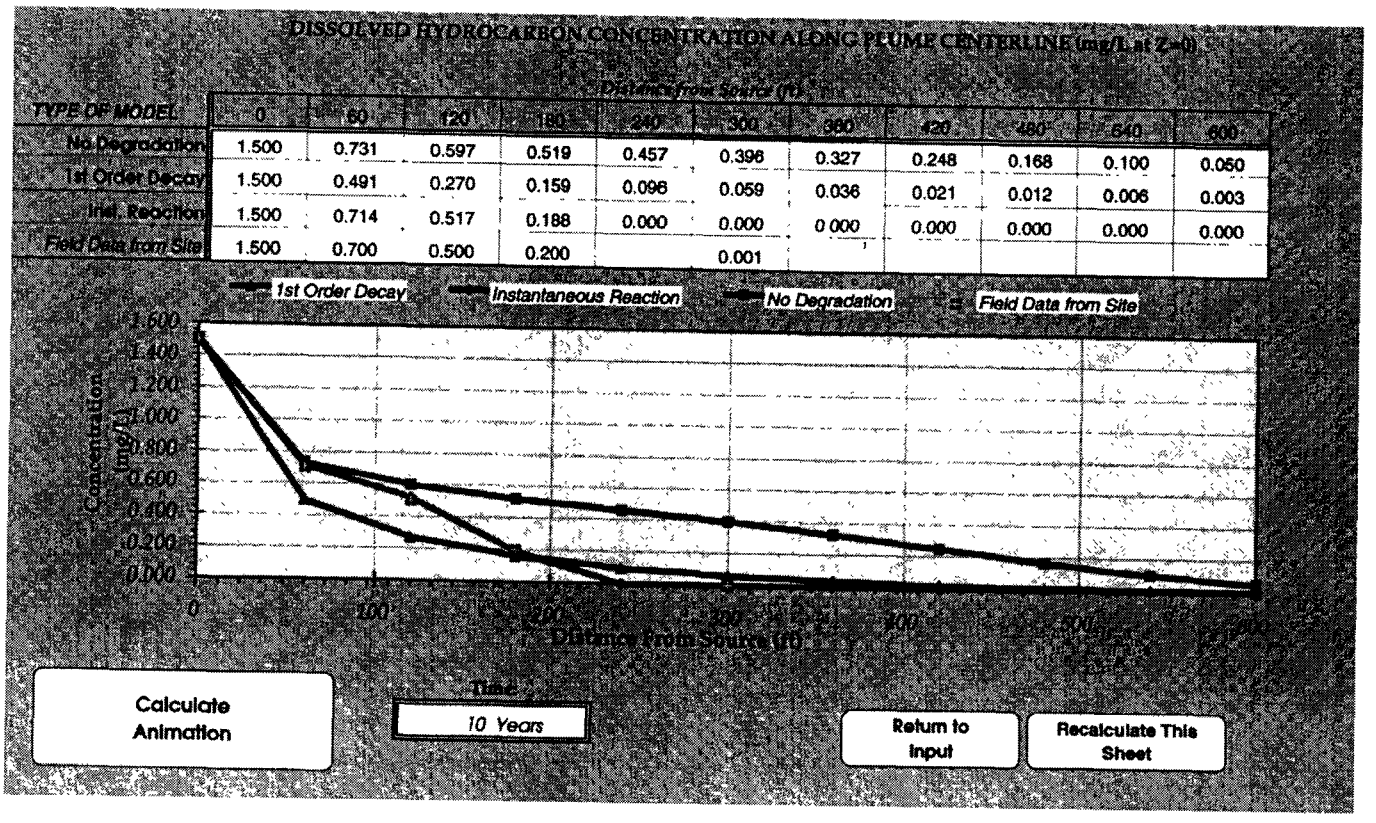

Figure 2. BIOSCREEN centerline output screen.

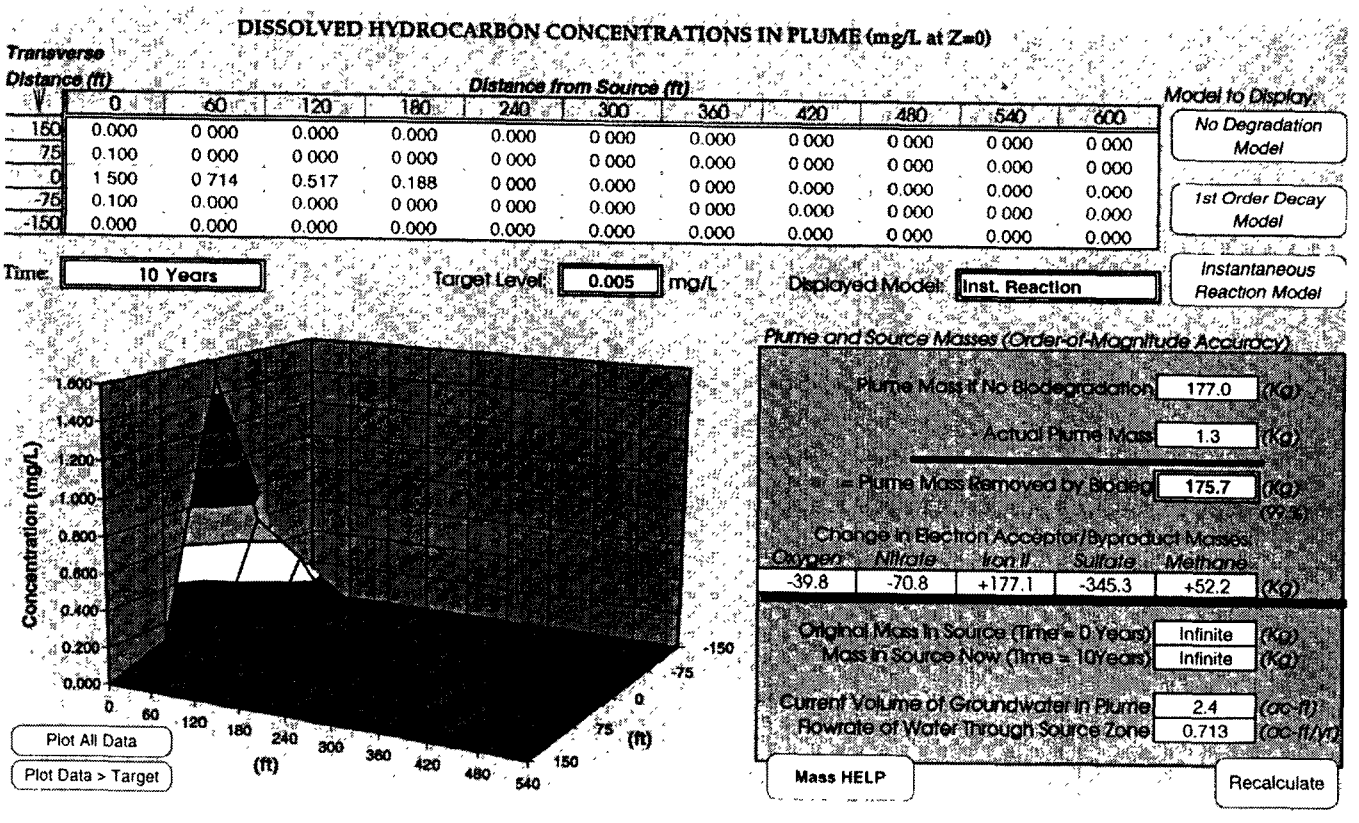

Figure 3. BIOSCREEN concentration array output screen.

(14,400 baud, 8 bits, 1 stopbit available, no parity), and Internet http://www.epa.gov/ada/kerrlab.html. Electronic manuals will be available in .pdf format; the Adobe Acrobat Reader is necessary to read and print .pdf files.)

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Case Study: Naval Air Station Cecil Field, Florida

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U.S. Geological Survey, Columbia, South Carolina

Redox processes at a fire-training area at Naval Air Station Cecil Field in Florida are segregated into distinct and clearly definable zones. Near the source of contamination, methanogenesis predominates. As ground water flows downgradient, distinct sulfate-reducing, iron(III)-reducing, and oxygen-reducing zones are encountered. This naturally occurring sequence favors the reductive dehalogenation of chlorinated ethenes near the contamination source, followed by oxidative degradation of vinyl chloride to carbon dioxide and chloride downgradient of the source. This sequence of redox processes has created a natural bioreactor that effectively treats contaminated ground water without human intervention. These results show that mapping the zonation of redox processes at individual sites is an important step in evaluating the potential for natural attenuation of chlorinated ethenes.

Case Study of Natural Attenuation of Trichloroethene at St. Joseph, Michigan

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Introduction

Trichloroethene (TCE) was found in ground water at the St. Joseph, Michigan, Superfund site in 1982. The site, located 4 miles south of St. Joseph and 0.5 mile east of Lake Michigan, has been used for auto parts manufacturing since 1942. The aquifer is primarily composed of medium, fine, and very fine glacial sands. The base of the aquifer is defined by a clay layer that lies between 21 and 29 meters below the ground surface, with elevation of the clay layer increasing toward Lake Michigan. Investigation at the site included an exhaustive study of 41 possible contaminant sources but did not definitively identify the source.

The source was apparently situated over a groundwater divide, however, as the contamination was divided into eastern and western plumes. Both plumes were found to contain TCE, cis- and trans-1,2-dichloroethene (cis-DCE and t-DCE), 1,1-dichloroethene (1,1-DCE), and vinyl chloride (VC). Initial investigation indicated that natural anaerobic degradation of the TCE was occurring in the western plume, because of the presence of transformation products and significant levels of ethene and methane (1, 2).

This paper describes the investigation at the site and presents the field evidence for natural attenuation of TCE. Since degradation of TCE is known to occur anaerobically under differing redox conditions and to produce specific daughter products, the relationships between measured concentrations of chlorinated ethenes and various redox indicators are emphasized.

Sampling Strategy

Water samples were taken in October 1991 and March 1992 from a 5-foot long slotted auger (3). Seventeen boreholes were completed near the source of the western plume (1), which formed three transect crossing the contaminant plume. Data from these first three transect were analyzed by Semprini et al. (4).

In 1992, two additional transect (4 and 5 on Figure 1) consisting of nine additional slotted auger borings were completed. These two transect were chosen to sample the plume in the vicinity of Lake Michigan. In each boring, water samples were taken in 5-foot intervals from the water table to the base of the aquifer. Onsite gas chromatography was used to determine the width of the plume and the point of highest concentration in each transect. The onsite gas chromatography ensured that the entire width of the contaminant plume was captured within each transect. In August 1994, data were collected from a transect located about 100 meters offshore that was roughly parallel to the shore line and contained four borings. Water samples were taken with a barge-mounted geoprobe (3). Data from the lake transect showed the location of the plume by the observed reduction in dissolved oxygen concentrations and the measured redox potentials.

Results

Figures 2 through 5 show the data from all the boreholes separated by transect, which in effect also separates them by sample date. By compositing the data set, sitewide trends can be seen. These figures are supplemented by Figures 6 through 9, which show contaminant distribution with depth in single boreholes from representative locations. Significant methane concentrations occurred where dissolved oxygen concentrations were low (Figure 2). Variation in concentration occurring on a scale smaller than the length of the auger is not accurately represented, as waters of differing chemistry may mix upon sampling. This may explain why a few data points simultaneously have high methane and high oxygen concentrations. Most importantly, the figure indicates that a large number of sample locations at the site had the necessary strong reducing conditions for reductive dechlorination to occur.

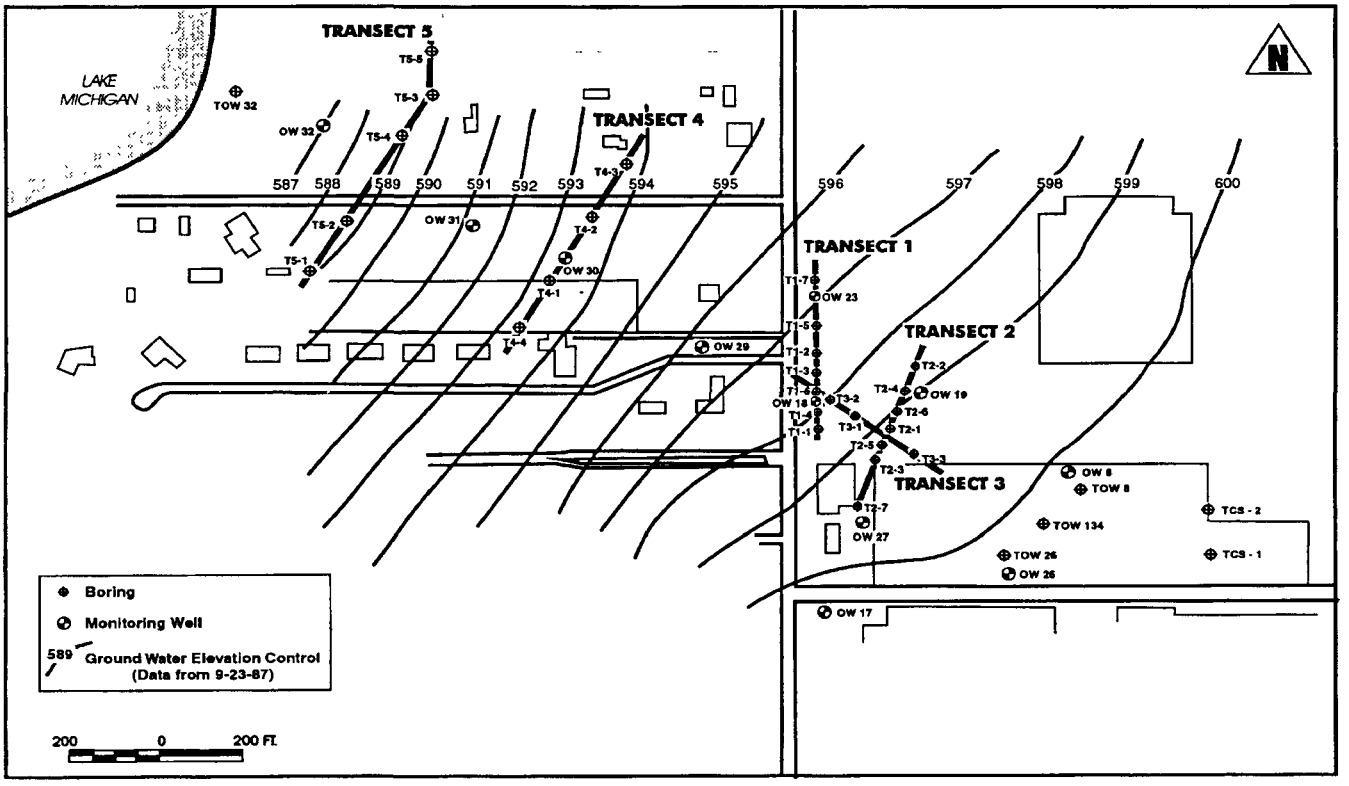

Figure 1. St. Joseph Superfund site plan.

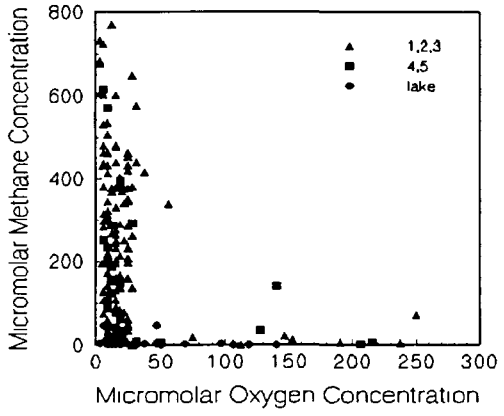

Figure 2. Scatter plot of methane and oxygen data.

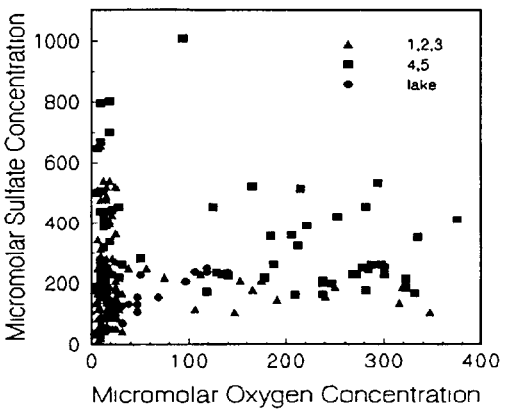

Figure 3. Scatter plot of sulfate and oxygen data.

Figure 3 shows the distribution of sulfate and oxygen. Many of the points cluster near the sulfate axis, which generally corresponds to the regions of high methane concentration. Generally the sulfate concentrations around the site are high, and completely clear patterns of sulfate depletion are not found in the composited data set. The trends that exist in the data are best illustrated by the contaminant distribution in individual boreholes. These data suggest that transformation of TCE to DCE occurred where the sulfate concentration showed some sign of decline. Clustering of the sulfate data occurred at sulfate concentrations of 300 micromolar (mM) or less and oxygen concentrations of 50 mM or less.

Many of these points occurred in the transition between the aerobic and methanogenic region. Compared with higher sulfate concentrations at other locations, these points tentatively indicate sulfate reduction zones, which may be concurrent with methanogenesis (5). In particular, in Transect 4 and 5 the uppermost sample locations

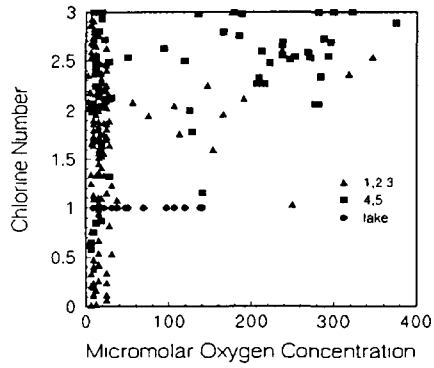

Figure 4. Composited chlorine number plotted against oxygen concentration.

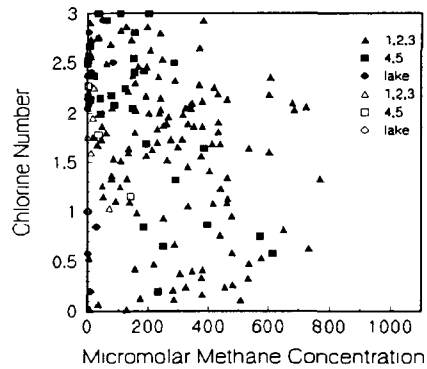

Figure 5. Composited chlorine number plotted against methane concentration.

were devoid of contaminants and were oxygenated. Sulfate concentrations in the range of 300 to 500 µM at these points indicate background sulfate levels.

The entire chlorinated ethene (TCE, DCEs, and VC) and ethene data set is plotted in Figures 4 and 5 as a chlorine number, N_{Cl}, that is defined by

$$N_{Cl} = \frac{\sum w_i C_i}{\sum C_i}$$

where w_i is the number of chlorine atoms in molecule i and C_i is the molar concentration of each ethene species. The chlorine number composites the ethene concentrations and scales them from 0 to 3. At 0 no chlorinated species are present, and at 3 all of the ethene is in the form of TCE. Generally, the integer chlorine numbers (0, 1, 2, 3) are obtained with non-0 concentration only of the ethene with that number of chlorine atoms. There are fortuitous combinations, however, of positive non-0 concentrations that give integer chloride numbers. None of these combinations occurred in the St. Joseph data set.

High chlorine numbers were associated with many of the high dissolved oxygen concentrations (Figure 4), indicating that most of the chlorine was contained in TCE molecules at these sampling points. Some of these had chlorine numbers of 3, indicating that TCE was the only species present. The majority of locations with chlorine numbers below 3 were anaerobic, which also corresponded to methanogenic locations. The latter condition, in conjunction with the presence of the TCE degradation products (indicated by the low chlorine numbers), indicates degradation of the TCE. When the data set is plotted against the methane concentration (Figure 5), the data appeared scattered over most of the graph. Some of the lowest chloride numbers were associated with the high methane concentrations.

Generally, many of the downgradient locations (squares on Figures 4 and 5) showed chlorine numbers above 2 and lower methane concentrations. These data suggest that in the downgradient transect, TCE degraded to DCE under other than methanogenic conditions.

Data from selected borings represent the general trends with depth in each of the transect (Figures 6 and 7). In Transect 2, located near the presumed source of contamination, dissolved oxygen was depleted below the 60-foot depth (Figure 6). Between 45 and 60 feet, the 45- and 55-foot depths showed significant dissolved oxygen as well as significant methane concentrations. Sulfate showed a weak declining trend with depth to about 70

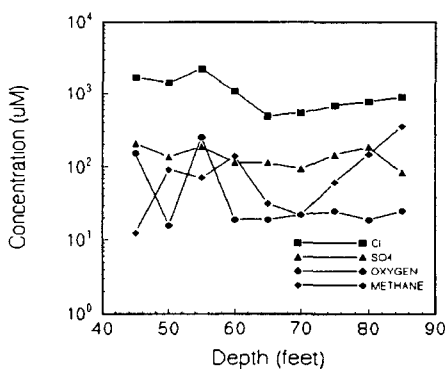

Figure 6. Distribution of chloride, sulfate, dissolved oxygen, and methane with depth in Borehole T23.

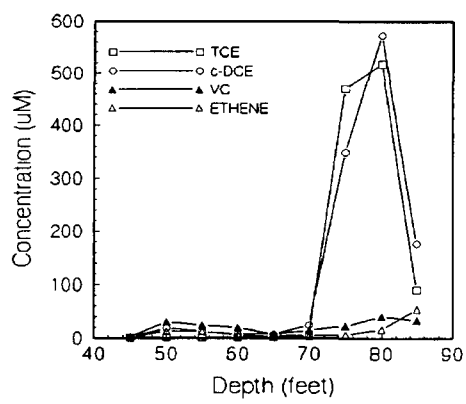

Figure 7. Distribution of ethenes with depth at Borehole T23.

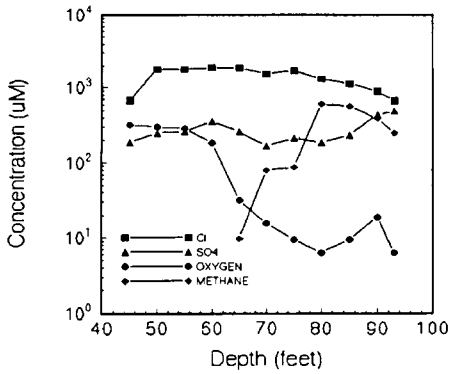

Figure 8. Distribution of chloride, sulfate, dissolved oxygen, and methane with depth in Borehole T42.

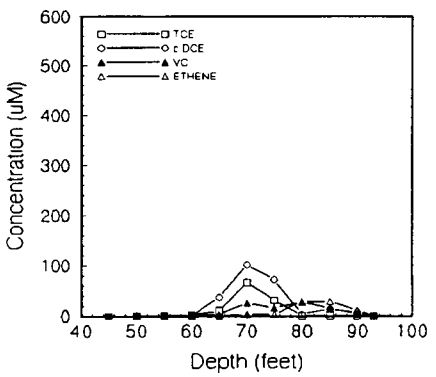

Figure 9. Distribution of ethenes with depth in Borehole T42.

feet. Significant TCE and cis-DCE concentrations were found only from 75 to 85 feet below the surface (Figure 7). VC was found at concentrations of 40 μM or less over most of the borehole. Ethene was found at highest concentrations at the bottom of the borehole, where methane concentrations also were highest.

Borehole T42 had the highest chlorinated ethene concentrations recorded for Transect 4, and it also represents the general chemical distribution for the downgradient transect (Figures 8 and 9). From the water table to the depth of 60 feet, oxygen concentrations were high but decreasing (Figure 8). This contrasts with the upgradient transects, which showed less consistent depletion of oxygen near the water table. Sulfate concentrations decreased from 60 to 70 feet, roughly the same zone in which oxygen was declining. From 70 to 85 feet, sulfate concentrations remained low but increased from 80 feet to the bottom of the borehole. Methane was not present in the aerobic zone above 65 feet, but it increased sharply in concentration from 70 to 80 feet before decreasing.

Figure 9 shows the distribution of the chlorinated ethenes and ethene in T42. TCE was found from 60 feet downward, with its maximum concentration occurring at the 70-foot depth. The region above the 60-foot depth was free from chlorinated ethenes, so the high sulfate and oxygen concentrations found there correspond with no activity due to TCE degradation.

The cis-DCE concentration was also highest at the 70-foot depth. Methane first appeared at 65 feet, and the peak cis-DCE concentration occurred where sulfate concentrations declined to the minimum. VC was found from 65 feet to the bottom of the borehole. Ethene was found from 70 feet downward, corresponding closely to the most methanogenic part of the borehole.

Conclusion

Because of a variety of evidence, the data set from St. Joseph suggest the occurrence of natural attenuation. The composited data set indicate that, with the exception of a few points, the oxygenated and methanogenic zones of the aquifer are clearly separated. The presence of many methanogenic locations in the aquifer show that the strongly reducing conditions required for production of VC existed in the aquifer. The distribution of the chloride number indicate that the majority of sample locations where daughter products were present were also anaerobic. Data from individual boreholes indicate that high cis-DCE concentrations were commonly associated with declines in oxygen and sulfate concentrations and appeared on the upper edge of the methanogenic zone. Generally, ethene was found in the most methanogenic portions of the aquifer and was also associated with relatively high VC concentrations, suggesting that the ethene production was limited to those sample locations.

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Extraction of Degradation Rate Constants From the St. Joseph, Michigan, Trichloroethene Site

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Background

Anaerobic biodegradation of trichloroethene (TCE) occurs through successive dechlorination from TCE to dichloroethene (DCE), vinyl chloride (VC), and ethene (1). The process produces three isomers of DCE: 1,1-DCE, cis-1,2-DCE, and trans-1,2-DCE. Although TCE was commonly used in industry, the DCEs were not, and ethene would not be expected in most ground waters. Thus, the presence of these compounds is indicative of degradation when found in anaerobic ground waters. Implicit in the work of Kitanidis et al. (2) and McCarty and Wilson (3) is the fact that degradation of TCE at the St. Joseph, Michigan, site was not predicted from theoretical considerations; rather, degradation of TCE was established from the field data as described in these proceedings (Weaver et al. *a*, this volume). The purpose of this paper is to present estimates of averaged concentrations, mass flux, and degradation rate constants.

Ground-Water Flow

Ground water flows at the St. Joseph site from the contaminant source toward Lake Michigan. The average hydraulic conductivity at the site was estimated at 7.5 meters per day from a calibrated ground-water flow model (4). The estimated travel time for TCE between the source and the lake is approximately 18 years (Table 1). If the contamination was released only in the aqueous phase, one would expect that contaminants released 18 years or longer ago would by now have discharged into the lake. The observed contaminant distribution suggests a continuing source, most likely a DNAPL.

Averaged Concentrations

Data were collected from the site from sets of borings that formed four on-shore and one off-shore transects that crossed the plume (Weaver et al. *a*, this volume). These range from 130 to 855 meters from the suspected source of contamination. From the borings, a three-dimensional view of the contamination was developed. A field gas chromatograph was used to determine the boundaries of the plume. Sampling continued until the entire width of the plume was crossed at each transect. By following this procedure, the transects are known to have contained the entire plume. This approach allows calculation of total mass that crosses each transect and thus gives an estimate of flux of each contaminant as a function of distance from the lake.

Table 1. Attenuation of the Chlorinated Ethenes Along the Length of the Plume

			Average Concentration (µg/L) *Highest Concentration (µg/L)*		
Distance From Source (m)	Transport Time (y)	Transect Width (m)	TCE	cis-DCE	Vinyl Chloride
130	3.2	108	6,500 *68,000*	8,100 *128,000*	930 *4,400*
390	9.7	150	520 *8,700*	830 *9,800*	450 *1,660*
550	12.5	192	15 *56*	18 *870*	106 *205*
855	17.9	395	<1 *0.4*	<1 *0.8*	<1 *0.5*

Transect-averaged concentration estimates were developed by using the SITE-3D graphics package (5). The data were represented as sets of blocks that are centered around each boring. The blocks were each 5 feet high, corresponding to the length of the slotted auger. At each transect, the average concentration was calculated

by summing over the blocks and dividing by the area of the transects.

In Table 2, concentration estimates are presented for the perpendicular transects ordered from furthest upgradient (Transect 2) to furthest downgradient (Transect 5). The concentration estimates are based only on blocks from the anaerobic portion of the aquifer (and thus differ from the averages in Table 1). All of the chlorinated ethenes show decreasing concentration with distance downgradient; thus, all of the rate coefficients developed below reflect a net loss of the species. The chloride concentrations increase downgradient as expected from the dechlorination of the ethenes. On a molar basis, however, the increase in average chloride concentration is greater than that which would result from dechlorination alone.

Mass Flux

The concentration results (Table 2) show that by the time the contaminants reach the lake, their concentrations are reduced to very low levels. It is equally important to determine the mass of chemicals released to the lake per year. Given the approximate ground-water velocities and the contaminant concentrations in the transects, an estimate of the mass flux of chemicals can also be estimated. Advective mass fluxes of each chemical were estimated per transect by multiplying the seepage velocity by concentration in each block formed, using SITE-3D. The results are given in Table 3, which shows a decline in the mass flux of each chlorinated ethene. The flux reduction ranged from a factor of 10 to 123. The flux of methane showed no consistent pattern. Chloride flux increased beyond Transect 1.

Table 2. Transect-Averaged Concentrations (μg/L) From the Anaerobic Zone

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7,411	864	30.1	(1.4)
cis-DCE	9,117	1,453	281	(0.80)
t-DCE	716	34.4	5.39	(1.1)
1,1-DCE	339	24.3	2.99	*blq*
VC	998	473	97.7	(0.16)
Ethene	480	297	24.2	No data
Sum of the ethenes	19,100	3,150	442	(3.5)
Chloride	65,073	78,505	92,023	44,418

Note: Values in parentheses were based on one or more estimated values; *blq* indicates no detection above the limit of quantitation.

Degradation Rates

The transport of each chemical is parametrized by the ground-water flow velocity, the retardation coefficient, the dispersivities, and the decay constant. Specifically, two-dimensional solute transport with first-order decay obeys

$$R\frac{\partial c}{\partial t} = D_{xx}\frac{\partial^2 c}{\partial x^2} + D_{yy}\frac{\partial^2 c}{\partial y^2} - v\frac{\partial c}{\partial x} - \lambda^* c \qquad \text{(Eq. 1)}$$

where R is the retardation coefficient; c is the concentration; t is time; D_{xx} and D_{yy} are the longitudinal and transverse dispersion coefficients, respectively; x is longitudinal distance; y is the distance transverse to the plume centerline in the horizontal plane; v is the seepage velocity; and λ^* is the first-order decay constant. First-order decay is assumed for this analysis because it is the usual way to report degradation rates of chlorinated hydrocarbons (6). This form of the transport equation assumes that ground-water flow is uniform and aligned with the axis of the plume, as observed for the plume. This assumption also allows application of analytic solutions as described in the appendix.

The concentration of dissolved chemicals can change because of the effect of the terms on the right-hand side of Equation 1. Dispersion is used to characterize apparent physical dilution in aquifers. Dispersion is currently

Table 3. Flux Estimates for Transects 1, 2, 4, and 5

	Mass Flux (kg/y)						
Transect	TCE	cis-DCE	VC	Ethene	Total Ethenes	Methane	Chloride
1 (August-September 1991)	50.0	45.2	16.8	7.95	125	49.2	545
2 (August-September 1991)	117	133	16.8	7.60	283	65.7	1,456
4 (March 1992)	30.9	41.7	3.87	10.8	88.4	101	4,610
5 (April 1992)	0.95	10.0	1.68	0.164	13.1	46.7	5,290
Reduction ratio	123	13	10	46	22		

Note: The reduction ratio is the ratio of mass flux at Transect 2 to that at Transect 5.

understood to result primarily from ground-water flow through heterogeneous materials. In multidimensional flow, advection can cause concentrations to decrease because of the divergence of flow lines. Advection does not directly change concentrations in one-dimensional flow but influences the contribution of dispersion. Decay changes concentration through removal of mass from the aquifer.

The significance of these observations is that when presented with a set of contaminant concentrations, the distribution of contamination may depend on physiochemical and biological processes. Observed concentrations in themselves do not indicate the contribution of each process to the plume shape. Extraction of apparent rates from the field data needs to account for the multiple processes. In Table 4, estimated rate constants are given for St. Joseph. These constants were determined from the solution of the transport equation presented in the appendix. The solution included advection, retardation, longitudinal and transverse dispersion, and first-order loss. Inclusion of transverse dispersion is important because this characterizes downgradient spreading of the plume. The observed widths of the plume at St. Joseph are given in Table 1 and were used to estimate the transverse dispersivity according to the procedure given in the appendix. The effect of transverse dispersivity on the estimated rate constants, however, decreases as the plume widens and the centerline concentrations decrease. Longitudinal dispersivity has been shown to have a minor impact on the estimated rate constants at distances between transects on the order of 100 meters (7).

Table 4. Apparent Degradation Rate Constants (One Per Year) From the Two-Dimensional Model (Equation 3) and the Gross Rate Correction Given by Equation 7

Chemical	Transect 2 to 4	Transect 4 to 5	Transect 5 to Lake
TCE	0.30	1.7	1.7
cis-DCE	0.54	1.1	4.0
Vinyl chloride	2.6	3.1	20

The rates given in Table 5 are called net rates because, for the daughter products, the observed concentrations are a result of production of the daughter from both decay of the parent and decay of the daughter itself. The gross rate of decay of the daughter (Table 4) does not include its production and was determined by the procedure given in the appendix. The two rates are the same for TCE, since no production of TCE occurred. The gross rates are, as expected, higher than the net rates, because production of a compound must be balanced by high gross rates to attain the observed net rate.

Table 5. Net Apparent Degradation Rate Constants (One Per Year) From the Two-Dimensional Model (Equation 3)

Chemical	Transect 2 to 4	Transect 4 to 5	Transect 5 to Lake
TCE	0.30	1.7	1.7
cis-DCE	0.26	0.58	3.3
Vinyl chloride	0.15	0.78	2.6

Conclusion

The western TCE plume at St. Joseph, Michigan, showed a decrease of maximum TCE concentration by a factor of 50,000 from the furthest upgradient transect to the lake transect. Concentrations of each contaminant declined to values below the respective maximum contaminant levels when sampled from the lake sediments. Mass fluxes decrease by factors of 10 to 123 from the source to the last on-shore transect (Transect 5); thus, not only do the concentrations decline, but so does the loading in the ground water. The reduction in loading is attributed to degradation, because of the geochemical evidence presented (Weaver et al. *a*, this volume).

Further, when site-specific estimates of the transport parameters are used in solutions of the transport equations, the apparent reduction in concentration is only accounted for by loss of mass. These apparent degradation rate constants were calculated from the St. Joseph data set through application of a two-dimensional analytical solution of the transport equation. Since transverse spreading of the plume reduces the contaminant concentrations, the effect of transverse dispersivity was included in the analysis.

Appendix

Extraction of Rate Constants via Two-Dimensional, Steady-State Transport Analysis

The two-dimensional transport equation, subject to the boundary conditions

$$c(x,y,0) = 0$$

$$c(0,y,t) = c_o \exp\left(\frac{-y^2}{2\sigma^2}\right)$$

$$c(\infty,y,t) = c(x,-\infty,t) = c(x,\infty,t) = 0$$

(Eq. 2)

has the approximate steady state solution (9)

$$c(x,y) = \frac{c_o \exp\left[\frac{vx}{2D_{xx}}\left(1 - \sqrt{1 + \frac{4\lambda^* R D_{xx}}{v^2}}\right) - \frac{\frac{y^2}{\sigma^2}}{2 + \frac{\frac{4xD_{yy}}{\sigma^2 v}}{\sqrt{1 + \frac{4\lambda^* R D_{xx}}{v^2}}}}\right]}{\sqrt{1 + \frac{\frac{2xD_{yy}}{\sigma^2 v}}{\sqrt{1 + \frac{4\lambda^* R D_{xx}}{v^2}}}}} \qquad \text{(Eq. 3)}$$

Vertically averaged concentrations and the distances between each borehole were used to develop the boundary condition (c(0,y,t) in Equation 2) for application of Equation 3. The unknown parameters are the up-gradient peak concentration, c_o, and the standard deviation, σ, of the distribution. Since the width of the plume, W, was established via the field sampling program, the standard deviation of the distribution can be estimated as $W = 6\sigma$. A mass balance can then be solved for the peak concentration of the Gaussian distribution, c_o, from

$$\int n\hat{c}dy = \int nc_o \exp\left(\frac{-y^2}{2\sigma^2}\right) dy = nc_o \sigma \sqrt{2\pi} \qquad \text{(Eq. 4)}$$

where n is the porosity, $\hat{c}$ is the vertically averaged concentration, and the y coordinate runs parallel to the transect.

The transverse dispersivity can also be estimated from the measured widths of the transects. The width of a contaminant distribution is related to the transverse dispersivity through

$$D_{yy} = a_{yy}\, v = \frac{1}{2}\frac{d\sigma^2}{dt} \qquad \text{(Eq. 5)}$$

where a_{yy} is the transverse dispersivity. By applying Equation 5 in a discrete form and substituting $\Delta t = \Delta xR/v$, an expression for a_{yy} is obtained in terms of the seepage velocity, retardation coefficient, distance between transects (Δx), and change in variance of the Gaussian distributions for the transect concentrations ($\Delta \sigma^2$):

$$a_{yy} = \frac{1}{2R}\frac{\Delta\sigma^2}{\Delta x} \qquad \text{(Eq. 6)}$$

The only remaining unknown in Equation 3 is the decay constant λ^*, which is determined through a bisection search. Table 5 gives the rate constants from the two-dimensional model.

Net and Gross Decay Rates

The rate constants derived from the solution (Equation 3 and Table 5) are net rates that include the production and decay of a given daughter product. It is necessary to separate production of the compound from its decay to estimate the gross apparent decay rates for cis-DCE, t-DCE, 1,1-DCE, and VC. Previous work (7) used a reaction rate model that simultaneously solved ordinary differential equations for this purpose. Here, simplified expressions for the rates were used to estimate the apparent decay rates:

$$\lambda_{j(n)} = f_j\, \lambda_{j+1(n)}\, S + \lambda_{j(g)} \qquad \text{(Eq. 7)}$$

where $\lambda_{j(n)}$ is the net decay rate determined by Equation 3, f_j is the fraction of an isomer (j) produced from the degradation of the parent (j+1), $\lambda_{j+1(n)}$ is the apparent decay rate of the parent defined from Equation 3, S is the ratio of molar concentration of parent j+1 to daughter j, and $\lambda_{j(g)}$ is the gross apparent decay rate of daughter j. For the DCE isomers, f_j is approximated by the average ratio of an isomer j to the sum of the DCEs over the pairs of transects. For VC, f_j is equal to 1.0. The gross apparent decay rates for cis-DCE, t-DCE, 1,1-DCE, and VC appear in Table 4. Although Equation 7 is concentration dependent because S was assumed to be the average of the up- and downgradient ratios, the results presented in Table 4 are essentially the same as determined from the reaction rate model (8).

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Natural Attenuation of Chlorinated Aliphatic Hydrocarbons at Plattsburgh Air Force Base, New York

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Introduction

Activities at a former fire training area (Site FT-002) at Plattsburgh Air Force Base (AFB) in New York resulted in contamination of shallow soils and ground water with a mixture of chlorinated solvents and fuel hydrocarbons. Ground water contaminants include trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride, and benzene, toluene, ethylbenzene, and xylenes (BTEX). Table 1 contains contaminant data for selected wells at the site.

Contaminant plumes formed by chlorinated aliphatic hydrocarbons (CAHs) dissolved in ground water can exhibit three types of behavior based on the amount and type of primary substrate present in the aquifer. Type 1 behavior occurs where anthropogenic carbon such as BTEX or landfill leachate is being utilized as the primary substrate for microbial degradation. Such plumes typically are anaerobic, and the reductive dechlorination of highly chlorinated CAHs introduced into such a system can be quite rapid. Type 2 behavior occurs in areas that are characterized by high natural organic carbon concentrations and anaerobic conditions. Under these conditions, microorganisms utilize the natural organic carbon as a primary substrate; if redox conditions are favorable, highly chlorinated CAHs introduced into this type of system will be reductively dechlorinated. Type 3 behavior occurs in areas characterized by low natural organic carbon concentrations, low anthropogenic carbon concentrations, and aerobic or weakly reducing conditions. Biodegradation of CAHs via reductive dechlorination will not occur under these conditions. Biodegradation of the less chlorinated compounds such as vinyl chloride, however, can occur via oxidation.

Plattsburgh AFB is located in northeastern New York State, approximately 26 miles south of the Canadian border and 167 miles north of Albany. Site FT-002 (Figure 1) is located in the northwest corner of the base on a land surface that slopes gently eastward toward the confluence of the Saranac and the Salmon Rivers, approximately 2 miles east of the site. The site, which is approximately 700 feet wide and 800 feet long, was used to train base and municipal fire-fighting personnel from the mid-1950s until it was permanently closed to fire-training activities in May 1989.

Four distinct stratigraphic units underlie the site: sand, clay, till, and carbonate bedrock. Figure 2 shows three of the four stratigraphic units at the site. The sand unit consists of well-sorted, fine- to medium-grained sand with a trace of silt, and generally extends from ground surface to as much as 90 feet below ground surface (bgs) in the vicinity of the site. A 7-foot thick clay unit has been identified on the eastern side of the site. The thickness of the clay on the western side of the site has not been determined. A 30- to 40-foot thick clay till unit is also present from 80 to 105 feet bgs in the vicinity of the site. Bedrock is located approximately 105 feet bgs.

Ground-Water Hydraulics

The depth to ground water in the sand aquifer ranges from 45 feet bgs on the west side of the site to zero on the east side of the runway, where ground water discharges to a swamp (Figure 2). Ground-water flow at the site is to the southeast, with the average gradient approximately 0.010 foot per foot (ft/ft). Hydraulic conductivity of the upper sand aquifer was measured using constant drawdown tests and rising head tests. Hydraulic conductivity values for the unconfined sand aquifer

Table 1. Analytical Data, Plattsburgh Air Force Base

Point	Date	Distance From Source (feet)	TMB (µg/L)	BTEX (µg/L)	TCE (µg/L)	Total DCE[a] (µg/L)	Vinyl Chloride (µg/L)	Methane (µg/L)	Ethene (µg/L)	Chloride (mg/L)	Dissolved Oxygen (mg/L)	Nitrate (mg/L)	Iron(II) (mg/L)	Sulfate (mg/L)	Hydrogen (nM)	Total Organic Carbon (mg/L)
A	Aug. 95	0	1,757	16,790	25,280	51,412	0	1,420	< 0.001	63	0.1	0.2	4.0	5.5	6.70	80
	May 96		828	6,598	580	12,626	0	1,600	< 0.001	82	0.5	0.0	45.6	1.0	2.00	94
B	Aug. 95	970	491	3,060	2	14,968	897	305	35.00	48	0.5	0.2	15.3	0.0	1.66	30
	May 96		463	4,198	1	9,376	1,520	339	13.00	43	0.1	0.0	16.0	0.0	1.40	31
C	Aug. 95	1,240	488	3,543	3	10,035	1,430	1,010	182.00	46	0.4	0.2	13.8	0.0	NA	21
	May 96		509	3,898	1	10,326	1,050	714	170.00	57	0.2	0.0	19.3	0.0	11.13	24
D	Aug. 95	2,050	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	May 96		9	89	0	1,423	524	617	4.00	14	0.2	0.1	2.5	1.5	NA	14
E	Aug. 95	2,560	0	40	24	2,218	8	3,530	< 0.001	20	0.9	0.3	0.7	0.5	NA	8
	May 96		0	40	17	1,051	12	1,800	< 0.001	18	0.1	0.0	0.0	1.0	0.81	8
F	Aug. 95	3,103	0	2	1	226	5	115	< 0.001	3	0.4	10.4	0.0	14.7	0.22	NA
	May 96		0	2	0	177	4	44	< 0.001	3	0.2	9.5	0.1	14.4	0.25	NA

[a] Greater than 99% of DCE is *cis*-1,2-DCE.
NA = Not analyzed.
Point A = MW-02-108, B = MW-02-310, C = 84DD, D = 84DF, E = 34PLTW12, F = 35PLTW13.

underlying the site range from 0.059 to 90.7 feet per day (ft/day). The average hydraulic conductivity for the site is 11.6 ft/day. Freeze and Cherry (1) give a range of effective porosity for sand of 0.25 to 0.50. Effective porosity was assumed to be 0.30. The horizontal gradient of 0.010 ft/ft, the average hydraulic conductivity value of 11.6 ft/day, and an effective porosity of 0.30 yields an average advective ground-water velocity for the unconfined sand aquifer of 0.39 ft/day, or approximately 142 feet per year. Because of low background total organic carbon (TOC) concentrations at the site, retardation is not considered to be an important transport parameter.

Ground Water and Light Nonaqueous-Phase Liquid Chemistry

Contaminants

Figure 1 shows the approximate distribution of light nonaqueous-phase liquid (LNAPL) at the site. This LNAPL is a mixture of jet fuel and waste solvents that partitions BTEX and TCE to ground water. Analysis of the LNAPL shows that the predominant chlorinated solvents are tetrachloroethane (PCE) and TCE; DCE and vinyl chloride are not present in measurable concentrations. For the most part, ground water beneath and downgradient from the LNAPL is contaminated with dissolved fuel-related compounds and solvents consistent with those identified in the LNAPL. The most notable exceptions are the presence of *cis*-1,2-DCE and vinyl chloride, which, because of their absence in the LNAPL, probably were formed by reductive dechlorination of TCE.

The dissolved BTEX plume currently extends approximately 2,000 feet downgradient from the site, and has a maximum width of about 500 feet. Total dissolved BTEX concentrations as high as 17 milligrams per liter (mg/L) have been observed in the source area. Figure 3 shows the extent of BTEX dissolved in ground water. As indicated on this map, dissolved BTEX contamination is migrating to the southeast in the direction of ground-water flow. Five years of historical data for the site show that the dissolved BTEX plume is at steady-state equilibrium and is no longer expanding.

Detectable concentrations of dissolved TCE, DCE, and vinyl chloride currently extend approximately 4,000 feet

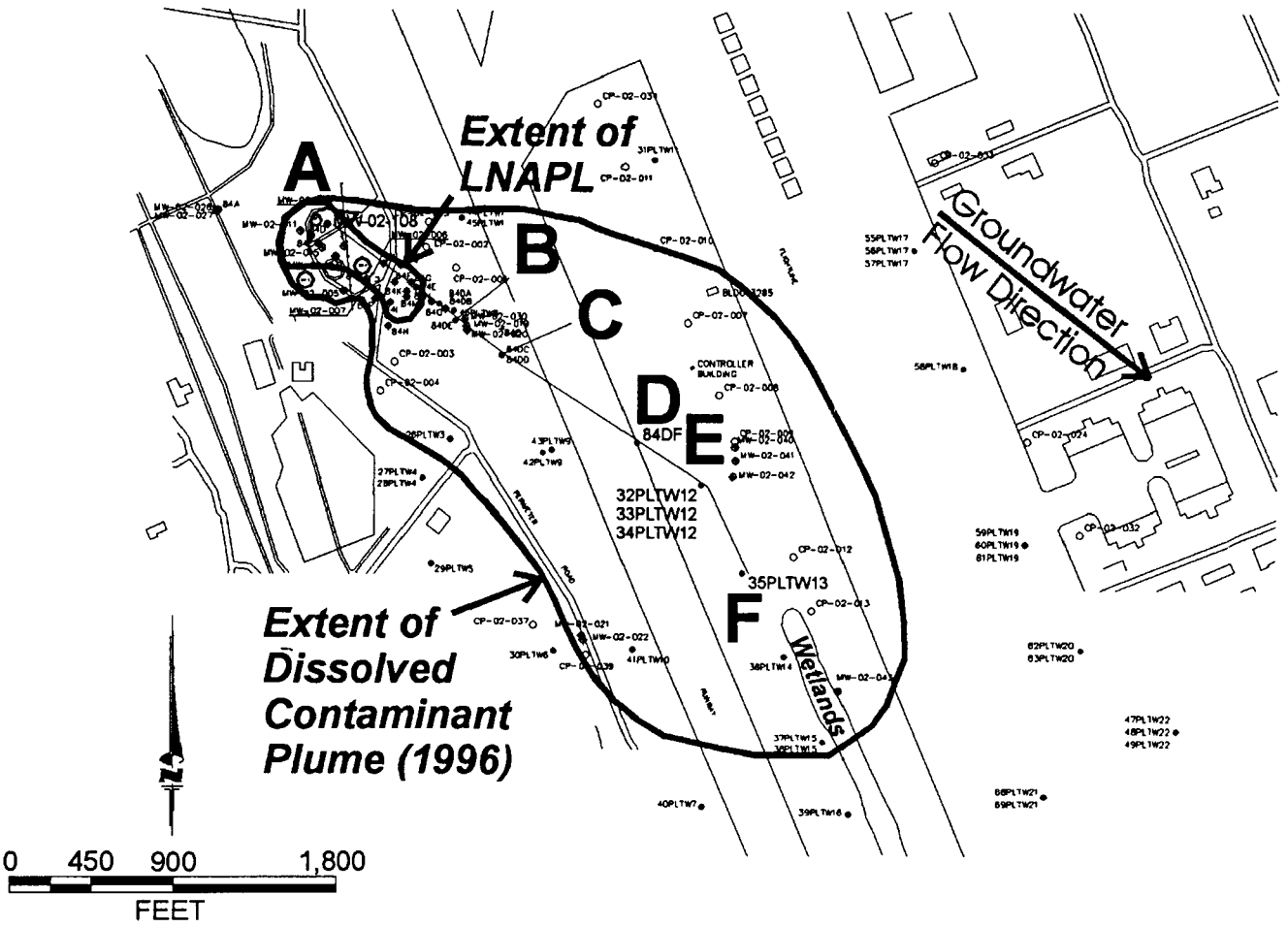

Figure 1. Site map.

downgradient from FT-002. Concentrations of TCE, DCE, and vinyl chloride as high as 25 mg/L, 51 mg/L, and 1.5 mg/L, respectively, have been observed at the site. As stated previously, no DCE was detected in the LNAPL plume at the site, and greater than 99 percent of the DCE found in ground water is the *cis*-1,2-DCE isomer. Figure 3 shows the extents of CAH compounds dissolved in ground water at the site. As indicated on this map, contamination is migrating to the southeast in the direction of ground-water flow. Five years of historical data for the site show that the dissolved CAH plume is at steady-state equilibrium and is no longer expanding.

Indicators of Biodegradation

The distribution of electron acceptors used in microbially mediated oxidation-reduction reactions is shown in Figure 4. Electron acceptors displayed in this figure include dissolved oxygen, nitrate, and sulfate. There is a strong correlation between areas with elevated BTEX concentrations and areas with depleted dissolved oxygen, nitrate, and sulfate. The absence of these compounds in contaminated ground water suggests that aerobic respiration, denitrification, and sulfate reduction are working to biodegrade fuel hydrocarbons at the site. Background dissolved oxygen, nitrate, and sulfate concentrations are on the order of 10 mg/L, 10 mg/L, and 25 mg/L, respectively.

Figure 5 shows the distribution of metabolic byproducts produced by microbially mediated oxidation-reduction reactions that biodegrade fuel hydrocarbons. Metabolic byproducts displayed in this figure include iron(II) and methane (Figure 5). There is a strong correlation between areas with elevated BTEX concentrations and areas with elevated iron(II) and methane. The presence of these compounds in concentrations above background in contaminated ground water suggests that iron(III) reduction and methanogenesis are working to biodegrade fuel hydrocarbons at the site. Background iron(II) and methane concentrations are less than 0.05 and 0.001 mg/L, respectively.

The pE of ground water is also shown in Figure 5. Areas of low pE correspond to areas with contamination, indicating that biologically mediated oxidation-reduction reactions are occurring in the area with ground-water contamination.

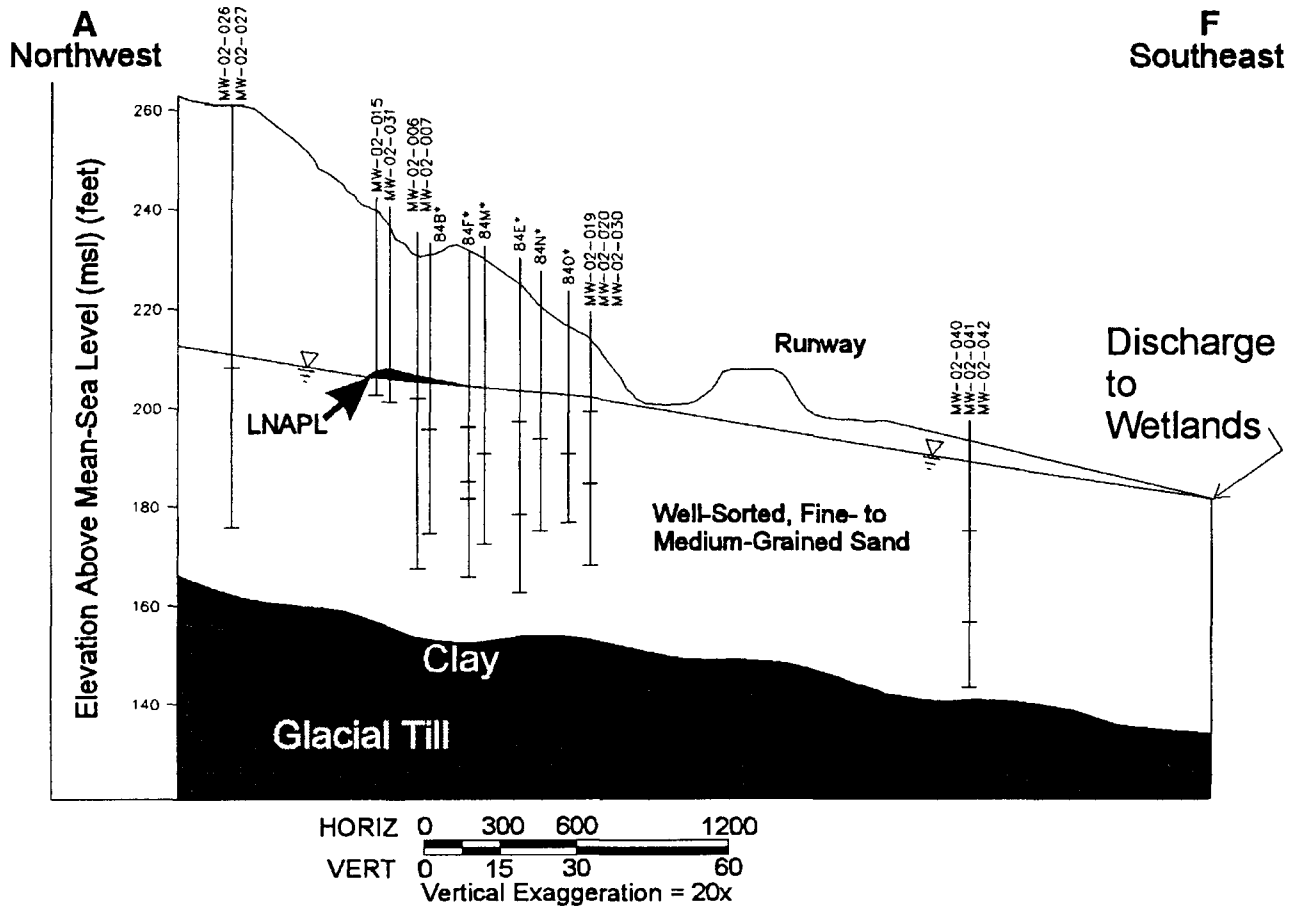

Figure 2. Hydrogeologic section.

Figure 3 illustrates the distribution of chloride in ground water and compares measured concentrations of total BTEX and CAHs in the ground water with chloride and ethene. There is a strong correlation between areas with contamination and areas with elevated chloride and ethene concentrations relative to measured background concentrations. The presence of elevated concentrations of chloride and ethene in contaminated ground water suggests that TCE, DCE, and vinyl chloride are being biodegraded. Background chloride concentrations at the site are approximately 2 mg/L; background ethene concentrations at the site are less than 0.001 mg/L.

Dissolved hydrogen concentrations can be used to determine the dominant terminal electron-accepting process in an aquifer. Table 2 presents the range of hydrogen concentrations for a given terminal electron-accepting process. Much research has been done on the topic of using hydrogen measurements to delineate terminal electron-accepting processes (2-4). Table 1 presents hydrogen data for the site.

Biodegradation Rate Constant Calculations

Apparent biodegradation rate constants were calculated using the method presented in Wiedemeier et al. (5, 6) for trimethylbenzene (TMB). A modified version of this method that takes into account the production of chloride during biodegradation also was used to calculate approximate biodegradation rates. Table 3 presents the results of these rate-constant calculations.

Table 2. Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

Terminal Electron Accepting Process	Hydrogen Concentration (nM/L)
Denitrification	< 0.1
Iron(III) reduction	0.2 to 0.8
Sulfate reduction	1 to 4
Methanogenesis	> 5

Primary Substrate Demand for Reductive Dechlorination

For reductive dechlorination to occur, a carbon source that can be used as a primary substrate must be present in the aquifer. This carbon substrate can be in the form of anthropogenic carbon (e.g., fuel hydrocarbons) or native organic material.

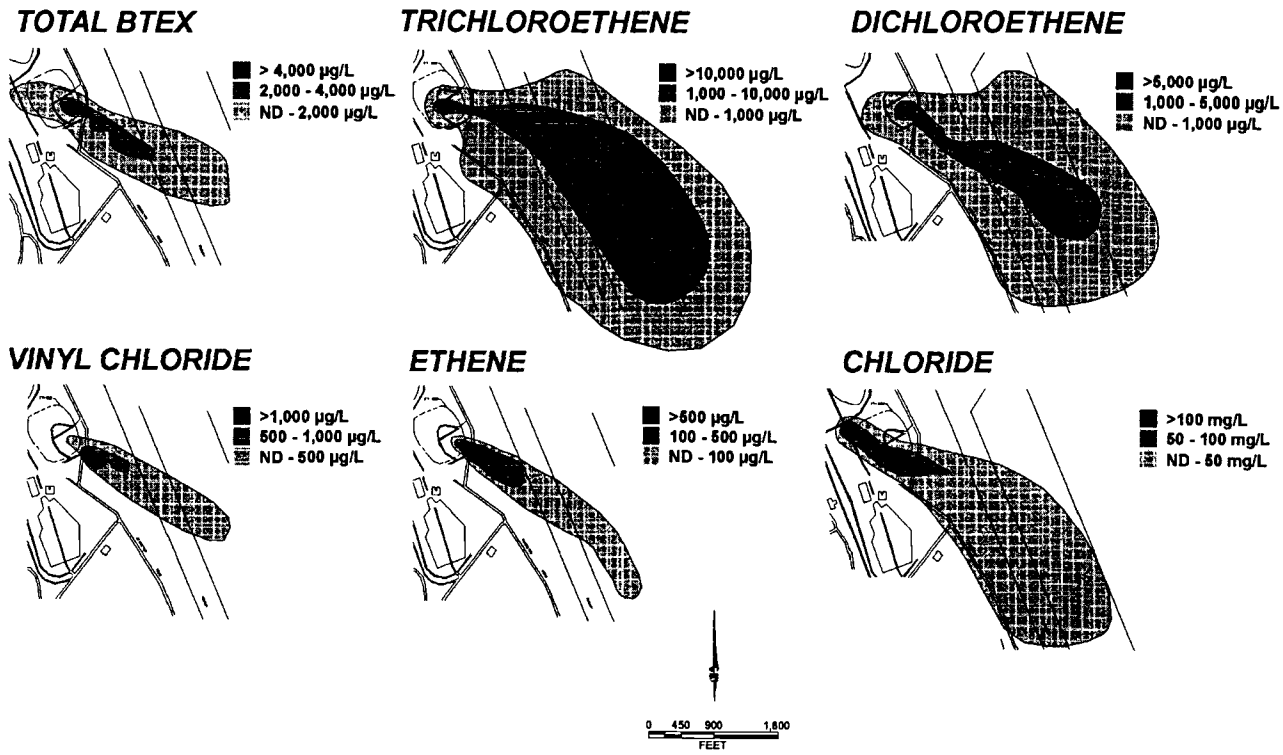

Figure 3. Chlorinated solvents and byproducts (1995).

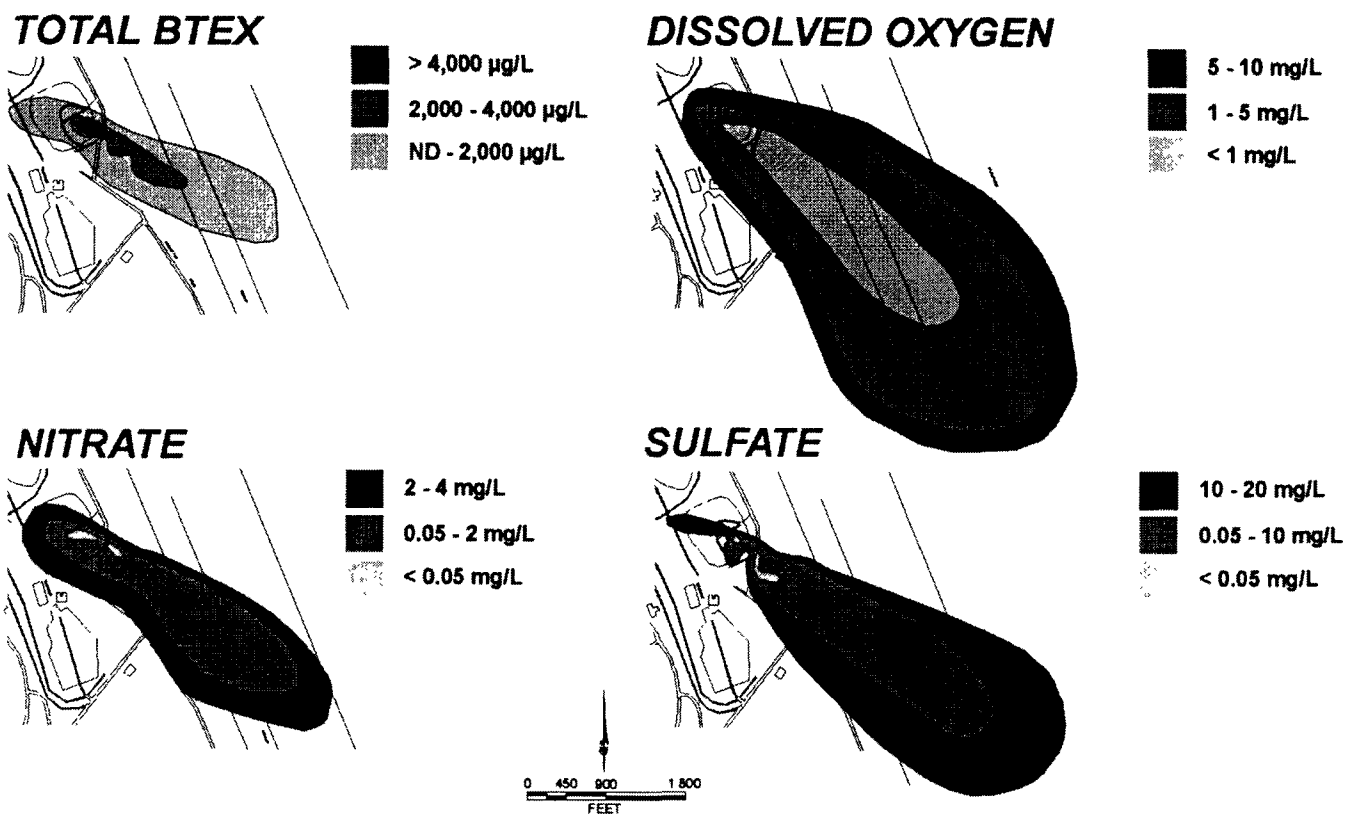

Figure 4. BTEX and electron acceptors (1995).

Table 3. Approximate First-Order Biodegradation Rate Constants

Compound	Correction Method	A - B 0 to 970 feet (1/year)	B - C 970 to 1,240 feet (1/year)	C - E 1,240 to 2,560 feet (1/year)
TCE	Chloride	1.27	0.23	-0.30
	TMB	1.20	0.52	NA
	Average	1.24	0.38	-0.30
DCE	Chloride	0.06	0.60	0.07
	TMB	0.00	0.90	NA
	Average	0.03	0.75	0.07
Vinyl chloride	Chloride	0.00	0.14	0.47
	TMB	0.00	0.43	NA
	Average	0.00	0.29	0.47
BTEX	Chloride	0.13	0.30	0.39
	TMB	0.06	0.60	NA
	Average	0.10	0.45	0.39

Reductive Dechlorination Supported by Fuel Hydrocarbons (Type 1 Behavior)

Fuel hydrocarbons are known to support reductive dechlorination in aquifer material (7). Equation 1 below describes the oxidation of BTEX compounds (approximated as CH) to carbon dioxide during reduction of carbon to chlorine bonds (represented as C-Cl) to carbon to hydrogen bonds (represented as C-H).

$$CH + 2H_2O + 2.5C\text{-}Cl \rightarrow CO_2 + 2.5H^+ + 2.5Cl^- + 2.5C\text{-}H \qquad \text{(Eq. 1)}$$

Based on Equation 1, each 1.0 milligram (mg) of BTEX that is oxidized via reductive dechlorination requires the consumption of 6.8 mg of organic chloride and the liberation of 6.8 mg of biogenic chloride. PCE loses two C-Cl bonds while being reduced to vinyl chloride. Based on Equation 1, ½ x 2.5 = 1.25 moles of TCE that would have to be reduced to vinyl chloride to oxidize 1 mole of BTEX to carbon dioxide. Therefore, each 1.0 mg of BTEX oxidized would consume 12.6 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of BTEX oxidized would consume 18.6 mg of DCE. To be more conservative, these calculations should be completed assuming that TCE and DCE are reduced to ethene. Because the amount of ethene produced is trivial compared with the amount of TCE and DCE destroyed, however, we have omitted this step here.

Reductive Dechlorination Supported by Natural Organic Carbon (Type 2 Behavior)

Wershaw et al. (8) analyzed dissolved organic material in ground water underneath a dry well that had received TCE discharged from the overflow pipe of a degreasing unit. The dissolved organic material in ground water exposed to the TCE was 50.57 percent carbon, 4.43 percent hydrogen, and 41.73 percent oxygen. The elemental composition of this material was used to calculate an empirical formula for the dissolved organic matter, and to estimate the number of moles of C-Cl bonds required to reduce one mole of dissolved organic carbon in this material:

$$C_{1.0}H_{1.051}O_{0.619} + 1.38H_2O + 1.91C\text{-}Cl \rightarrow CO_2 + 1.91Cl^- + 1.91C\text{-}H + 1.91H^+ \qquad \text{(Eq. 2)}$$

Based on Equation 2, each 1.0 mg of dissolved organic carbon that is oxidized via reductive dechlorination requires the consumption of 5.65 mg of organic chloride and the liberation of 5.65 mg of biogenic chloride. Using Equation 2, ½ x 1.91 = 0.955 moles of TCE that would have to be reduced to vinyl chloride to oxidize 1 mole of organic carbon to carbon dioxide. Therefore, 1.0 mg of organic carbon oxidized would consume 10.5 mg of TCE. If DCE were reduced to vinyl chloride, each 1.0 mg of organic carbon oxidized would consume 15.4 mg of DCE.

Table 4 compares the electron donor demand required to dechlorinate the alkenes remaining in the plume with the supply of potential electron donors. Table 3 reveals that removal of TCE and *cis*-1,2-DCE slows or ceases between points C and E. This correlates with the exhaustion of BTEX in the plume. Over this interval, the supply of BTEX is a small fraction of the theoretical demand required for dechlorination. There are adequate supplies of native organic matter, suggesting that native organic matter may not be of sufficient nutritional quality to support reductive dechlorination in this aquifer.

Table 4. Comparison of the Estimated Electron Donor Demand To Support Reductive Dechlorination to the Supply of BTEX and Native Organic Carbon

Point	Chloride (mg/L)	Organic Chloride (mg/L)	BTEX Available (mg/L)	BTEX Demand (mg/L)	TOC Supply (mg/L)	Organic Carbon Demand (mg/L)
A	63	58.1	16.8	8.5	80.4	10.3
B	43	7.72	4.2	1.13	31.1	1.37
C	57	8.26	3.9	1.21	24.3	1.46
D	13.6	1.34	0.09	0.20	13.8	0.24
E	18.4	0.78	0.04	0.114	8.2	0.14

Discussion and Conclusions

Available geochemical data indicate that the geochemistry of ground water in the source area and about 1,500 feet downgradient is significantly different than the ground water found between 1,500 and 4,000 feet downgradient from the source. Near the source the plume exhibits Type 1 behavior. At about 1,500 feet downgradient from

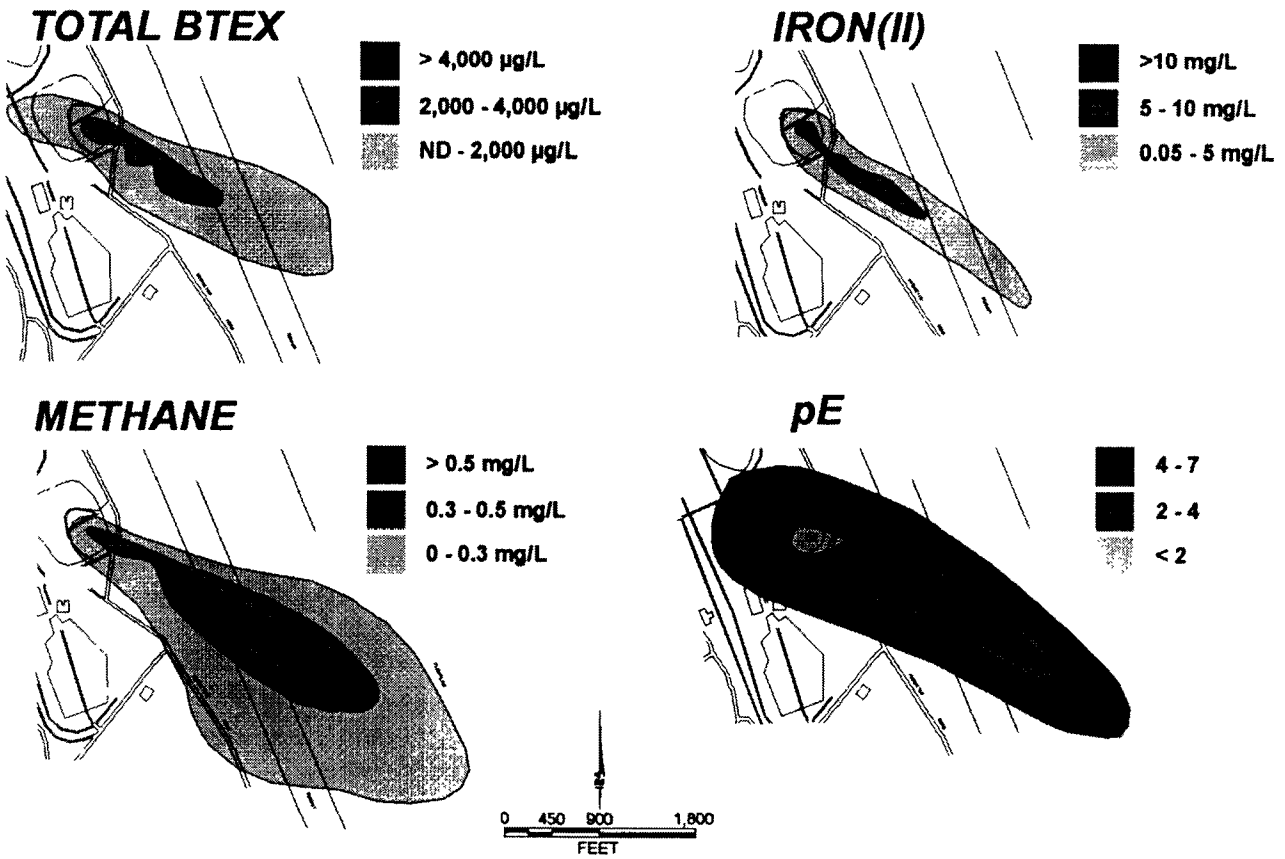

Figure 5. BTEX and metabolic byproducts (1995).

the source, the plume reverts to Type 3 behavior. Figure 6 shows the zones of differing behavior at the site.

Type 1 Behavior

In the area extending to approximately 1,500 feet downgradient from the former fire- training pit (source area), the dissolved contaminant plume consists of commingled BTEX and TCE and is characterized by anaerobic conditions that are strongly reducing (i.e., Type 1 behavior). Dissolved oxygen concentrations are on the order of 0.1 mg/L (background = 10 mg/L), nitrate concentrations are on the order of 0.1 mg/L (background = 10 mg/L), iron(II) concentrations are on the order of 15 mg/L (background = less than 0.05 mg/L), sulfate concentrations are less than 0.05 mg/L (background = 25 mg/L), and methane concentrations are on the order of 3.5 mg/L (background = mg/L). Hydrogen concentrations in the source area range from 1.4 to 11 nanomoles (nM). As shown by Table 2, these hydrogen concentrations are indicative of sulfate reduction and methanogenesis, even though there is no sulfate available and relatively little methane is produced. Thus, reductive dechlorination may be competitively excluding these processes.

In this area BTEX is being used as a primary substrate, and TCE is being reductively dechlorinated to *cis*-1,2-DCE and vinyl chloride. This is supported by the fact that no detectable DCE or vinyl chloride was found in the LNAPL present at the site and is strong evidence that the DCE and vinyl chloride found at the site are produced by the biogenic reductive dechlorination of TCE. Furthermore, the dominant isomer of DCE found at the site is *cis*-1,2-DCE, the isomer preferentially produced during reductive dechlorination. Average calculated first-order biodegradation rate constants in this zone are as high as 1.24, 0.75, and 0.29 per year for TCE, *cis*-1,2-DCE, and vinyl chloride, respectively. Figure 6 shows the approximate extent of this type of behavior. Because reductive dechlorination of vinyl chloride is slower than direct oxidation, vinyl chloride and ethene are accumulating in this area (Figure 7).

Type 3 Behavior

Between 1,500 and 2,000 feet downgradient from the source area, the majority of the BTEX has been biodegraded and the system begins to exhibit Type 3 behavior. Dissolved oxygen concentrations are on the order of 0.5 mg/L (background = 10 mg/L). Nitrate concentrations start increasing downgradient of where Type 3 behavior begins and are near background levels of 10 mg/L at the downgradient extent of the CAH plume. Iron(II) concentrations have significantly decreased and are on the

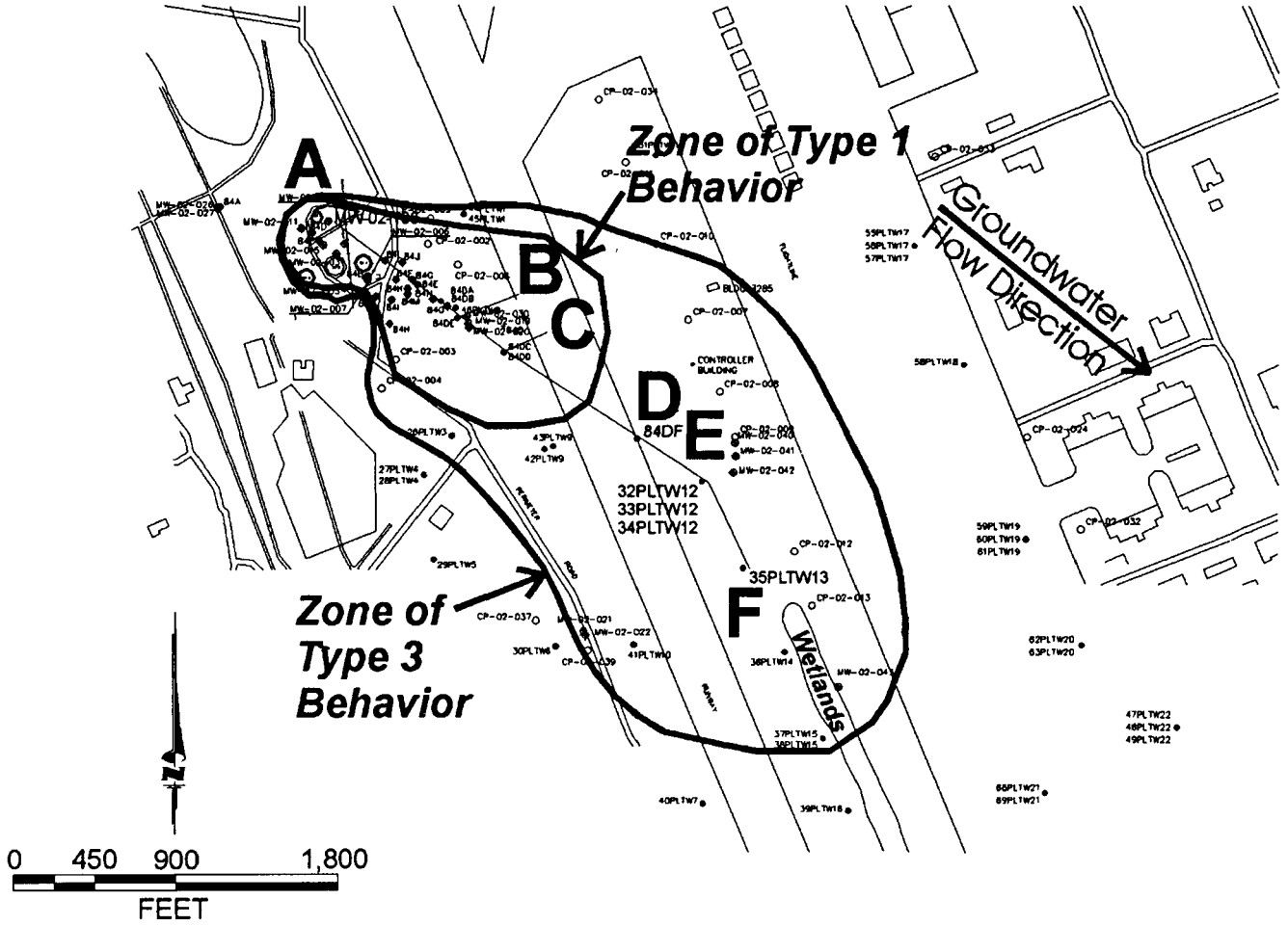

Figure 6. Zonation of CAH plume.

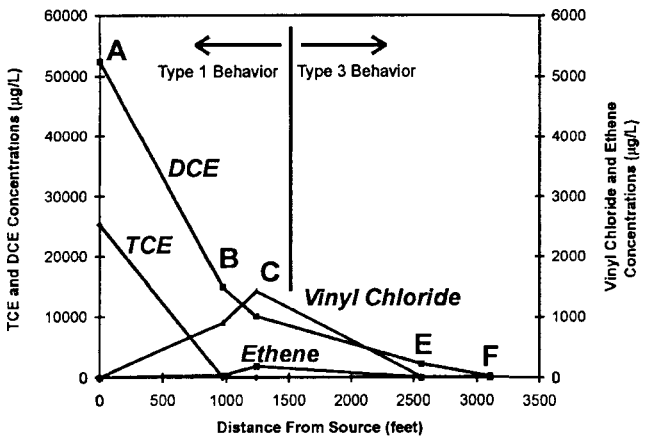

Figure 7. Plot of TCE, DCE, and ethene versus distance downgradient.

order of 1 mg/L (background = less than 0.05 mg/L). Sulfate concentrations start increasing to 15 mg/L at the downgradient extent of the CAH plume. Methane concentrations are the highest in this area but could have migrated from upgradient locations. The hydrogen concentrations at Points E and F are 0.8 nM and 0.25 nM, respectively, suggesting that the dominant terminal electron-accepting process in this area is iron(III) reduction.

These conditions are not optimal for reductive dechlorination, and it is likely that vinyl chloride is being oxidized via iron (III) reduction or aerobic respiration. Average calculated rate constants in this zone are -0.3, 0.07, and 0.47 per year for TCE, cis-1,2-DCE, and vinyl chloride, respectively. The biodegradation rates of TCE and DCE slow because reductive dechlorination stops when the plume runs out of primary substrate (i.e., BTEX). The rate of vinyl chloride biodegradation in this area increases, probably because vinyl chloride is being oxidized. Because biodegradation of vinyl chloride is faster under Type 3 geochemical conditions than the biodegradation of other CAH compounds, the accumulation of vinyl chloride ceases and the accumulated vinyl chloride rapidly degrades. Ethene concentrations also begin to decrease because ethene is no longer being produced from the reductive dechlorination of vinyl chloride (Figure 7).

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Case Study: Natural Attenuation of a Trichloroethene Plume at Picatinny Arsenal, New Jersey

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Introduction

Past efforts to clean up aquifers contaminated with chlorinated solvents typically have relied on engineered remediation systems that were costly to build and operate. Recently, environmental regulatory agencies have begun to give serious consideration to the use of natural attenuation as a more cost-effective remediation option. The successful use of natural attenuation to remediate chlorinated-solvent contaminated sites depends on understanding the processes that control the transport and fate of these compounds in the ground-water system.

To this end, the U.S. Geological Survey, as part of its Toxic Substances Hydrology Program, has been conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents at Picatinny Arsenal, New Jersey. The objectives of the study are to identify and quantify the physical, chemical, and biological processes that affect the transport and fate of chlorinated solvents, particularly trichloroethene (TCE), in the subsurface; determine the relative importance of these processes at the site; and develop predictive models of chlorinated-solvent transport that may have transfer value to other solvent-contaminated sites in similar hydrogeologic environments.

This paper reports on the results of efforts to identify and quantify the natural processes that introduce and remove TCE to and from the plume at Picatinny Arsenal, and to determine which natural TCE-attenuation mechanisms are the most important on a plume-wide basis.

Geohydrology

Picatinny Arsenal is a weapons research and development facility located in a narrow glaciated valley in north central New Jersey (Figure 1). The site is underlain by a 15- to 20-meter thick unconfined aquifer consisting primarily of fine to coarse sand with some gravel and discontinuous silt and clay layers. Ground-water flows from the sides of the valley toward the center, where it discharges to Green Pond Brook. Within the unconfined aquifer, flow is generally horizontal, with some downward flow near the valley walls and upward flow near Green Pond Brook. Estimated ground-water flow velocities range from 0.3 to 1.0 meters per day (m/d) at the site on the basis of hydraulic conductivities that range from 15 to 90 m/d, gradients that range from 1.5 to 3.0 m per 500 m, and an average porosity of 0.3 (1-4).

Ground-Water Contamination

Ground water at Picatinny Arsenal was contaminated over a period of 30 years as a result of activities associated with metal plating and degreasing operations in Building 24 (5, 6). The areal and vertical extent of TCE contamination at the site, determined using data from October and November 1991, is shown in Figure 1. Areally, the plume, as defined by the 10 micrograms per liter (µg/L) line, extends about 500 m from Building 24 to Green Pond Brook and is approximately 250 m wide where it enters the brook. Vertically, TCE contamination is found at shallow depths near the source, over the entire 15- to 20-m thickness of the unconfined aquifer in the plume center, and at shallow depths as it discharges upward to the brook (Figure 1B). Whereas TCE concentrations greater than 1,000 µg/L are found in the source area, the TCE concentrations are highest (greater than 10,000 µg/L) near the base of the aquifer midway between the source and discharge.

Geochemistry of the Plume

Determination of the pH and redox conditions present in a plume is essential to predicting the types of natural biological interactions that may take place in the aquifer.

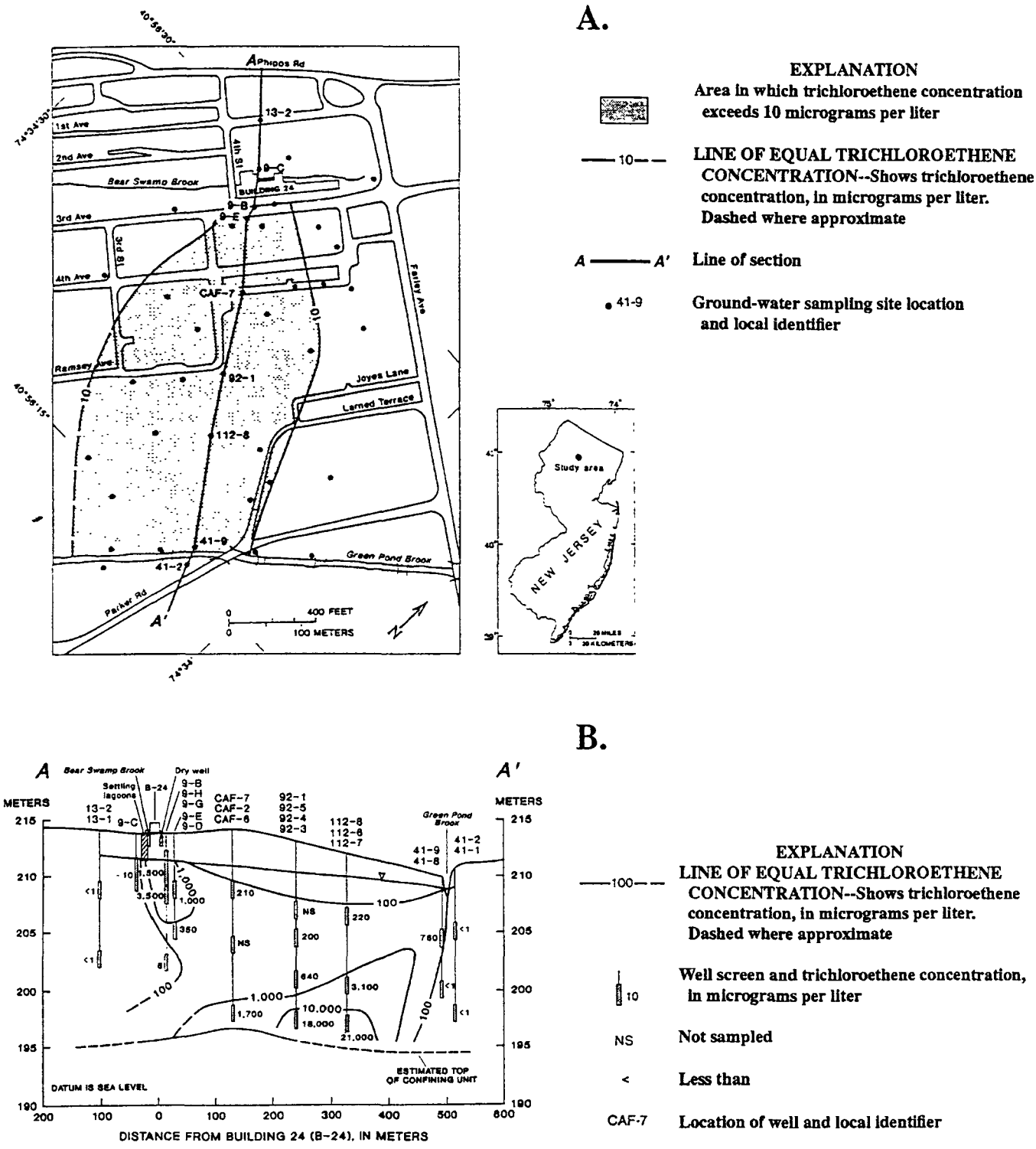


Figure 1. Location of Building 24 study area at Picatinny Arsenal, New Jersey: (A) areal extent of ground-water trichloroethene plume and (B) vertical distribution of ground-water trichloroethene concentrations, October to November 1991. (Location of section A-A' is shown in Figure 1A.)

Results of water-quality analyses indicate that the pH of ground water in the plume is near neutral (6.5 to 7.5), and concentrations of both dissolved oxygen (less than 0.5 milligrams per liter [mg/l]) and nitrate (less than 1 mg/L) are very low. Concentrations of iron(II) are greater than 1 mg/L in some areas of the plume, whereas sulfate and carbon dioxide are consistently plentiful (greater than 40 mg/L and 100 mg/L as bicarbonate, respectively) as

potential terminal electron acceptors. In addition, sulfide odor was noted in water from many wells within the plume, and methane was present at concentrations ranging from 1 to 85 µg/L.

These findings indicate the plume is primarily anaerobic and contains a variety of reducing redox environments controlled in different areas by iron(III) reduction, sulfate reduction, and methanogenesis. Under these conditions, reductive dechlorination of TCE can take place if sufficient electron donors are available. Dissolved organic carbon (DOC), consisting primarily of humic and fulvic acids, may fulfill the electron donor requirement in this system. Concentrations of DOC are highest immediately downgradient from the source area (5 to 14 mg/L) and also are elevated near the discharge point (1 to 2 mg/L).

The presence of cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC)—TCE breakdown products—in 75 percent of the wells sampled in and around the plume indicates that reductive dechlorination of TCE is taking place in the aquifer. Because neither of these compounds was used in Building 24, they are believed to originate from the biologically mediated breakdown of TCE. Further evidence for reductive dechlorination of TCE is the similarity among the distributions of TCE, cis-DCE, and VC in the aquifer, although the concentrations of cis-DCE and VC are highest in the downgradient portion of the plume near the discharge point.

Trichloroethene Mass Distribution

The mass of TCE dissolved in the ground water in the plume was estimated on the basis of results of six synoptic sampling taken from 1987 to 1991. By using a plume volume of 2.3 x 10^6 cubic meters (m^3) and a porosity of 0.3, and by assuming that each well represents a finite volume of the aquifer, the average mass of TCE dissolved in the plume was determined to be 1,000 ± 200 kilograms (kg) (7). This estimate did not show a consistent increasing or decreasing trend over the six sampling, which implies that the plume was essentially at steady state. Most of the dissolved TCE mass (57 percent) is present in the ground water near the base of the unconfined aquifer, where TCE concentrations are greater than 10,000 µg/L.

The mass of sorbed TCE within the plume was estimated from methanol-extraction analyses of sediments from six sites along the centerline of the plume (8). The ratio of the masses of sorbed TCE to dissolved TCE per unit volume of aquifer ranged from 3:1 to 4:1 at these six sites. Therefore, 3,000 to 4,000 kg of TCE is calculated to be sorbed to aquifer sediments within the plume. A sorbed mass of 3,500 kg of TCE was used in all calculations.

Trichloroethene Mass-Flux Estimates

The major naturally occurring processes that affect the input or removal of TCE to or from the plume were identified and studied independently as part of the Toxic Substances Hydrology Program project at Picatinny Arsenal (9, 10). The TCE removal processes that were considered include advective transport, lateral dispersion, anaerobic biotransformation, diffusion-driven volatilization, advection-driven volatilization, and sorption. The TCE input processes evaluated include desorption, infiltration, and dissolution. Each of these processes is described briefly below, and a TCE mass-flux estimate is made for each on the basis of the results of research conducted in the Picatinny Arsenal plume.

Removal-Process Flux Estimates

Advective transport is the process by which dissolved TCE is removed from the plume in ground water that is discharging to Green Pond Brook. The mass flux of TCE was calculated by using an advective flux rate of 800 liters per meter squared per week (based on modeling analyses [4, 11]), a median ground-water TCE concentration of 1,200 µg/L, and a cross-sectional area of 980 square meters where the aquifer discharges to the brook. On the basis of these values, approximately 50 kilograms per year (kg/yr) of TCE are removed from the plume by discharge to Green Pond Brook.

Lateral dispersion is the process that causes plume spreading by transport of TCE out of the side boundaries of the plume where the concentration is 10 µg/L (Figure 1). Using Fick's Law, the lateral TCE-concentration gradient, and the estimated area of the sides of the plume, researchers calculated that less than 1 kg/yr of TCE is lost from the plume by this mechanism.

Anaerobic biotransformation is the biologically mediated process of reductive dechlorination whereby TCE undergoes the sequential replacement of the chlorine atoms on the molecule with hydrogen atoms to form cis-DCE, VC, and ethene as breakdown products (12, 13). Biotransformation rate constants were determined in laboratory batch microcosm studies of core samples from five sites along the centerline of the plume (14, 15). The first-order TCE-degradation rate constants obtained in these studies range from -0.004 to -0.035 per week, with a median of -0.007 per week. If this latter rate constant is applied to the 1,000 kg of TCE dissolved in the plume, about 360 kg/yr of TCE are removed from the plume by naturally occurring anaerobic biotransformation.

Volatilization is the loss of TCE from ground water into the soil gas of the unsaturated zone across the water table. Volatilization is driven by diffusive and advective mechanisms. The rate of loss of TCE in diffusion-driven volatilization is determined by the TCE gradient in the soil gas of the unsaturated zone. Diffusion-driven vola-

tilization was estimated using Fick's Law, field-measured unsaturated-zone soil-gas TCE gradients, bulk diffusion coefficients from the literature for sites with similar soils, and the area of the plume. Removal of TCE from the plume by diffusion-driven volatilization is calculated to be less than 1 kg/yr over the area of the plume (7, 16). In advection-driven volatilization, the rate of loss of TCE is controlled by pressure and temperature changes in the unsaturated-zone soil gas. Advection-driven volatilization was investigated using a prototype vertical-flux measuring device at Picatinny Arsenal (16). On the basis of flux measurements made with the device at eight sites and the area of the plume, the TCE removed from the plume by advection-driven volatilization is calculated to be approximately 50 kg/yr.

Sorption is the partitioning of TCE from the ground water into the organic-carbon fraction of the aquifer sediments. Field partition coefficients measured at several locations within the plume (8) indicate that more TCE was sorbed to aquifer organic materials at all sites than would be predicted if the sorbed TCE concentrations were in equilibrium with the ground-water TCE concentrations. Therefore, desorption processes rather than sorption processes most likely predominate. Removal of TCE by sorption is estimated to be less than 1 kg/yr.

Input-Process Flux Estimates

Desorption is the process by which TCE partitions out of the organic phase on the contaminated sediments back into the ground water in response to concentration gradients. This process at Picatinny Arsenal was characterized as having two parts: an initial rapid phase of desorption, in which 0 to 10 percent of the TCE releases, and a second, slower phase of desorption, in which most of the TCE releases over a longer period (8). First-order desorption rate constants ranging from -0.003 to -0.015 per week were measured in flow-through column experiments. Because these experiments were conducted with clean water, the desorption rates obtained probably are higher than in situ desorption rates. For this reason, the smaller of the desorption rate constants (-0.003 per week) and the total amount of TCE estimated to be sorbed to the plume sediments (3,500 kg) were used to calculate that 550 kg/yr of TCE is being input to the plume by means of desorption.

Infiltration, the process by which TCE in the soil gas or on the unsaturated-zone soil is dissolved by percolating recharge to the ground water, was studied with laboratory soil columns, field infiltration experiments, and multiphase solute-transport modeling (17). Because concentrations of TCE in the soil gas generally are low over most of the plume, and because infiltration occurs only during recharge events rather than continuously throughout the year, it was estimated that the input of TCE to the plume by this process is less than 1 kg/yr.

Dissolution is the process by which dense nonaqueous-phase liquid (DNAPL) TCE dissolves into the ground water. The presence of DNAPL TCE at the base of the unconfined aquifer midway between the source and the brook has been suspected because concentrations of TCE in ground water at this location are much higher than those immediately upgradient. Concentrations of TCE in deep wells in this area consistently exceed 2 percent of saturation, which is one indication of DNAPL presence (18). DNAPL TCE has not been confirmed by measurement or observation of free-phase TCE in any water or soil sample from the arsenal. Consequently, the mass of DNAPL TCE that is input by dissolution cannot be calculated directly but can only be estimated by the difference between the sum of the mass removed by all removal processes and the sum of the mass introduced by all other input processes.

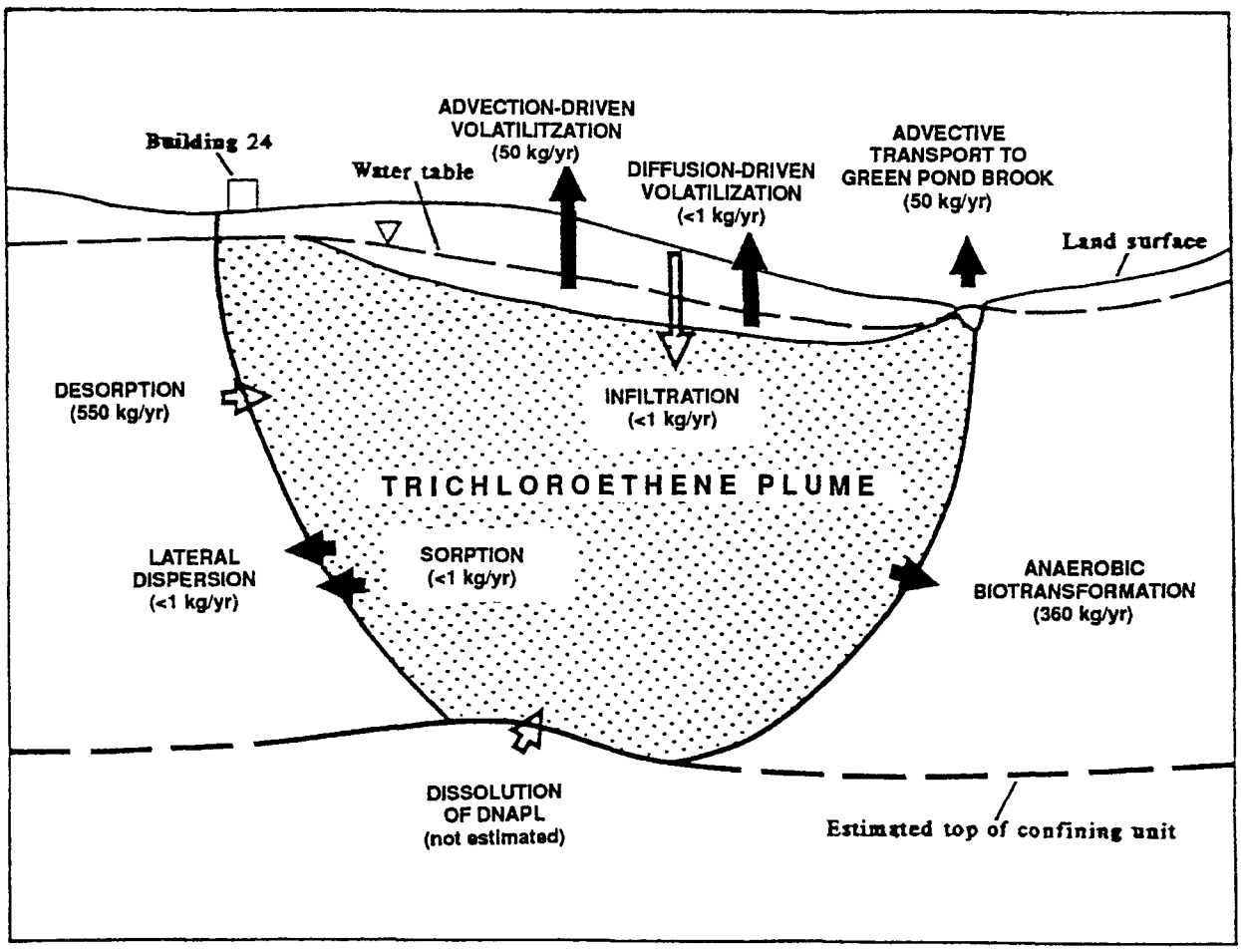
Mass-Balance Analysis

The estimated mass balance for the TCE plume at Picatinny Arsenal is shown in Figure 2. All inputs are represented with open arrows; all outputs are represented with solid arrows.

Approximately 460 kg/yr of dissolved TCE is estimated to be removed from the plume by natural processes. Of this, 360 kg/yr, or 78 percent of the TCE removed annually, is removed as a result of anaerobic biotransformation. This is by far the most important TCE removal process operating in the Picatinny Arsenal plume. Removal by advective transport to Green Pond Brook and advection-driven volatilization are each estimated at 50 kg/yr. Therefore, each of these processes is responsible for the removal of about 11 percent of the total TCE removed annually from the plume. Lateral dispersion, diffusion-driven volatilization, and sorption are all of minor importance compared with these major processes.

The finding that natural anaerobic biotransformation is the principal mechanism for removal of TCE from the plume at Picatinny Arsenal is significant. Anaerobic biotransformation has been reported to be a major natural removal process for TCE at only a few sites (19), and this conclusion has not previously been reached by quantifying and comparing the magnitude of all other removal processes occurring at a site. This result is likely to have great transfer value to other sites with similar geochemistry, hydrology, and geology.

The process of desorption is the most important input mechanism evaluated at Picatinny Arsenal; it accounts for the introduction of an estimated 550 kg/yr of TCE. Input by infiltration is very small in comparison (less than 1 kg/yr). Because the sum of the inputs is larger than the sum of the outputs, dissolution of DNAPL TCE in the system cannot be estimated.



NOT TO SCALE

TRICHLOROETHENE MASS-BALANCE COMPONENTS
[kg/yr, kilograms per year; <, less than]

GAINS	
DESORPTION	550 kg/yr
INFILTRATION	<1 kg/yr
DISSOLUTION OF DENSE NONAQUEOUS PHASE LIQUID	not estimated
TOTAL	550 kg/yr

LOSSES	
ANAEROBIC BIOTRANSFORMATON	360 kg/yr
ADVECTIVE TRANSPORT TO BROOK	50 kg/yr
ADVECTION-DRIVEN VOLATILIZATION	50 kg/yr
LATERAL DISPERSION	<1 kg/yr
DIFFUSION-DRIVEN VOLATILIZATION	<1 kg/yr
SORPTION	<1 kg/yr
TOTAL	460 kg/yr

Figure 2. Mass-balance estimates of fluxes of naturally occurring processes that affect the fate and transport of trichloroethene in the ground-water system at Picatinny Arsenal, New Jersey.

The fact that long-term desorption is a significant continuing source of TCE to the aquifer may explain why the TCE concentrations are still relatively high in the source area (greater than 1,000 µg/L) 13 years after TCE use was discontinued at the site. This finding is significant because it shows that desorption can be an important input mechanism even at sites where the sediment organic content is low (less than 0.5 percent).

Because the mass of TCE in the plume was at steady state during these studies, the sources of TCE ideally should equal the sinks of TCE. Although the estimated inputs do not equal the estimated outputs in the mass balance, they are of the same order of magnitude. Additional study of the individual processes would be necessary to refine the mass balance further. Because confidence in the output-process mass-flux estimates is

high and the TCE desorption rate constants used probably were on the high side, the desorption mass-flux estimate may be higher than the actual value.

Field-Scale Estimate of Natural Attenuation Rate

The natural attenuation rate of TCE at Picatinny Arsenal was calculated from field data and compared with the anaerobic biotransformation rates calculated in the laboratory microcosm studies. Assuming first-order kinetics and considering the decrease in TCE concentrations from the source area to the discharge area (1,900 µg/L to 760 µg/L), the time of travel for TCE between these two points in the plume (3.1 years), and the distance between these two sites (470 m), then the field-scale natural attenuation rate constant is calculated to be -0.006 per week. This field-calculated rate constant is nearly identical to the median rate constant of -0.007 per week determined in the laboratory microcosm experiments. That both methods yield rate constants of similar magnitude confirms that most of the natural attenuation that occurs in the Picatinny Arsenal plume is due to anaerobic biotransformation. In addition, it indicates that the methods used to make these estimates and measurements are valid.

Comparison of Natural Attenutation Processes to Pump-and-Treat Remediation

A pump-and-treat system was installed in the Picatinny Arsenal TCE plume as an interim remediation measure in September 1992. It consists of a set of five withdrawal wells from which an average of 440,000 liters per day are pumped to a treatment system equipped with stripping towers and granulated activated carbon filters. On the basis of average pumpage values and ground-water TCE concentrations in each withdrawal well during 1995, the pump-and-treat system is currently removing about 70 kg/yr at a cost of $700,000 per year. This is about one-fifth the amount of TCE being removed from the plume each year by anaerobic biotransformation, and just slightly more than the mass of TCE being removed by each of the processes of advective transport and advection-driven volatilization.

Conclusion

The relative importance of all naturally occurring processes that introduce or remove TCE to or from a contamination plume at Picatinny Arsenal, New Jersey, was determined. Anaerobic biotransformation is the most important process for TCE removal from the plume by almost an order of magnitude over advective transport and advection-driven volatilization. Anaerobic biotransformation accounts for an estimated 78 percent of the total mass of TCE removed from the plume annually. Other removal processes—lateral dispersion, diffusion-driven volatilization, and sorption—are minor in comparison. Desorption is the most significant TCE input process evaluated. A mass-balance analysis shows that the removal of TCE from the plume by natural attenuation processes is of the same order of magnitude as the input of TCE to the plume. The natural attenuation rate constant calculated from field TCE concentrations and time-of-travel data is in close agreement with anaerobic biotransformation rate constants measured in laboratory microcosm studies.

Anaerobic biotransformation removes approximately five times the mass of TCE removed by an interim pump-and-treat remediation system operating at the Picatinny Arsenal site. The pump-and-treat system removes just slightly more mass per year than each of the processes of advective transport to Green Pond Brook and advection-driven volatilization.

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Case Study: Plant 44, Tucson, Arizona

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Introduction

A pump-and-treat remediation system operating for the past 10 years at the Plant 44 site in Tucson, Arizona, allowed hydraulic control of the dissolved chlorinated solvents contaminant plume. Additionally, the pump-and-treat network removed a total of approximately 6,000 kilograms (kg) of trichloroethene (TCE) in its first 5 years of operation. Recent observations using site data, however, include resurgence of TCE concentrations after pump turnoff and the emergence of the "tailing" phenomenon at a number of the pumping wells.

A detailed analysis of the site's historical information as well as extensive data collected before and after system startup suggested the presence of dense nonaqueous phase liquids (DNAPLs) at the site and revealed that the pump-and-treat system would not achieve the desired site cleanup within a reasonable time frame.

Plant 44 Site Description

The site hydrogeology consists of four stratigraphic units (1): a relatively thick unsaturated zone extending between 110 to 130 feet below the surface; an upper zone extending to a depth of 180 to 220 feet; an aquitard consisting of 100 to 150 feet of low-permeability clay; and a lower zone. Pump tests indicate that hydraulic conductivity ranges from 2×10^{-4} to 3×10^{-3} feet per second for the upper zone. The background hydraulic gradient is 0.006 feet per foot toward the northwest, and the groundwater velocity ranges from 250 to 800 feet per year (2).

Activities at Plant 44 include development, manufacturing, testing, and maintenance of missile systems from 1952 until the present. Historical data indicate that greater than 50 drums per year of TCE, 1,1-dichloroethene (1,1-DCE), and 1,1,1-trichloroethane (1,1,1-TCA) were used at the site. The resulting area of TCE contamination was approximately 5 miles long by 1.6 miles wide in 1986, before remediation startup (Figure 1). A maximum TCE concentration of 2.7 parts per million (ppm) was measured in 1986, although concentrations of up to 15.9 ppm have been observed in the ground water (2). Potential sources of contamination include pits, ponds, trenches, and drainage ditches in which disposal of solvents and waste water was reported from 1952 through 1977 (Figure 2).

Ground-Water Extraction System

The pump-and-treat system began operation in April 1987. The system consists of 17 extraction wells and 13 recharge wells, shown in Figure 1. Water-level elevation and contaminant concentration data for the pumping wells and 40 monitoring wells are collected monthly. The total dissolved mass removed by the system in its first 5 years of operation (approximately 6,000 kg) exceeds the 3,800 kg dissolved mass present in the plume in 1986. This would suggest the presence of a continuing source of contamination in the aquifer.

The concentration of dissolved TCE in the extracted ground water decreases during remediation, particularly in those wells with initially high TCE concentrations. In the majority of cases, the TCE concentration appears to level out between 3 and 5 years, usually to a value that exceeds the TCE drinking water standard of 5 parts per billion (ppb). Numerous spikes of high TCE concentration are observed in a number of the pumping wells, possibly due to continuing sources.

Fate-and-Transport Modeling

Modeling of the TCE plume at the site was completed to evaluate the time required for cleanup. Aqueous-phase flow in the upper zone was simulated along with the pump-and-treat remediation system. Source locations used in the modeling were based on the location

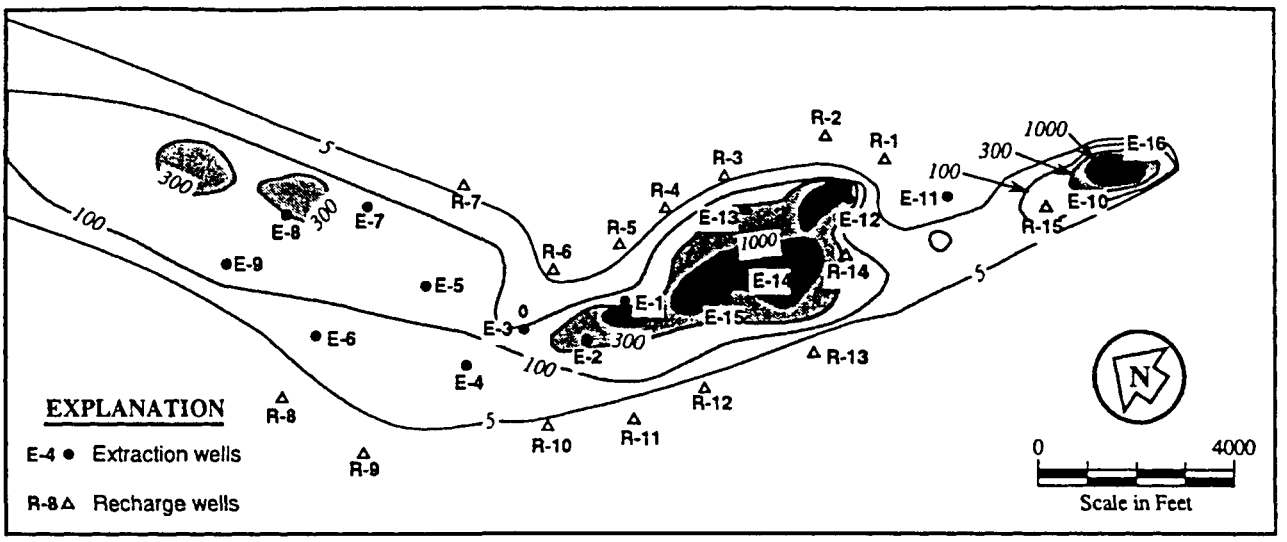

Figure 1. TCE plume prior to remediation, December 1986 (ppb).

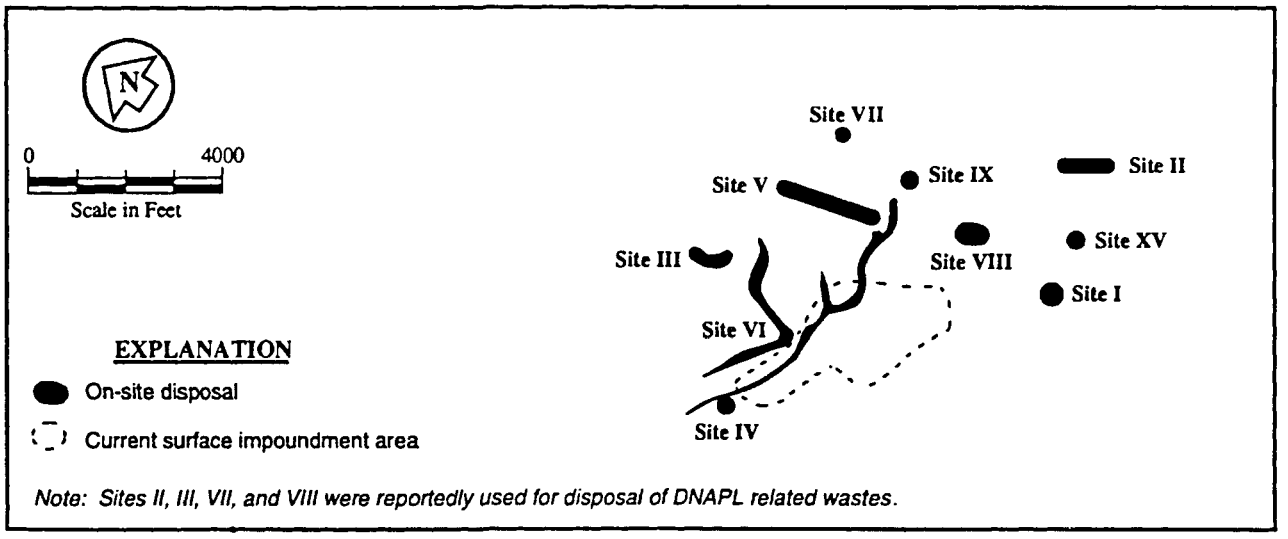

Figure 2. Historical onsite disposal locations.

of "hot spots" in the plume, areas where formation of DNAPL pools is likely and areas where the confining clay layer is thin. An overall mass transfer rate due to a continuing source of contamination was estimated based on the difference between the mass pumped in the first 5 years of operation of the system and the mass present in the aquifer.

Additionally, source dissolution mechanisms were analyzed assuming the following four potential configurations of DNAPL in the subsurface: unsaturated zone residual, a DNAPL pool, saturated zone residual, and DNAPL located in a nonadvective zone. Dissolution times, for example, due to unsaturated zone source areas ranged from 1,100 to 13,000 years, while those for DNAPL pools ranged from 1 to 60,000 years depending on the source assumptions that were made.

A comparison between the estimated mass transfer rate and the dissolution data indicated that the two most likely dissolution mechanisms present at the site include unsaturated zone residuals and DNAPL pools. The associated dissolution times ranged from 100 to 1,000 years. The fate-and-transport modeling results, assuming no continuing sources of TCE into the aquifer, indicate that 50 more years of the remediation system's operation are required. If the estimated mass transfer rates are incorporated into the model, the required remediation time exceeds hundreds of years.

Conclusion

Data from the Plant 44 site indicate that DNAPL may be present. Further contamination of the ground water might occur because of sources present in the unsaturated zone and the potential dissolution from TCE plumes.

Complete dissolution of the DNAPL pools may take as long as 100 years under pumped conditions, while dissolution of unsaturated residual by infiltrating ground water may continue for thousands of years. The groundwater extraction system at the site has contained the dissolved plume and removed significant amounts of chlorinated compounds. If DNAPL is present at the site, however, complete removal of TCE using pump-and-treat will require a very lengthy and costly operation period.

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Remediation Technology Development Forum Intrinsic Remediation Project at Dover Air Force Base, Delaware

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Introduction

The Remediation Technology Development Forum (RTDF) Bioremediation Consortium is conducting a large, integrated field and laboratory study of intrinsic remediation in a plume at the Dover Air Force Base (AFB) in Delaware. The work group is a consortium of industrial companies and government agencies working on various aspects of bioremediation of chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethene (TCE). The intrinsic bioremediation program is part of an integrated study that also includes cometabolic bioventing and accelerated anaerobic treatment. The combination of these three methods can treat all parts of a solvent contamination area.

The goals of the 4-year intrinsic remediation study are to evaluate whether the contaminants at the site are being destroyed through intrinsic remediation, to identify the degradation mechanisms, and to develop and validate protocols for implementing intrinsic remediation at other sites.

A wide variety of geological, geochemical, and biological research is being integrated into this study. This presentation emphasizes the geochemical aspects of the study for the following reasons: the geochemical data were available early in the study; it clearly shows that solvent destruction is happening; and the primary author's expertise lies in geochemistry. The participants who focused on the biological aspects of this study will undoubtedly be presenting their conclusions at future meetings.

Background

The RTDF Bioremediation Consortium initiated this study in February 1995. Dover AFB was chosen over the many other sites evaluated for the study because:

- The plume is well-characterized.
- Analyses of ground-water chemistry provided clear evidence that chlorinated solvent contaminants are being biodegraded.
- The deep zone of the aquifer has relatively simple geology and is underlain by a thick confining layer.
- Access for sampling and testing is good, and the site is easily reached by offsite personnel and visitors.
- The base has a proactive environmental program.

The plume contains primarily TCE and dichloroethene (DCE), with smaller amounts of vinyl chloride (VC). It occupies an area north and south of U.S. Highway 113 approximately 9,000 feet long and 3,000 feet wide. There are multiple sources of solvent contamination in the area north of the highway, as well as several minor sources of petroleum hydrocarbons. There appear to be at least three sources of TCE.

The water-bearing unit in the study area is composed of fine- to coarse-grained sands ranging in thickness from 30 to 60 feet. The ground-water elevation ranges from approximately 13 feet mean sea level (MSL) at the north end of the plume to less than 3 feet MSL near the southern end. Ground water flows to the south. The plume velocity ranges from about 150 feet per year in the northern portion of the study area to over 200 feet per year beneath the southern area. The consortium believes that the aquifer contains aerobic and anaerobic microzones. This simple sand aquifer exhibits complex metabolic activity that might not be apparent from a cursory examination of geochemical information.

This paper focuses on the lower third of the aquifer, which has the highest permeability and contains the majority of the contaminants.

Current Findings

Intrinsic remediation is clearly occurring in the ground water, and results suggest that multiple biodegradation pathways are operating. These findings are based on data on the plume profile, contaminant concentrations and geochemical markers, and the presence of the soluble chloride ion produced by biodegradation of the solvents.

Plume Profile

Figure 1 shows the relationship of the constituents within the plume. Note that the plumes of the different solvent species are "stacked." There is no chromatographic separation, as would be expected based on the much different mobilities of these compounds in ground water. This suggests that the more mobile compounds, such as VC, are degrading before they can move away from the less mobile ones.

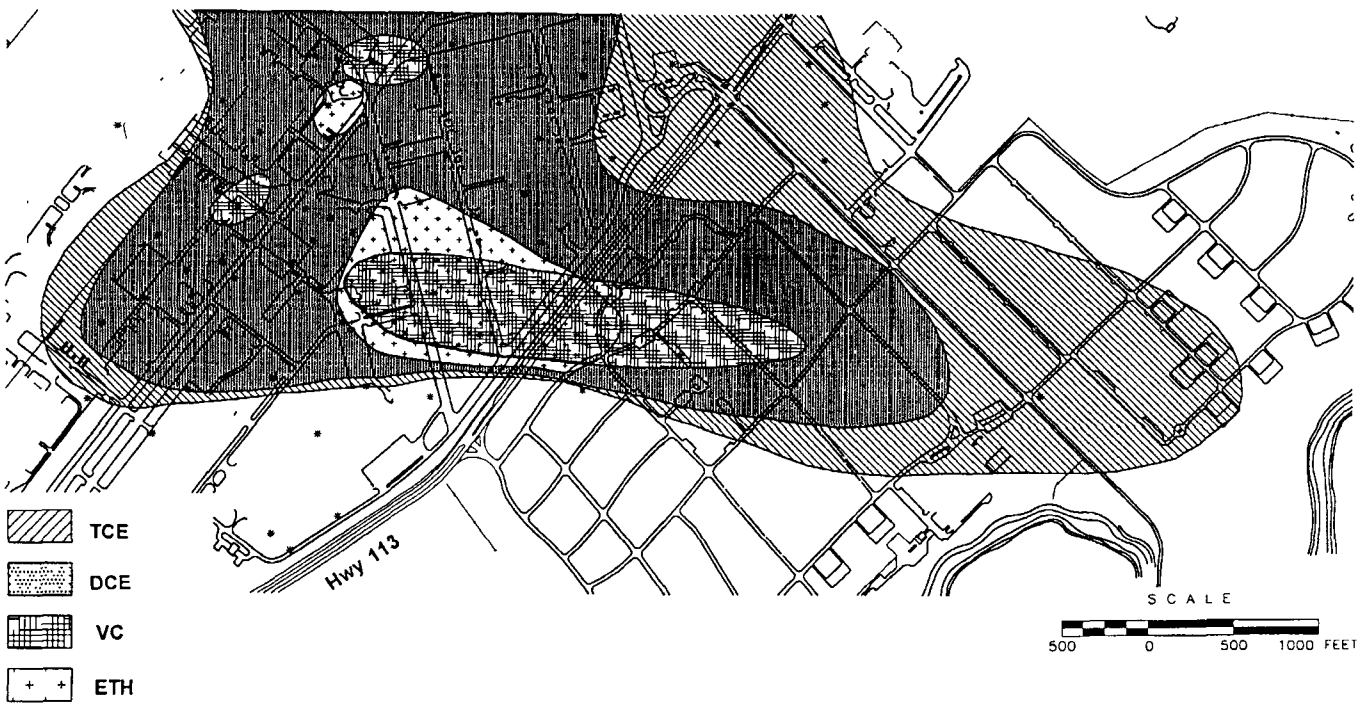

Figure 1. Plume configuration in the deep zone at Dover AFB.

Contaminants and Geochemical Markers

TCE

TCE concentrations in the ground water range up to 20 milligrams per liter (mg/L.) The TCE concentration declines rapidly near Highway 113. TCE is degraded before reaching the St. Jones River to the south of the plume.

DCE

DCE concentrations are over 10 mg/L in two areas. The DCE is primarily cis-1,2-DCE, the isomer produced by biodegradation of TCE. Chemically manufactured DCE can be distinguished from biogenic DCE because chemically manufactured DCE contains a mixture of isomers, of which cis-DCE is a minor component. The DCE plume overlaps the TCE plume. DCE concentrations also decline rapidly south of Highway 113.

VC

There is a smaller VC plume with concentrations up to 1 mg/L. Since VC was never used on the base, the consortium believes that it is present as a biodegradation product of DCE. If DCE were being lost primarily by reduction to VC, we should be able to detect low, transient concentrations of VC throughout the area containing DCE, regardless of the relative degradation rates of the two compounds. The area containing VC, however, is considerably smaller than the DCE plume.

Ethylene

Ethylene is also present, showing that complete reductive dehalogenation of TCE does occur in the deep zone. The amount of ethylene is small, however: 50 micrograms per liter (µg/L) or less. This is much too low to account for the observed losses of TCE and DCE.

Soluble Chloride Ion

The best evidence that chlorinated solvents are being destroyed is the simultaneous increase in soluble chloride ions and decrease in solvent concentrations. This is clearly observable at Dover AFB, as shown in Figures 2 and 3. While the total chlorocarbon concentrations decrease from 15 to around 1 mg/L in the area of Highway 113 (Figure 2), the dissolved chloride concentration increases to over 40 mg/L. Background chloride levels are approximately 10 mg/L. The dissolved chloride (Figure 3) increases in the deep zone of the aquifer but not the shallow zone. This eliminates other, extraneous chloride sources such as road salt. This evidence clearly supports the hypothesis that solvents are being destroyed by an intrinsic process.

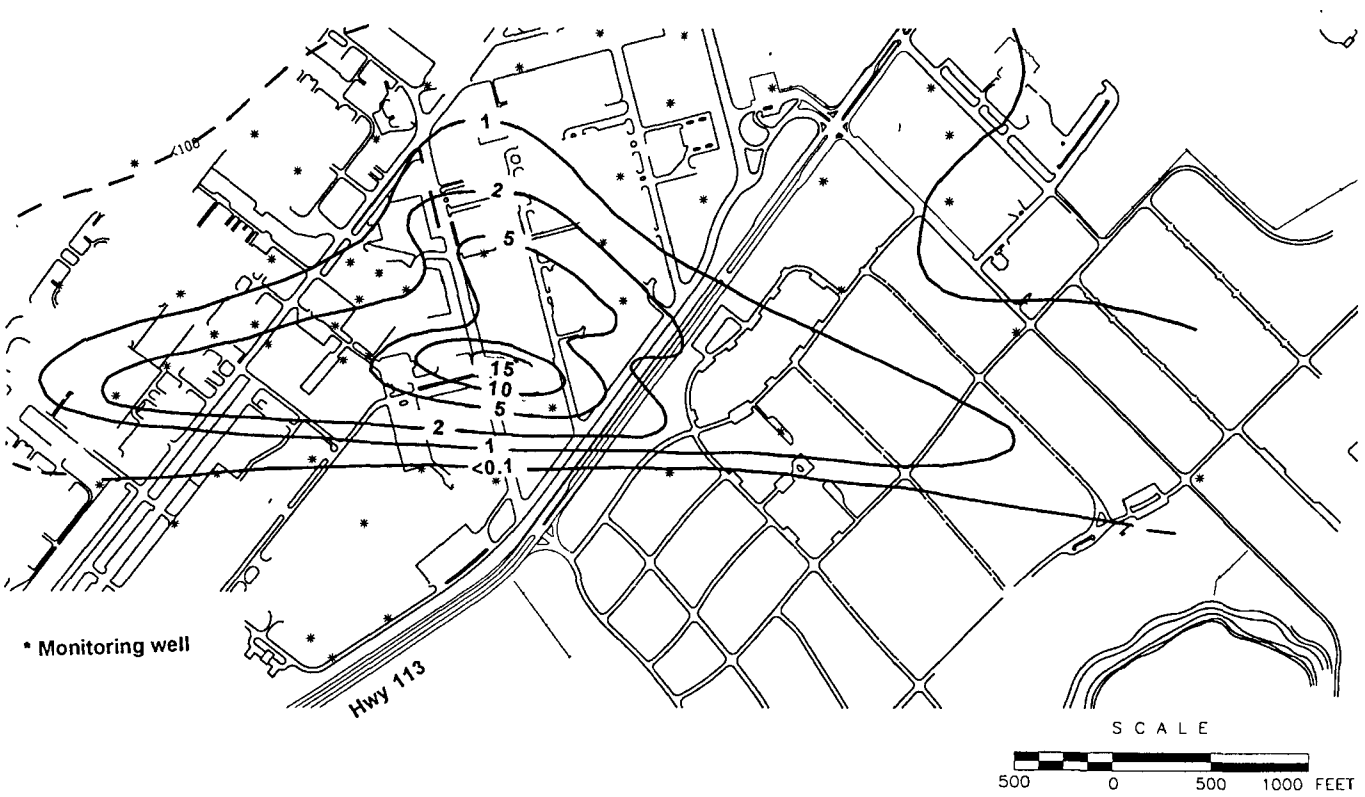

Figure 2. Total chlorinated compounds (mg/L) in the deep zone at Dover AFB.

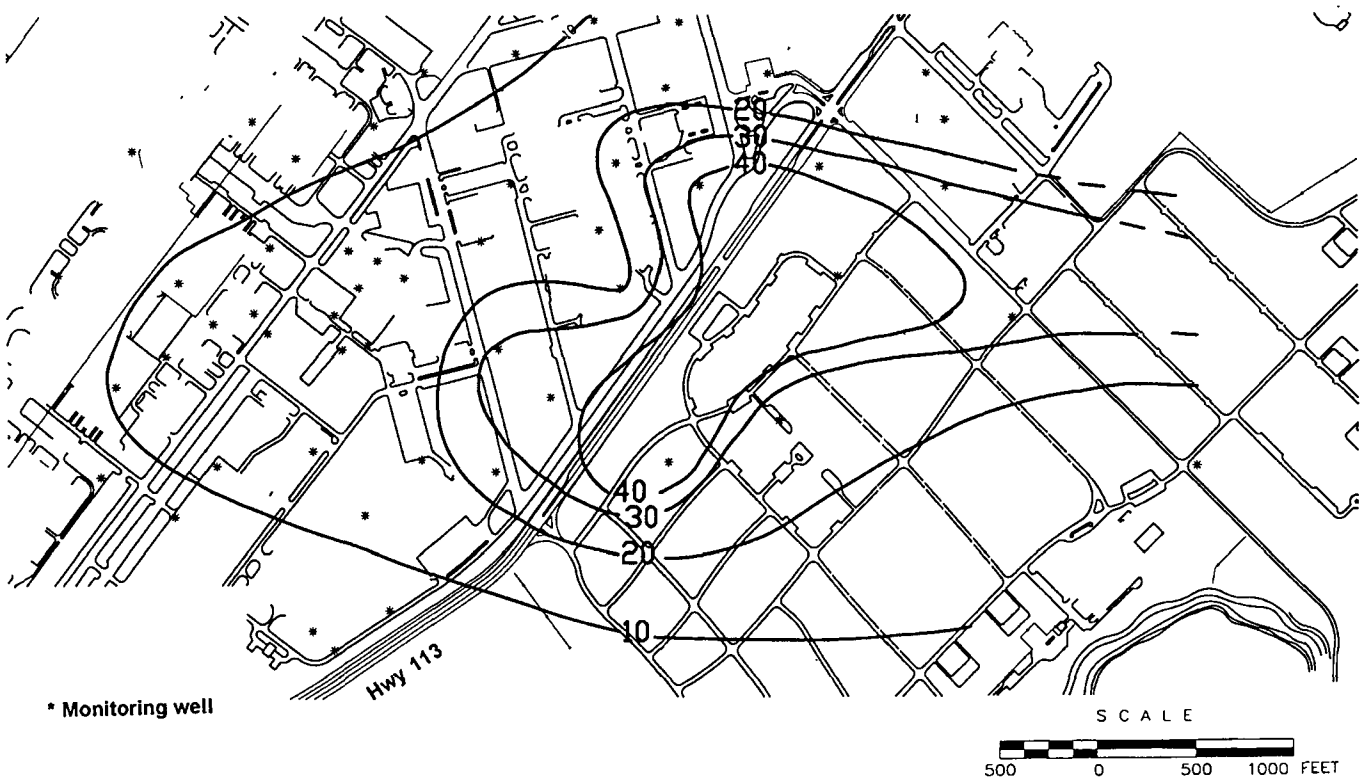

Figure 3. Dissolved chloride in the deep zone at Dover AFB.

Biodegradation Mechanisms

Processes other than reductive dehalogenation account for the majority of the degradation of DCE because of low levels of VC and ethylene. The consortium has extensively measured the geochemistry of the ground water to understand this environment. Clues to the mechanisms are found in dissolved oxygen levels, methane data, the redox state of the aquifer, and laboratory studies.

In the vicinity of the plume, the dissolved oxygen concentration is depleted to below 1 mg/L in the ground water. Dissolved oxygen begins increasing in the vicinity of Highway 113. Outside the contaminated zone, dissolved oxygen is greater than 4 mg/L.

The methane data show a pattern generally the inverse of the dissolved oxygen data. Methane concentrations ranging from 20 to greater than 500 µg/L are found within the contaminated zone, while no methane is observed outside of the plume. This indicates that methanogenesis appears to be an important microbial process in the anaerobic portion of the aquifer. The occurrence of both methane and oxygen south of Highway 113 suggests that cooxidation is likely occurring at Dover AFB.

The redox state of the deep zone at Dover AFB is relatively high. In most of the plume, the bulk phase redox is above 200 millivolts. All redox potentials are above 50 millivolts. Sharma and McCarty (1) showed that bacterial reductive dehalogenation of PCE and TCE to DCE can occur in relatively oxidizing conditions, requiring only the absence of oxygen or nitrate, similar to conditions at Dover AFB. Reductive dehalogenation of DCE to VC or ethylene, however, appears to require sulfate-reducing or methanogenic conditions (2, 3), processes that occur at redox levels below -200 millivolts. These low oxidation states are probably found in microenvironments but do not dominate the aquifer. Finally, ongoing RTDF microcosm studies of Dover AFB samples are showing clear production of $^{14}CO_2$ from ^{14}C-labeled DCE under oxygenated conditions. Therefore, the consortium believes that at Dover AFB TCE is transformed to DCE by reductive dehalogenation and that DCE is then biodegraded by a combination of direct oxidation and cooxidation, with a minor component of reductive dehalogenation to VC and ethylene.

Biodegradation Rates

Table 1 gives estimated half-lives and goodness of fit values (r^2) at Dover AFB as calculated by two different

Table 1. Half-Life Calculations for Dover AFB

Method	PCE → TCE	TCE → DCE	DCE → VC	VC → ETH
Buscheck	2.4	2.8	1.4	2.2
r^2	0.99	0.94	0.94	0.93
Graphical extraction	2.80	4.19	2.81	1.84

methods. The method developed by Buscheck et al. (4) gives the values shown in the first row of the table. The values in the second row were calculated by a simple graphical extrapolation method. The values in both rows are fairly consistent, all on the order of 1 to 2 years. These rate constants are consistent with other chlorinated solvent rate constants determined to date. This consistency suggests that a similar set of degradation mechanisms operates at other sites as well.

If the plume is assumed to be in a steady state, isoconcentration maps can be used to calculate that about 250 pounds of chlorinated solvents are being biodegraded each year. This is equivalent to destroying 25 gallons of dense nonaqueous-phase liquid every year.

Conclusion

The RTDF project at Dover AFB is in the second of 4 years. The evidence clearly demonstrates that active intrinsic remediation of chlorinated solvents is occurring. The key evidence supporting this conclusion is:

- The contaminant plumes are "stacked," indicating that the more mobile contaminants are being destroyed before they can move away from the less mobile contaminants.
- The chloride ion concentration in solution increases as the solvent concentration declines. The increase is large enough to account for the entire observed loss of solvents.
- There is clear field evidence of reductive dehalogenation and oxidation, and possible evidence for co-oxidation.

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Case Study: Wurtsmith Air Force Base, Michigan

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Introduction

Wurtsmith Air Force Base (WAFB) in Oscoda, Michigan, was decommissioned in June of 1993. Shortly thereafter, the U.S. Environmental Protection Agency (EPA), the Strategic Environmental Research and Development Program (SERDP) of the Department of Defense (DoD), the University of Michigan, and the Michigan Department of Environmental Quality contributed resources to develop the National Center for Integrated Bioremediation Research and Development (NCIBRD). NCIBRD is a DoD National Environmental Technology Test Site (NETTS) whose mission is to provide a well-defined and controlled research and development platform for the evaluation of in situ site characterization and remediation technologies. The emphasis is on bioremediation techniques applied to subsurface and sediment contamination problems. In situ biological technologies with the potential to remediate unsaturated- and saturated-zone fuel and organochlorine solvent contamination in subsurface and sediment systems are of particular interest. NCIBRD focused its early activities on the development of an expanded database of contaminant, hydrogeologic, and geochemical conditions at several contamination sites. Spatial and temporal variability in these conditions makes evaluating the progress of intrinsic bioremediation technology applications difficult.

Physical Setting

WAFB is located in Iosco County in northeast Michigan, in the coastal zone of Lake Huron north of Oscoda. Oscoda is accessible by rail, highway, and commercial air routes north of Saginaw-Bay City, Michigan. WAFB is under the authority of the Oscoda-Wurtsmith Airport Authority and the Wurtsmith Area Economic Development Commission. The U.S. Air Force Base Conversion Authority (BCA) is charged with remediating contaminated sites to enable the transition of site facilities to civilian use. At present, 10 private or public concerns have leased sites on the base for operations, including an aircraft maintenance facility, a plastics manufacturer, engineering firms, and educational institutions. The base occupies 7 square miles bounded by the AuSable River/AuSable River wetlands complex to the south, Lake Van Etten to the east, and bluffs fronting a 5-mile-wide plain extending onto the base to the west. Lake Huron receives the discharge from the associated ground-water flow system and the Au Sable River approximately 0.5 mile south of the base boundary. The altitude of the land surface ranges from 580 to 750 feet above mean sea level. Figure 1 shows the base detail, with an emphasis on Installation Restoration Program (IRP) sites.

Mean monthly temperatures range from 21°F (-6°C) in January to 68°F (20°C) in July. The lowest recorded temperature was -22°F (-30°C), the highest 102°F (39°C). Average annual precipitation is 30 inches (76 centimeters), and average snowfall is 44 inches (112 centimeters). Surficial geologic materials are of quaternary glaciofluvial and aeolian origins, made up largely of medium to fine sands and coarse sand and gravel deposits to depths of 60 to 90 feet (18 to 27 meters). Below the glacial deposits, a confining lacustrine clay layer (125 to 250 feet thick) separates the upper aquifer ground water from lower, more saline waters in bedrock units. In the eastern regions of the area, intermittent sand, sand/gravel, and clay layers of 1 to 3 feet (less than 0.3 to approximately 1 meter) thickness have been observed in the saturated zone. These features are site specific. Depths to ground water in the upper aquifer range from less than 10 to approximately 30 feet (less than 3 to 9 meters) in areas remote from pumping. Average ground-water recharge rates range from 8 to 18 inches per year (20 to 46 centimeters per year). The aquifer solids are greater than 85 percent quartz minerals, with organic carbon and inorganic carbon contents below 0.1 and approximately 6.0 percent, respectively.

Hydraulic conductivities at the base range from 75 to 310 feet per day (23 to 95 meters per day), with a weighted

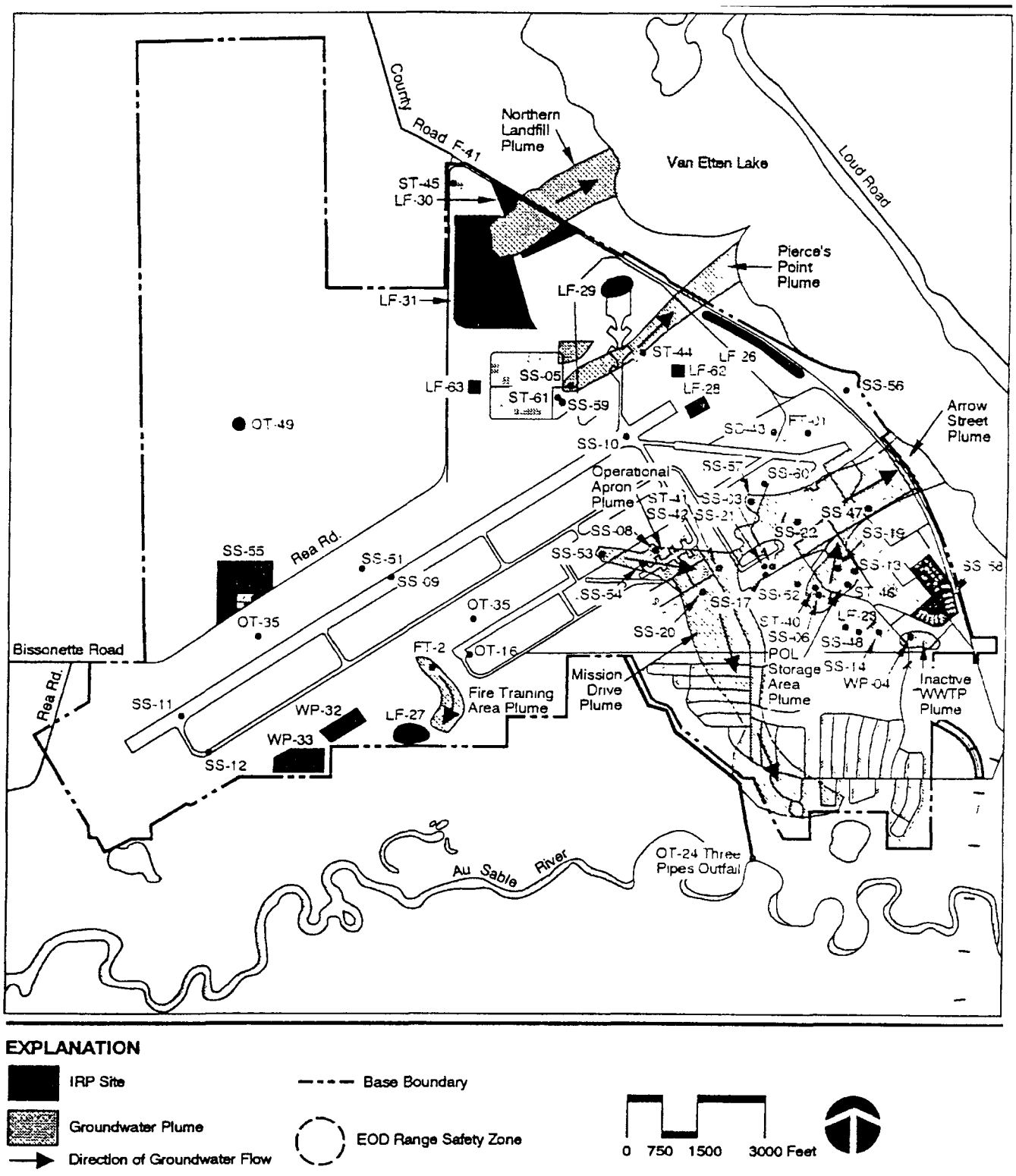

Figure 1. Map of Installation Restoration Program sites at WAFB.

average of approximately 100 feet per day (31 meters per day) based on selected slug or pump tests and estimations from particle size distributions. Flow in the sand and gravel upper aquifer is generally eastward towards Lake Van Etten and south-southeast to the AuSable River discharge areas at average rates of 1.0 to 0.3 feet per day (0.3 to 0.1 meter per day). In general, vertical flow gradients are negligible except in zones of ground-water discharge to surface-water bodies or near pumping centers.

Contaminant Profile

Contaminant investigations at the base began in the late 1970s. The Air Force and the U.S. Geological Survey had been involved in formal studies since 1979. More than 50 known and potential contamination sites have been identified at the base through their efforts and those of other contractors. Principal contaminants of concern at the base include components of petroleum hydrocarbon fuels, oils, and lubricants (POLs); organochlorine solvents (e.g., trichloroethylene [TCE], dichloroethylene [DCE]); fire-fighting compounds; combustion products (e.g., naphthalene and phenanthrene); and chlorinated aromatic compounds (e.g., dichlorobenzenes). Soil, aquifer solids, sediments, and ground water are the major environmental media involved. Of the 58 high-priority sites at the base, 13 include chlorinated solvents or partial microbial degradation products as primary contaminants. Twelve of these 13 sites identify perchloroethylene (PCE) and TCE as primary contaminants in soil, aquifer solids, and ground water, and show evidence of reductive dechlorination processes (i.e., the presence of cis-1,2-DCE, vinyl chloride monomer). These sites have abundant levels of nonchlorinated organic matter and exhibit reduction to suboxic redox conditions, as evidenced by the results from Fire Training Area 2. The only major site at which sparse evidence for microbial dechlorination of TCE exists is the Pierces Point Plume, where oxic to transitional redox conditions exist in the dissolved plume. The extent of contamination of aquifer materials remains unknown.

Facilities

EPA (Region 5), Michigan Department of Natural Resources, and the BCA actively cooperate in the ongoing IRP activities as well as the efforts of NCIBRD. Currently, NCIBRD occupies seven buildings on the base in addition to 10,000 square feet of office and laboratory space in Ann Arbor. Facilities for offices, laboratories, storage, field operation, staging, and decontamination have been developed to support activities at three sites of intensive investigations. Mobile laboratory and drilling vehicles provide additional support for year-round in-field sampling and analysis assisted by experienced field and laboratory staff. A basewide ground-water flow model has been developed and refined by estimates of hydraulic conductivity and mass water level measurements at more than 500 wells. Site-wide water balance and refined ground-water transport models exist for sites of current or future technology demonstration activity as well as for a controlled in situ injection experimental facility. This facility, the Michigan Integrated Remediation Technology Laboratory (MIRTL), will be the site of a natural gradient reactive tracer test in the summer of 1996 for aerobic fuel bioremediation. MIRTL will eventually consist of instrumented parallel test lanes for both natural and induced gradient in situ testing of cleanup technologies.

Case Study

Fire Training Area 2, in the southwest portion of the base, has been the site of the most intensive monitoring attention in the past decade at the base. Forty years of fire training exercises using waste solvents and fuels have resulted in soil and subsurface contamination with hydrocarbons, chlorinated alkenes, aromatics, and polycylic aromatics. Early detective monitoring results were collected by the U.S. Geological Survey from a network of shallow and deep wells developed in 1987 (1). Focusing on the dissolved volatile organic compounds (i.e., aromatics and chlorinated alkenes), the plume was delineated to be approximately 200 to 300 feet (30 to 90 meters) wide, approximately 1,800 to 2,000 feet (550 to 610 meters) long, and approximately 6 to 25 feet (2 to 8 meters) thick. Concentrations of benzene, toluene, ethylbenzene, and xylene compounds ranged from greater than 2,000 to less than 10 micrograms per liter. In both cases, the contaminant concentrations were highest near the pad at the site (Figure 2). Although not the source, the pad was certainly the locus of recent fire training activity. Figure 2 shows the rough outline of the major chlorinated alkene (i.e., principally cis-1,2-dichloroethylene, trichloroethylene, and perchloroethylene) plume, which was restricted to the upper 6 feet (approximately 2 meters) of this water table aquifer in 1993. Here, the cis-1,2-DCE metabolite of PCE and TCE was the major constituent, accounting for over 90 percent of the dissolved contaminants.

In 1994, quarterly contaminant and geochemical monitoring in the ground water was undertaken as the initial part of a demonstration of intrinsic bioremediation. Quarterly monitoring results since that time have disclosed variable dissolved concentrations of the chlorinated parent compounds as well as the DCE major metabolite. It should be noted that vinyl chloride has been detected only once in mid-field shallow wells. Figure 3 shows representative dissolved concentration variability of TCE and DCE in the major portion of the plume from available data over the past 9 years. Far-field wells have generally shown diminished concentrations of DCE, while near-field (i.e., near-pad) wells have shown some increase, particularly in the last year. The major plume dimensions evidenced in 1993 (Figure 2) have remained stable, and iron- and sulfate-reducing or methanogenic conditions prevail in its interior.[1]

The question arises in this case whether significant mass removal has occurred during the course of the investigation. Based on dissolved concentrations, distribution

[1] Chapelle, F.H., S.K. Haack, P. Adriaens, M.A. Henry, and P.M. Bradley. 1996. Comparison of Eh and H_2 measurements for delineating redox processes in a contaminated aquifer. In preparation.

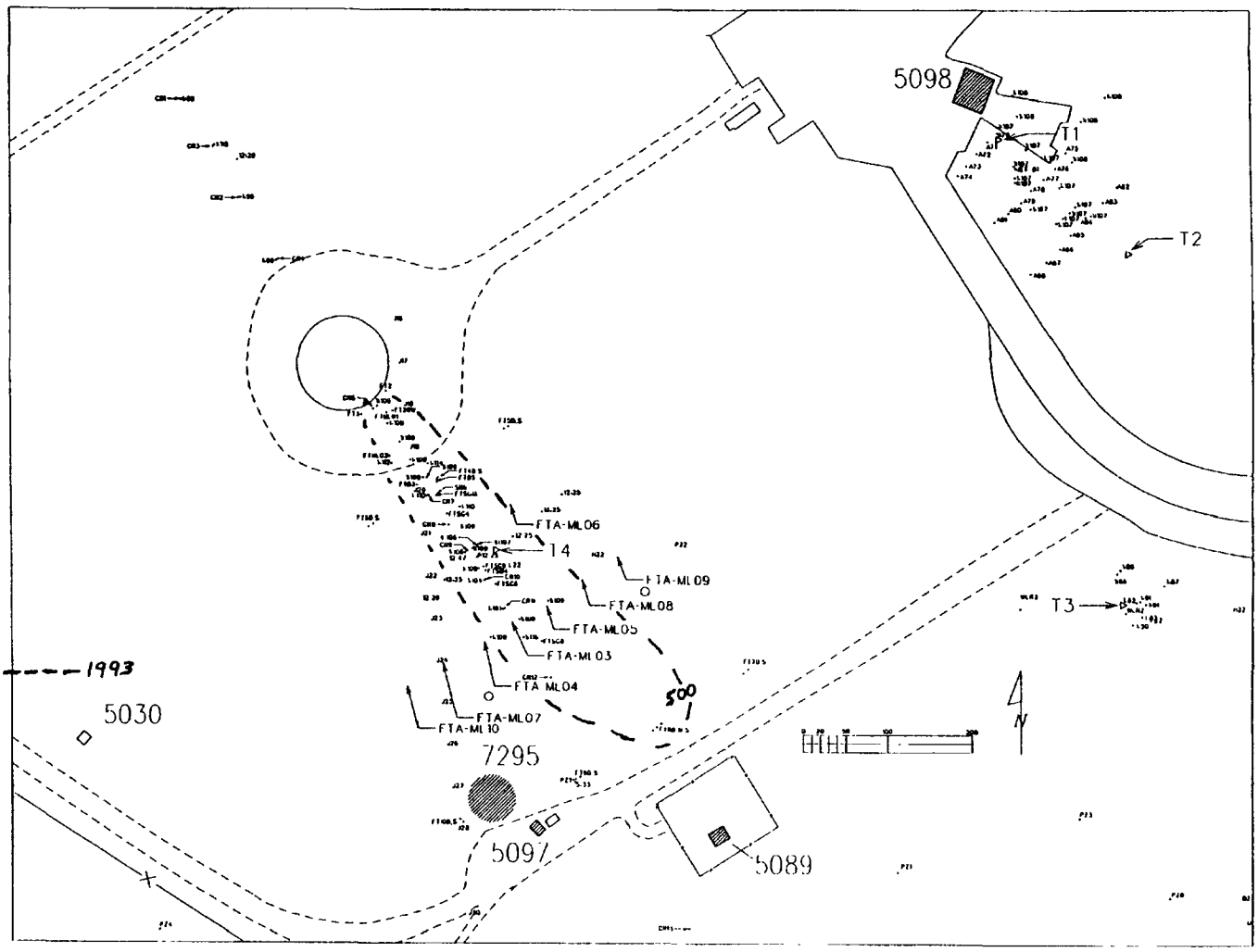

Figure 2. Plan view of Fire Training Area 2 showing dimensions of major chlorinated VOC plume in ground water in 1993.

variability and roughly ±20 percent precision of sampling and analysis would have to conclude that no significant reduction in dissolved mass has occurred in the main body of the plume.

To approach the net loss of chlorinated alkene compound mass from the plume, 13 borings were made in 1994 along the axis of the plume coincident with dominant ground-water flow direction. A total of 300 core subsamples were taken by Geoprobe techniques collecting field-preserved samples subsequently analyzed for major contaminants by static headspace techniques (2). Companion cores were collected adjacent to these locations for determination of oily phase, porosity, and water contents by the methods of Hess et al. (3).

Table 1 contains the average results of these determinations at the near- and mid-field locations of the monitoring wells. It should be noted that, in contrast to the water samples, which were contaminated by reductive dechlorination metabolites, the solid-associated chlorinated hydrocarbon distributions were dominated by parent compounds, principally PCE and TCE. It is clear

Table 1. Comparison of Average Dissolved and Aquifer Solid-Associated Masses of Total Volatile Chlorinated Compounds in the Fire Training Area 2 Plume (masses expressed in milligrams per liter aquifer material)[a]

Location in Major Plume	Ground Water (mg/L)	Aquifer Solids (mg/L)	% of Total Associated With Solids	Volume % of Oily Phase[b]
Near field (Approximately 200 feet downgradient from Pad Boring 6; Well 4S)	0.08	10.5	99%	2.9
Mid-field (Approximately 450 feet downgradient from Pad Boring 12; Wells 8S and 8M)	0.003	6.3	99%	0.006

[a] One liter of aquifer material was assumed to contain approximately 1.75 kilograms of aquifer solids and 300 milliliters of ground water in average unit volume in major plume.
[b] Oily phase determined on field preserved (dry ice freezing) of cores B-10 and B-12 respectively by the method of Hess et al. (3).

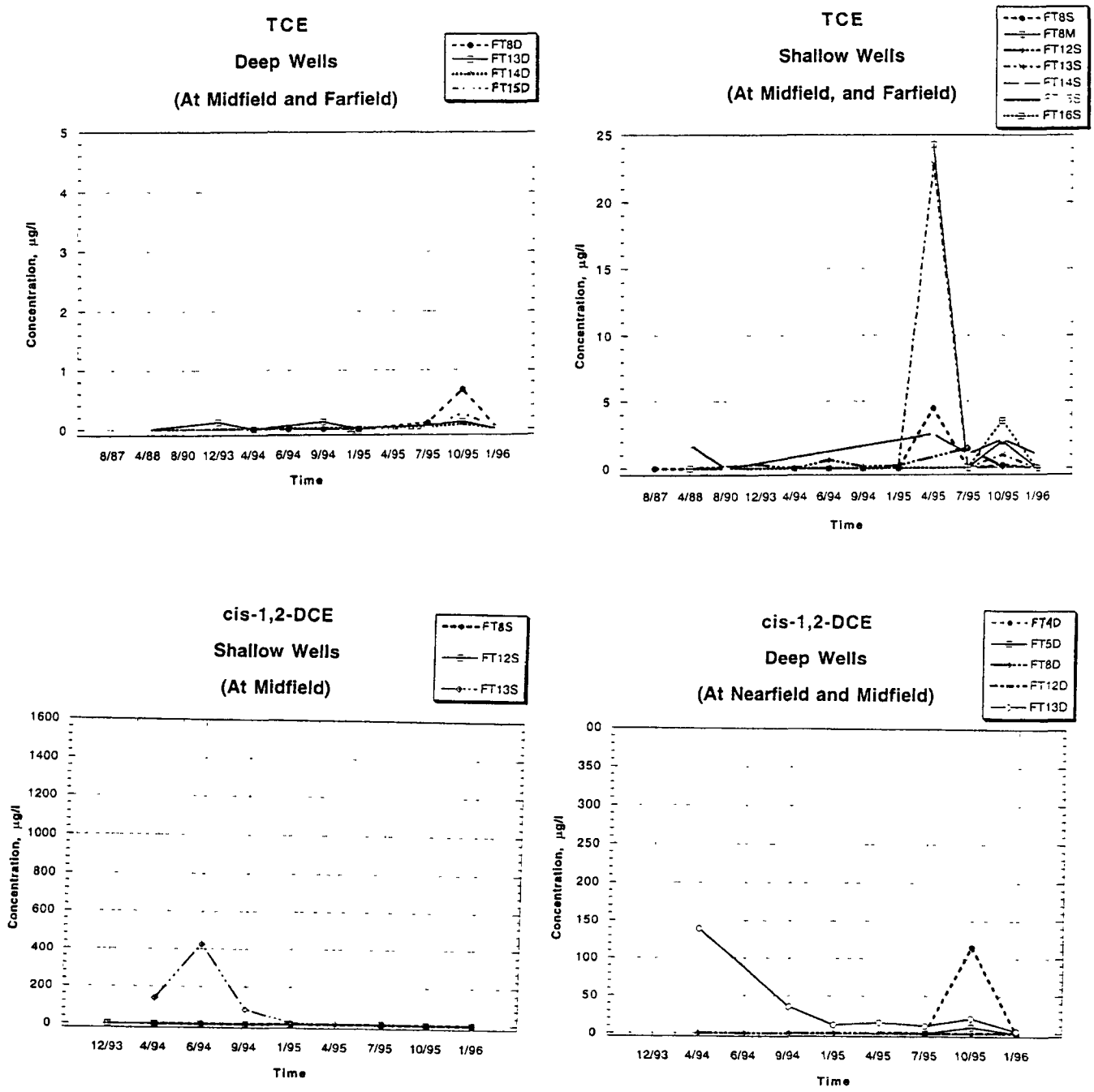

Figure 3. Concentration trends over time for TCE and DCE at Fire Training Area 2 wells.

from these data that aqueous concentration variability in determinations of metabolite concentrations are a negligible portion of the total mass of chlorinated hydrocarbon contaminants. The determinations must include considerations of oily-phase, solid-associated, and aqueous masses on a volume basis. It is therefore necessary to determine the *relative* mass distributions of both parent and metabolite compounds to evaluate net mass losses due to intrinsic bioremediation via reductive dechlorination processes. The apparent trends in aqueous contaminant concentrations represent symptoms of the ensemble processes contributing to net mass loss, particularly in the near field of the presumed contaminant source.

Acknowledgments

The author would like to thank his staff, all collaborators, and students for their constructive inputs to this slowly developing but important field. Special thanks to Mark Henry, Chris Till, Ron Lacasse, Amir Salezedeh, Debbie Patt, and Patty Laird. NCIBRD staff and collaborators welcome the contributions and participation of interested

groups in future investigations of promising site characterization and bioremediation cleanup technologies.

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Case Study: Eielson Air Force Base, Alaska

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Introduction

One innovative plume management approach that has been the subject of a great deal of recent interest is that of intrinsic remediation or natural attenuation, the process of site assessment and data reduction and interpretation that focuses on the quantification of the capacity of a given aquifer system to assimilate ground-water contaminants through physical, chemical, and/or biological means. The intrinsic remediation approach is appropriate for a given site if the plume has not affected a downgradient receptor and if the rate of contaminant release from the source area is equal to or less than the contaminant degradation rate observed at the site.

While many field sampling protocols are available from a variety of sources describing approaches for collecting and analyzing data necessary to verify that intrinsic remediation processes are taking place at a given site, the connection between these data and decisions regarding source removal activities or estimates of source lifetime has not generally been presented in the literature. An approach for implementing intrinsic remediation concepts from data collection through source removal and source lifetime considerations has been developed for the U.S. Environmental Protection Agency and the U.S. Air Force (1-3), and these concepts and procedures are presented in this paper through a case study at a mixed solvent/hydrocarbon contaminated site (Site 45/57) at Eielson Air Force Base (AFB), Alaska.

Intrinsic Remediation Protocol

The intrinsic remediation assessment carried out at the field site at Eielson AFB involved the seven-step process outlined in Figure 1. This process provides a logical approach to evaluating the feasibility and appropriateness of implementing intrinsic remediation at a given site and includes: 1) determining whether steady-state plume conditions exist; 2) estimating contaminant degradation rates; 3) estimating the source mass; 4) estimating the source lifetime; 5) predicting long-term plume behavior with and without source removal; 6) making decisions regarding the use of intrinsic remediation and the impact and desirability of source removal at a given site; and 7) developing a long-term monitoring strategy if intrinsic remediation is selected for plume management. Elements of this methodology will be highlighted through the following case study.

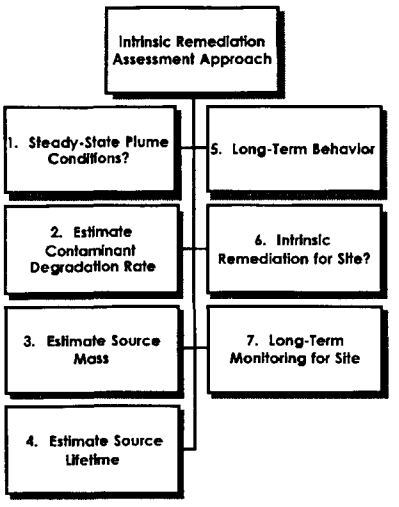

Figure 1. Components of the intrinsic remediation assessment approach.

Site Description

Eielson AFB is located in the Tanana River Valley in Central Alaska, approximately 200 kilometers south of the Arctic Circle. Most of the base is constructed on fill material underlain by an unconfined aquifer consisting of 60 to 90 meters of alluvial sands and gravels overlying a low-permeability bedrock formation (4). The aquifer

system below the base is bounded to the northeast by the Yuon-Tanana uplands and is approximately 70 to 80 kilometers wide in the area of the base (5). The direction of ground-water flow throughout the base is generally to the north, with ground-water encountered at 2.5 to 3.5 meters below ground surface at various times of the year.

Fire training and fueling operations are believed to be the source of ground-water contamination at Site 45/57. Dissolved trichloroethene (TCE) concentrations as high as 90 milligrams per liter (mg/L) have been observed at the site and are thought to have resulted from releases occurring within the last 20 to 40 years. No evidence of free-phase TCE exists from soil boring or ground-water monitoring data collected from 1992 through 1995. Anaerobic dechlorination reactions, evident as dechlorination products (cis- and trans-dichlorethene [DCE], vinyl chloride [VC], and ethylene), have been observed in the ground water at the site (Figure 2).

Assessment of Intrinsic Remediation at Site 45/57

Steady-State Conditions

Steady-state conditions were assessed by inspection of plume centerline concentrations over time (Figure 3), and through an analysis of integrated plume mass data for the site. Center of mass (CoM) and total mass results for Site 45/57 were generated from ground-water concentration data collected in this field study using a Thiessen area approach (1-3). Both TCE centerline concentrations and dissolved plume mass estimates using a consistent set of sampling locations over time indicated a decreasing plume mass, with CoM locations indicating no net plume migration over the sampling interval. The data indicated a finite source producing a stable TCE plume at Site 45/57 (2, 3, 6).

Estimation of Contaminant Degradation Rate

Estimation of contaminant degradation rates can be carried out using dissolved contaminant mass data if a declining mass of contaminant is observed over time in the plume. With estimated dissolved TCE concentrations in May 1994 (Mo) and July 1995 (M) being 40.1 and 33.1 kilograms, respectively, and assuming first-order degradation of TCE in the plume, the estimated TCE degradation rate (k1) is found by:

$$k1 = -\ln (M/Mo)/t = -\ln(33.1/40.1)/420 = 0.0005/d \qquad \text{(Eq. 1)}$$

where t = the time between sampling events = 14 months = 420 days.

In addition, degradation rates can be estimated through the calibration of contaminant fate-and-transport models to field ground-water data. These models provide improved estimates of contaminant degradation and mobility because they integrate transport, retardation, and degradation processes using site-specific contaminant and aquifer properties. An analytical, three-dimensional model developed by Domenico (7), the subject of a previous

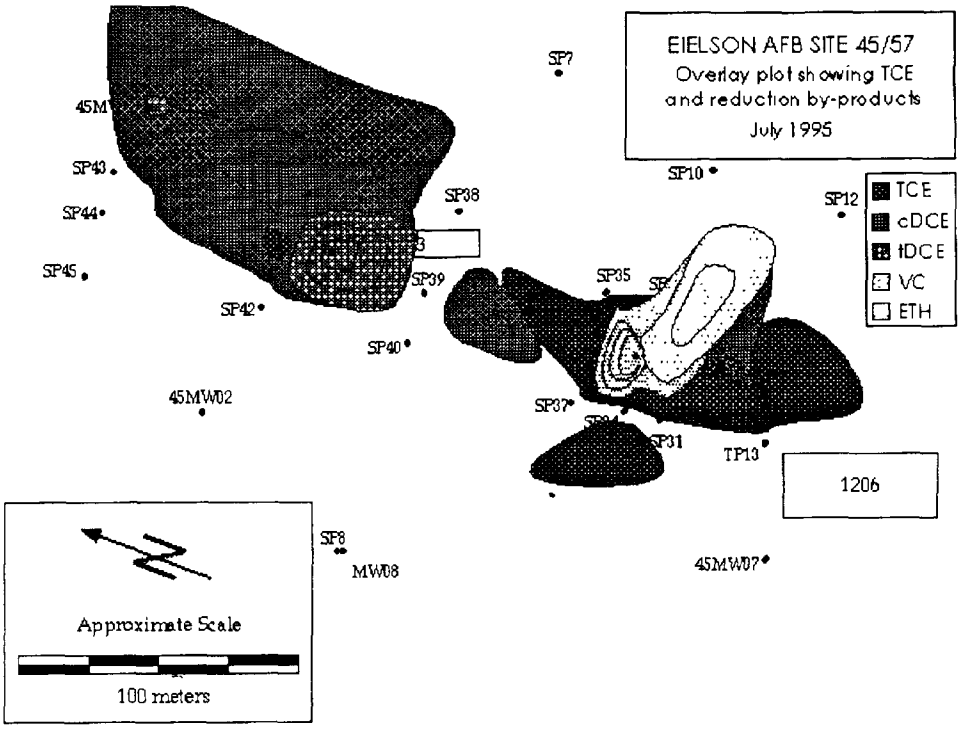

Figure 2. Overlay plot of TCE and its degradation products measured in July 1995 at Site 45/57, Eielson AFB, Alaska.

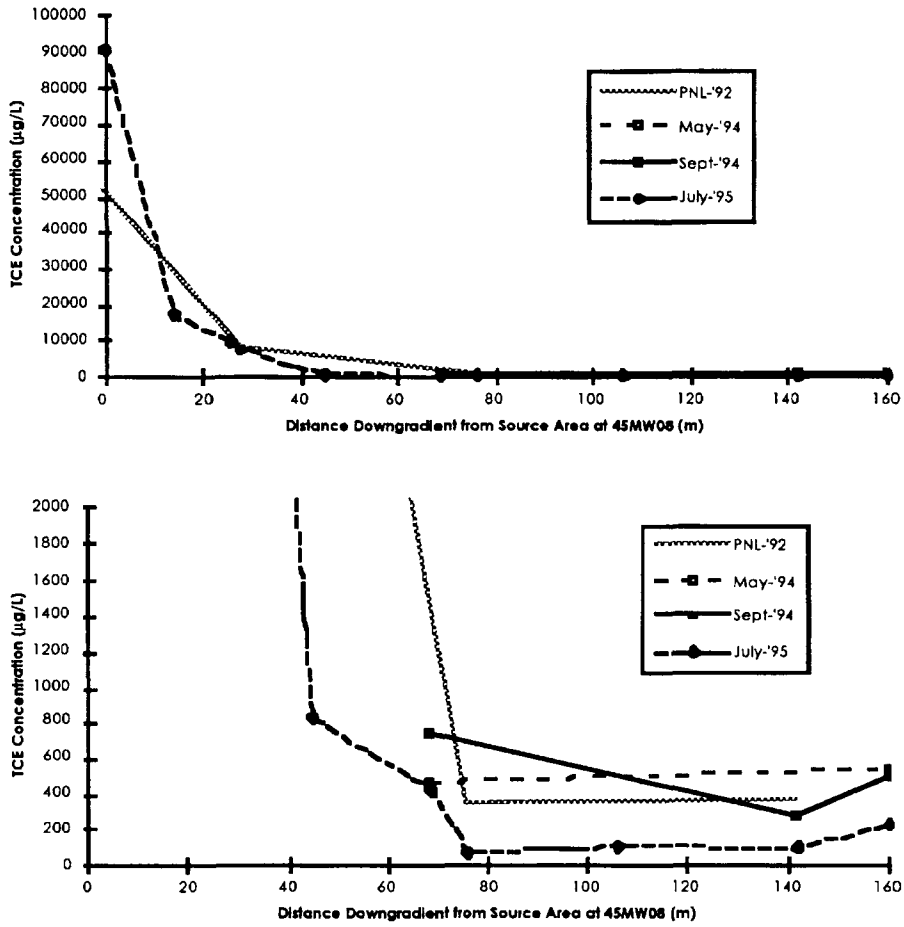

Figure 3. Plume centerline TCE concentrations measured from fall 1992 through July 1995 at Site 45/57, Eielson AFB, Alaska.

paper by Gorder et al. (8), has been incorporated into the intrinsic remediation methodology described in this paper and was used to develop an independent estimate of a TCE degradation rate at Site 45/57 based on July 1995 ground-water data. Calibration of this model is described elsewhere (7, 8) and involves matching predicted and measured centerline and cross-plume contaminant concentrations through the adjustment of aquifer dispersion properties and contaminant degradation rates. Through this process, a mean TCE degradation rate of 0.0026 per day (0.0006 to 0.007 per day) was determined.

Estimation of Source Mass and Source Lifetime

The source of the TCE plume at Site 45/57 had not been completely identified. Site investigations conducted in the past by the Pacific Northwest Laboratory and Harding Lawson Associates, as well as soil and ground-water sampling conducted in the source area by the Utah Water Research Laboratory, have not identified residual phase TCE in either the vadose zone or capillary fringe, nor below the ground-water table. In addition, the finding of a decreasing dissolved TCE plume mass over time strengthens the argument that a residual phase does not exist at the site. If it is assumed that a distinct free-product phase does not exist in the source area, an estimate of source mass can be made assuming contaminated soil in equilibrium with the measured source area dissolved TCE concentration, Co. Using this approach, the source area mass was estimated using the following equation:

$$M_{source} = Co\ (Y)\ (L)\ (b)\ (R)\ (\theta) \qquad \text{(Eq. 2)}$$

where Y = transverse source dimension = 22.5 meters; L = source length in direction of ground-water flow = 15 meters; b = source area thickness = 3 meters; R = TCE retardation factor = 2.5; and θ = aquifer total porosity = 0.38. Source dimensions were estimated based on interpolation of ground-water data collected within and outside the source area, while R and θ were based on aquifer-specific characteristics determined from cores collected from the site. Using these values, a source mass of 37.5 kilograms was estimated to exist at the site.

If the assumption of a finite source is appropriate at Site 45/57, then Equation 1 applies. With maximum source area TCE concentrations of 90 mg/L and a ground-water

impact concentration (maximum contaminant level [MCL]) of 5 micrograms per liter (µg/L) established for TCE, an estimated source lifetime for TCE at this site is:

$$\text{Source lifetime} = \ln(5/90{,}000)/k1 = \ln(5.6 \times 10^{-5})/(-0.0026) = 10.3 \text{ years} \quad \text{(Eq. 3)}$$

A worst-case scenario can be formulated for contamination at Site 45/57 using an assumption that a small mass of residual phase material, which has been undetected in site investigation activities, exists within the source area. The dimensions of this residual-phase source area are defined by the sampling grid within which it must exist, making its aerial extent no more than 15 by 5 meters (Ys by Ls). The residual phase volume, Sr, contained within the sandy aquifer at Site 45/57 is approximated to be 25 percent of the pore volume (9), or 9.5 percent of the source area volume. Based on a measured source area TCE concentration of 90 mg/L and a TCE solubility of 1,377 mg/L, the mole fraction of TCE in residual-phase material is estimated from Raoult's law to be 90/1,377 = 0.065, making the estimated concentration of TCE in the residual phase, C_{TCE}:

$$(\text{Mass}_{TCE})/(\text{Mass}_{\text{Residual Phase}}) = 0.065\ (\text{MW}_{TCE}/\text{MW}_{\text{Residual Phase}}) = 0.065\ (131.4/120) = 0.071$$

Based on these calculations, the estimated mass of TCE that could exist at Site 45/57 in an unidentified residual phase is:

$$\text{Mass}_{TCE\ \text{Residual}} = Ys\ (Ls)\ (b)\ (\theta)\ (Sr)\ (\rho_{\text{Residual Phase}})\ (C_{TCE}) \quad \text{(Eq. 4)}$$

$$\text{Mass}_{TCE\ \text{Residual}} = (15\text{ m})\ (5\text{ m})\ (3\text{ m})\ (0.38)\ (0.25)\ (1{,}200\text{ kg/m}^3)\ (0.071) = 1{,}677\text{ kg}$$

With this estimate of residual-phase source mass, the lifetime of the source can be predicted based on the mass flux of TCE out of this source area, as indicated below:

$$\text{Mass flux} = Ys\ (b)\ (v)\ (\theta)\ (Co) = (15\text{ m})\ (3\text{ m})\ (0.1\text{ m/d})\ (0.38)\ (0.09\text{ kg/m}^3) = 0.15\text{ kg/d} \quad \text{(Eq. 5)}$$

where v = ground-water velocity. With this mass flux value, an estimate can be made for the source lifetime assuming a residual-phase TCE mass of 1,677 kilograms exists at the site:

$$\text{Source lifetime} = \text{Mass}_{TCE\ \text{Residual}}/\text{Mass flux} = (1{,}677\text{ kg})/(0.15\text{ kg/d}) = 10{,}897\text{ d} = 29.9\text{ yy} \quad \text{(Eq. 6)}$$

As this example illustrates, if residual mass does exist, the lifetime of the plume is extended significantly, increasing the overall cost of plume management at the site. More information regarding residual-phase distribution at the site is needed to narrow the range of source lifetime predictions.

Prediction of Long-Term Plume Behavior

Consideration of long-term plume behavior involves an evaluation of the plume footprint over time with and without source removal implemented at a given site. Following source depletion or removal, the dissolved plume will begin to contract as the assimilation of contaminants in the aquifer exceeds their release rate from the source area. The impact of source removal can be modeled by superimposing a plume with a negative source concentration, initiated at the time of source removal or depletion, on top of the existing contaminant plume (7). This allows the prediction of the time required for the entire dissolved plume to degrade below a level of regulatory concern. Based on this information, a decision can be made regarding the expected benefit from source removal in terms of reducing the time required for management of the site to ensure long-term risk reduction.

If it is assumed that no free-phase product exists within the source area of Site 45/57, then the projected source lifetime is relatively short: approximately 10 years. With a residual phase existing at the site, the projected source lifetime is increased to approximately 30 years. Using the field-data-calibrated Domenico model (6, 7), a rapidly shrinking plume is predicted to be assimilated to below MCL values within 8 years following 100 percent source removal, as shown in Figure 4. While removal of the source reduces the projected lifetime of contamination at the site by a factor of two to five, the cost of such a removal action is high, it is highly disruptive of current site uses, and the efficiency of contaminant removal is uncertain. The recommendation made for this site was against an active source removal effort because of the marginal and high-cost benefit expected from such an action.

Long-Term Monitoring Plan for the Site

With implementation of intrinsic remediation recommended at Site 45/57, a long-term monitoring network is required. To have this network serve multiple purposes, a combination of upgradient, downgradient, and within-plume monitoring locations is desirable.

Two sets of wells would be installed at Site 45/57 as part of the long-term monitoring strategy for the intrinsic remediation plume management approach. The first set, the long-term monitoring wells, consists of a transect of plume centerline wells composed of a proposed well located upgradient of the TCE source area at monitoring point SP16, three existing wells (45MW01, 45MW03,

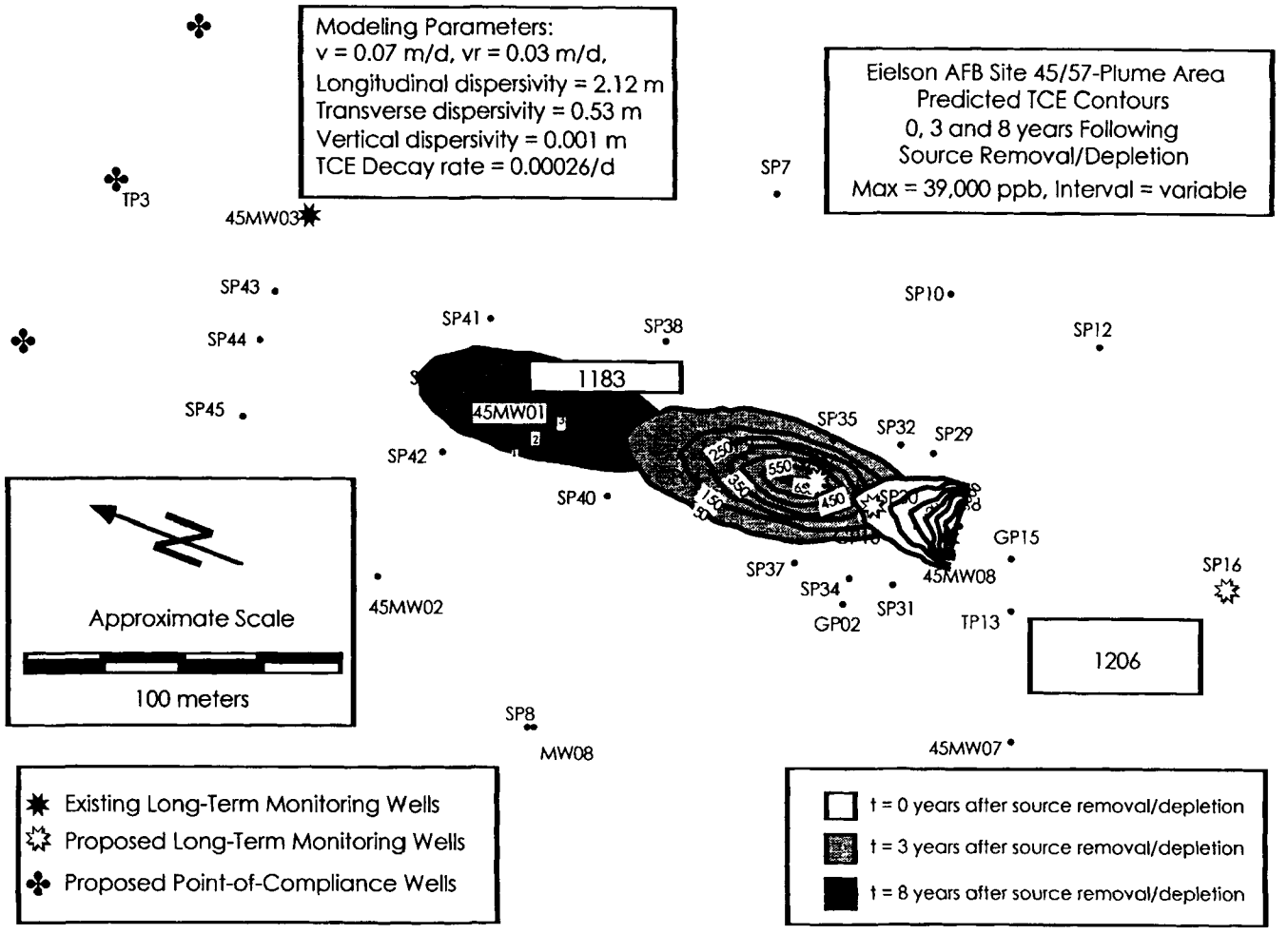

Figure 4. Projected TCE plume concentrations 0, 3, and 8 years following source removal or depletion and proposed long-term monitoring network at Site 45/57, Eielson AFB, Alaska.

and 45MW08) located within the observed TCE plume, and two additional monitoring wells located near the TCE source area. These wells are used to verify the functioning of the intrinsic remediation process and allow updating of the conceptual model for plume and source area configuration over time. The second set of monitoring wells consists of a transect of three wells perpendicular to the direction of plume migration, approximately 250 feet (75 meters) downgradient from Monitoring Well 45MW04 to establish the point-of-compliance (POC) for this site. The purpose of the POC wells is to verify that no TCE exceeding the federal MCL (5 µg/L) migrates beyond the area under institutional control.

A sampling frequency of 1 to 2 year intervals was recommended for this site. This interval provides sufficient data over time to verify plume stability and source area depletion, at a reasonable frequency based on cost considerations without compromising human health or environmental quality.

Conclusion

This paper highlights the application of an intrinsic remediation protocol to a hydrocarbon/solvent contaminated site, Site 45/57, at Eielson AFB, Alaska. This process involves 1) assessment of steady-state plume conditions; 2) determination of degradation rates; 3) estimation of the source term; 4) estimation of the source lifetime; 5) prediction of the long-term behavior of the plume with and without source removal; 6) assessment of aquifer assimilative capacity and the desirability of source removal at the site; and 7) development of a long-term monitoring strategy for verification of intrinsic remediation process performance and regulatory compliance purposes.

Intrinsic remediation of solvent contaminated ground water was demonstrated at Site 45/57 through the identification of TCE dechlorination products in the plume (Figure 1), the recognition of decreasing TCE dissolved plume mass over time, and calibration of field data to a

fate-and-transport model. No residual-phase product was identified within the source area based on historical and recent site investigation activities; however, a worst-case estimate was made of the potential residual TCE mass that might exist within the source area. Source lifetime estimates ranged from approximately 10 years without residual-phase TCE to approximately 30 years with residual-phase material remaining at the site. From an analysis of source depletion and plume attenuation rates, it was determined that source removal may reduce the projected site management lifetime from approximately 20 to 40 years to less than 10 years. Due to the difficulty and expense of source removal, and to the overall short timeframe for complete site remediation by intrinsic processes without source removal, long-term monitoring without source removal was recommended and has become the basis of the record of decision for this site.

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Considerations and Options for Regulatory Acceptance of Natural Attenuation in Ground Water

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Introduction

When approaching areas of ground-water contamination, both technical and regulatory options must be identified and evaluated to ensure compliance with state and federal regulatory requirements. A strong technical defense presented in the appropriate regulatory framework is necessary for the selection of natural attenuation as a component of the remedy. At Eielson Air Force Base (AFB) near Fairbanks, Alaska, this approach was used to select natural attenuation as a major component of the remedy for all areas of ground-water contamination. This paper summarizes the various options evaluated for addressing both the technical and regulatory issues associated with the selection of natural attenuation for ground-water contamination.

Background

Ground-water contamination at Eielson AFB generally consists of relatively limited areas of contamination that have an adverse impact on the beneficial uses of the aquifer but are not currently posing an immediate risk to receptors. This type of situation is frequently encountered under the Superfund program and poses a difficult dilemma from both technical and regulatory perspectives for compliance with the U.S. Environmental Protection Agency's (EPA's) Ground Water Protection Strategy. This strategy, which is outlined in the preamble to the National Contingency Plan (NCP), includes a goal to return usable ground waters to their beneficial uses within a timeframe that is reasonable given the particular circumstances of the site. The preamble to the NCP further states that ground-water remediation levels should generally be attained throughout the contaminated plume, or at and beyond the edge of the waste management area when waste is left in place.

To comply with the Ground Water Protection Strategy, it was necessary to first gain an understanding of the source of the contamination, its fate and transport, and the feasibility of contaminant removal. Once it was clear what the technical approach should be, the second task was to identify the most appropriate regulatory approach to accommodate the proposed technical solution. Options and combinations considered and used to address ground-water contamination at Eielson AFB are outlined below.

Technical Options

The first task in the Superfund process is to gain a thorough understanding of the type of contamination, the location and extent of the remaining source in both the unsaturated and saturated zones, and the anticipated fate and transport of the contamination. Once this is accomplished, alternatives for addressing the contamination can be evaluated.

In the feasibility study, a range of alternatives are developed and evaluated to determine the appropriate level of source reduction and/or ground-water treatment. The alternatives considered at Eielson AFB included:

- No action.
- Limited action, including institutional controls and ground-water monitoring.
- Source removal (either in situ or ex situ) in the subsurface soils and smear zone combined with institutional controls and ground-water monitoring.
- Ground-water extraction and physical/chemical treatment combined with institutional controls and ground-water monitoring.

The limited action alternative differed from the no action alternative by the inclusion of institutional controls to prevent exposure to contaminated ground water. This definition comes from the NCP (55 *Federal Register [FR]* 8711), which states that institutional controls, while not actively cleaning up the contamination at the site,

can control exposure and, therefore, are considered to be limited-action alternatives.

The selected remedy could be one of the alternatives or a combination, depending on the degree of active restoration required. Considerations for remedy selection were the amount of contamination remaining in the unsaturated and saturated zones and the availability of the contamination for removal and treatment. The technical evaluation is largely an issue of a balance between the need for and feasibility of contaminant removal in the unsaturated and/or saturated zones and the efficiency of natural attenuation. The NCP (55 *FR* 8734) addresses this balance by describing ground-water extraction and treatment as generally the most effective method of reducing concentrations of highly contaminated ground water. It subsequently notes, however, that pump-and-treat systems are less effective in further reducing low levels of contamination to achieve remediation goals and allows for the use of natural attenuation to complete cleanup actions in some circumstances. If ground-water extraction and treatment is not warranted due to the low levels present, then the attention is directed at any residual source of contamination.

At Eielson AFB, residual source contamination typically fit into two categories. In one category, an equilibrium existed in which the rate of contaminant migration from the source was approximately the same as the rate of natural attenuation in the aquifer. In the second category, the source was continuing to overwhelm the rate of natural attenuation, resulting in an expanding contaminant plume.

Even in situations in which the system was in equilibrium and the plume was not expanding, source removal was evaluated to determine whether reduction of contaminant mass would return the aquifer to its beneficial uses throughout the plume in a significantly greater timeframe than natural attenuation alone. This evaluation was not a trivial task given the difficulties in estimating the source term, accurately evaluating the contaminant fate and transport in the subsurface, and assessing the effectiveness of source removal. In evaluations conducted at Eielson AFB, modeling was generally the mechanism chosen to evaluate the benefits of source removal. Generally, these modeling efforts used conservative assumptions for fate-and-transport analysis and potentially overly optimistic assumptions for source removal. In combination, the modeling results indicated a significant benefit of source removal. Results from subsequent pilot studies, however, indicated low removal rates for the subsurface contamination, and contradicted the conclusions of the model. Source removal, therefore, was not expected to significantly reduce risks or remediation timeframes.

Regulatory Options

If, based on the technical evaluation, natural attenuation was identified as a major component of the selected remedy, regulatory options were reviewed to determine the most relevant approach for the specific situation. All of the regulatory options considered have several common requirements or considerations, which are outlined below.

- The contaminant plume must be contained by the contaminant source leach rate being in equilibrium with the rate of natural attenuation or by hydraulic containment of the leading edge of the aqueous plume.
- Institutional controls must be effective, reliable, and enforceable in preventing exposure to the contaminated ground water.
- Further contaminant reduction in the subsurface is not indicated either due to technical impracticability or because contamination reduction would not result in significant risk reduction.
- Ground-water monitoring is necessary to confirm the conceptual site model developed during the investigation and to ensure that the remedy remains protective.
- Statutory 5-year reviews are required whenever the selected remedy will leave contamination on site above levels that allow for unlimited use and unrestricted exposure (NCP §300.430(f)(4)(ii)).

At Eielson AFB, the regulatory options considered are described below.

Alternate Concentration Limits

Alternate concentration limits (ACLs, 55 *FR* 8732) are considered when the ground water has a known or projected point of entry to surface water with no statistically significant increases in contaminant concentration in the surface water. Natural attenuation is the mechanism for cleanup in ground water between the contamination and the point of surface-water discharge. If ACLs are used, the remedial action must include enforceable measures (e.g., institutional controls) that will preclude human exposure to the contaminated ground water. ACLs should only be used when active restoration of the ground water is not practicable (55 *FR* 8754).

For Eielson AFB, ACLs were not applicable because contaminated ground water did not discharge into surface water on base.

Alternate Points of Compliance

As stated previously, remediation levels should generally be attained throughout the contaminated plume, or at and beyond the edge of the waste management area.

For situations in which the risk of exposure is very slight (i.e., because of remoteness of the site), however, alternate points of compliance may be considered in combination with natural attenuation provided contamination in the aquifer is controlled from further migration (55 *FR* 8735). When releases from several distinct sources in close geographical proximity cause a plume, the most effective cleanup strategy may address the problem as a whole, with the point of compliance encompassing the sources of release (55 *FR* 8753).

For Eielson AFB, an alternate point of compliance was established for a previously used base landfill. Consistent with expectations outlined in the Ground Water Protection Strategy, an alternate point of compliance was established at the edge of the waste management area (i.e., the landfill boundary).

Technical Impracticability Waiver

The Superfund regulations allow Applicable or Relevant and Appropriate Standards, Limitations, Criteria, and Requirements (ARARs) to be waived under certain circumstances if the remedy can be demonstrated to be protective. One of the six ARAR waivers provided by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA §121(d)(4)) is technical impracticability (TI). The use of the TI waiver requires a demonstration that compliance with ARARs, including maximum contaminant levels (MCLs) or non-zero maximum contaminant level goals (MCLGs), is technically impracticable from an engineering perspective. A demonstration that ground-water restoration is technically impracticable generally should be accompanied by a demonstration that contaminant sources have been or will be identified and removed or treated to the extent practicable.

In the event that the requirements outlined above are demonstrated and a TI waiver is invoked, an alternative remedial strategy must be established that includes 1) exposure control using enforceable, reliable institutional controls such as deed notifications and restrictions on water supply well construction and use; 2) source control through treatment or containment where feasible and where significant risk reduction will result; and 3) aqueous plume remediation by preventing contaminant migration (e.g., through hydraulic containment), establishing a less-stringent cleanup level, and/or using natural attenuation.

At Eielson AFB, TI waivers are being invoked for two lead contamination plumes caused by leaded gasoline releases. The lead has degraded from the organic lead contained in the gasoline to a relative immobile inorganic lead. Ground-water contamination is confined to areas approximately 600 feet in length. Ground-water remediation is technically impracticable because the inorganic lead is so strongly adsorbed to the soils. Reliability of institutional controls is very good; Eielson AFB is not a target of base closure. These institutional controls preventing use of the ground water will protect human health.

Selection of Natural Attenuation With or Without Institutional Controls

Natural attenuation is generally recommended only when more active restoration is not practicable, cost-effective, or warranted because of site-specific conditions (e.g., ground water that is unlikely to be used in the foreseeable future and therefore can be remediated over an extended timeframe), or in situations in which the method is expected to reduce the concentration of contaminants in the ground water to remediation goals in a reasonable timeframe (i.e., in a period comparable to that achievable using other restoration methods). Institutional controls may be necessary to ensure that such ground waters are not used before levels protective of human health are reached (55 *FR* 8734).

The limited action alternative (natural attenuation with institutional controls and ground-water monitoring) has been selected for numerous areas at Eielson AFB contaminated with both petroleum compounds and chlorinated organics. For all of these areas, the plume is believed to have reached equilibrium where the rate of contaminant leaching from the source is balanced with the rate of natural attenuation. The use of institutional controls was also a critical component of the selected remedy to prevent exposure to contaminated ground water until ARARs are achieved throughout the aquifer and beneficial uses are restored.

Building a "Safety Net"

As with any environmental decision, it is prudent to develop a "safety net" of contingencies to alleviate apprehensions associated with the selection of natural attenuation.

The uncertainty associated with environmental decisions, specifically the selection of natural attenuation, was addressed at Eielson AFB through the use of the observational method. Key components of the observational method are 1) a decision based on the most probable site conditions; 2) identification of reasonable deviations from those conditions; 3) identification of parameters to monitor to detect deviations; and 4) preparation of contingency plans for each potential deviation (1). The conceptual site model developed through the investigation will be tested and confirmed through continued ground-water monitoring. A phased approach with contingencies for additional remediation was established in the event that the conceptual site model is not confirmed.

In addition, statutory 5-year reviews require an evaluation for additional remediation if it becomes apparent that the remedy is not protective of human health or the environment.

For sites where natural attenuation is selected and ground-water contamination remains, reliable institutional controls are a critical component for a protective remedy. For federal facilities, institutional controls to prevent exposure to contaminated ground water are generally effective and reliable and are further enhanced by the statutory requirements for property transfer under Section 120(h) of CERCLA.

Summary

Existing regulations and guidance were used to support a technically defensible selection of natural attenuation as a component of the selected remedy for all ground-water contamination areas at Eielson AFB. The selected remedies included a sound regulatory framework that is consistent with EPA's Ground Water Protection Strategy.

Continued monitoring, contingencies for implementing additional remediation if necessary, statutory 5-year protectiveness reviews, and the base closure requirements of CERCLA Section 120 provide additional checks and reviews to ensure that the selected remedy remains protective.

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Lessons Learned: Risk Based Corrective Action

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Introduction

With over 300,000 leaking underground storage tanks (LUSTs) nationwide (1) that have contaminated soil, ground-water, and surface-water resources, operation of an underground storage tank (UST) clearly is no longer a casual undertaking. U.S. Environmental Protection Agency (EPA) regulations (2) created guidelines and requirements for safe and responsible operation of USTs, with provisions for early leak detection, leak reporting, financial responsibility, and cleanup of leaks. Using a franchise approach, these EPA regulations have been adopted—and sometimes supplemented—by state UST programs in an effort to clean up existing leaks and prevent future leaks. Most state programs also instituted petroleum cleanup funds to assist owners and operators of USTs in complying with financial responsibility requirements and to provide money for cleanup of existing releases.

Initially many state programs required cleanup of LUST sites to very low levels of compounds of concern (petroleum products) or in some cases even to background or nondetectable levels at all sites, regardless of the actual hazard posed by the site. These levels often proved to be unattainable both technologically and economically, however, making site closure difficult to obtain, stalling property transfers, driving cleanup costs higher, and frustrating all parties concerned. Even though state UST programs have made strong efforts to prioritize sites for cleanup and streamline oversight, only about 45 percent (1) of known LUST sites nationwide had cleanups completed by the end of 1995, and some state cleanup funds were almost exhausted, bordering on insolvency.

The American Society for Testing and Materials' document "Standard Guide for Risk-Based Corrective Action (RBCA) Applied at Petroleum Release Sites" (3) was introduced as a logical framework for determining the extent and urgency of corrective action required at a LUST site. The RBCA standard provides a tiered approach to evaluating risk, progressing from generic, conservative calculation of risk-based screening levels (RBSLs) to more site-specific target levels (SSTLs) derived from increasingly site-specific data. Only completed pathways from contaminant source to potential receptors are evaluated. Risk levels are used to back-calculate acceptable concentrations (RBSLs or SSTLs) for each compound of concern for each completed pathway. Site conditions are then compared with the RBSLs or SSTLs to determine the extent of cleanup required.

Currently 43 states have entered the RBCA training process. Of these, 6 have implemented RBCA, 12 are working on the program design, and 25 are still training (4). This paper presents some of the lessons learned during the process of developing and implementing RBCA.

Lessons Learned

RBCA Program Development

The process of implementing an RBCA program at the state level requires commitment on the part of the entire organization. Training is usually required for all interested parties, including state regulators, environmental consultants, UST owners and operators, and the general public. All of these interested parties or stakeholders must be involved in the process up front to avoid misconceptions and misunderstandings. It is especially important that key decision-makers understand and "buy into" the process early on.

All interested parties must be involved in making the risk management decisions necessary for implementing RBCA. This includes determination of risk levels, pathways to be considered, compounds of concern, and other key parameters used to calculate Tier 1 RBSLs. Once the RBSLs have been calculated, it is important to avoid the temptation to adjust the parameters in an effort to make the RBSLs fit some preconceived or pre-existing level.

Creation of RBCA lookup tables and cleanup numbers can be a contentious process. The general public and many regulators often want to retain cleanup to background for Tier 1 regardless of the actual hazard posed by the site. Education is the only way to solve this problem. People must be made aware that background levels are unrealistic and often unattainable goals at most sites, given available technologies and resources. The RBCA process provides a method for determining cleanup goals to adequately protect human health and the environment.

Because RBCA often involves some major philosophical changes, regulatory and policy changes may also be needed. Stakeholders may feel wary if a state changes from fixed, numerical cleanup standards to risk-based cleanup goals without legislative authority to do so. These stakeholders may feel more comfortable if the law says the change is appropriate. Legislative mandates, however, may also impose limitations that impede or compromise RBCA implementation. Therefore, a balanced approach is required to ensure that regulators and other stakeholders feel that the implementation process is legitimate but not that RBCA is being forced upon them against their will.

RBCA Program Implementation

Implementation can be difficult initially. States should have a clear and thorough strategy for implementing as complete a RBCA program as possible before they start. If not, the state may end up haphazardly creating pieces of the program in response to problems and issues as they arise. For example, requirements and definitions relating to key issues such as alternate points of compliance, acceptable sampling methodologies, and extent of site assessment for Tier 1 versus Tier 2 should be available before program implementation.

Modeling data can sometimes be misleading. In particular, estimates of indoor air concentrations that result from a given soil concentration are often overestimated. Monitoring and sampling are important to confirm any modeling estimates used in the RBCA process.

RBCA is not a cure-all—some difficult issues will remain. For example, third party liability for compounds of concern left behind at LUST sites following property transfer may still cause uncertainty and potential problems. A site closed using cleanup levels determined through RBCA or by previous standards will leave some level of compounds of concern in place. In most cases, however, RBCA provides a more sound and defensible basis for site closure and levels of compounds of concern left in place should third-party issues arise. Another issue is the fear of having sites reopened after a closure letter has been granted. Again, RBCA provides a clear, logical framework for making site closure decisions that can be easily revisited should the closure be questioned in the future.

Some consultants and regulators may view RBCA as a threat to their livelihood. Long cleanup times and low site closure rates ensure continued work for both consultants and regulators. Sites will have to be closed eventually, however, and the RBCA process is one of the best ways to achieve this goal.

Considerations for the Future

The implementation and acceptance of RBCA involves a shift in perspective from asking the question "How much or what levels of the compounds of concern can we cleanup?" to asking "How much of the compounds of concern can we safely leave in place?" Again, this is not a significant change in the way we manage sites because some level of compounds of concern have always been left in place. RBCA simply asks the question early in the cleanup process to better utilize resources to clean up sites posing the most threat. We must, however, guard against allowing ourselves to ask "How much contamination can we allow to happen?" It is extremely important to supplement an RBCA program with a strong program of leak prevention and early leak detection.

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Informal Dialog on Issues of Ground-Water and Core Sampling

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An assessment of natural attenuation can be no better than the site characterization activities that collect the data used in the assessment. The following issues should be considered when planning for field sampling:

- When is a conventional well required, and when can a Geoprobe or CPT push technology be used for well installation?
- What are the advantages and disadvantages of conventional wells, mini wells, or water samples collected with a Hydropunch and a CPT rig?
- How much water should be purged to prepare a well for sampling?
  - What is the evidence that a well is ready for sampling?
  - What should be measured: conductivity, temperature, pH, turbidity, oxygen, or redox potential?
- What flow rate should be used to purge a well?
- What flow rate should be used to sample a well?
- What is the best way to measure oxygen in ground water?
  - What are the relative advantages of oxygen-sensing electrodes and indicator dye kits?
  - What level of training is required to use the equipment intelligently?
  - What problems may arise?
- What is the best way to measure sulfide in ground water?
  - What are the relative advantages of lead acetate indicator paper, colorimeter assays, or ion specific electrodes?
  - How accurate should the measurement be?
  - What problems may arise?
- What is the best way to measure iron(II) in ground water?
  - What field methods are available?
  - How accurate should the measurement be?
  - What problems may arise?
- How should samples for methane, ethylene, and ethane be collected?
  - Where can the samples be analyzed, and how much should analysis cost?
- What is the best preservative for ground-water samples?
- How is ground water sampled for hydrogen?
  - What are the limitations of this technique?
  - What problems may arise?
- Must alkalinity be analyzed in the field, or can samples be shipped back to the laboratory?
- When should ground-water samples be acquired for volatile fatty acids (VFAs)?
  - How are VFA samples stabilized and extracted?
- What is the best way to collect core samples?
  - What are the advantages and disadvantages of available equipment?
  - How should the samples be stabilized for analysis of contaminants?
  - What is the best way to screen samples in the field?
  - How should the samples be stabilized for analysis of microbial indices?
- How is soil gas analysis used to locate and identify nonaqueous-phase liquid source areas?
  - What parameters should be measured?
  - What equipment is available?
- What new analyses could be developed to improve understanding of natural attenuation?
  - What new tracers might be used?

- What are the cost tradeoffs of these analyses compared with the benefit of improved understanding of plume behavior?
- What should be the relative investment in sample acquisition, sample analysis, data reduction, mathematical modeling, and report preparation?
- How many wells or cores samples are needed?
  - To examine plume flow velocity?
  - To examine proximity to sensitive receptors?

Introductory Remarks: Appropriate Opportunities for Application—Civilian Sector (RCRA and CERCLA)

Fran Kremer
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(Paper unavailable at press time.)

Introductory Remarks: Appropriate Opportunities for Application—U.S. Air Force and Department of Defense

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(Paper unavailable at press time.)

Intrinsic Remediation in the Industrial Marketplace

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Introduction

Intrinsic remediation of chlorinated solvents is a common phenomenon. Most sites contain bacteria that can both dechlorinate and oxidize chlorinated solvents to nontoxic compounds. The challenge for site owners and for regulators is to determine whether intrinsic remediation is a safe and effective remedy at individual sites. Intrinsic remediation is an important development for industry because it protects human health and the environment yet is more cost-effective than the competing, intrusive ground water remediation techniques.

When To Consider Intrinsic Remediation

Decision-makers should determine whether the following criteria are met when evaluating the appropriateness of intrinsic remediation for a given site:

- Intrinsic remediation protects human health and the environment.
- Geochemical and volatile organic compound (VOC) analyses demonstrate that intrinsic degradation of contaminants is occurring.
- The contaminant source is continuing or cannot be removed (e.g., dense nonaqueous-phase liquids [DNAPLs]), so ground water will need long-term treatment.
- Ground water receptors are not affected or can be protected.
- Minimal disruption of plant operations or property is desired.
- Alternative remedial technologies pose additional risks, such as transferring contaminants to other environmental media or disrupting adjacent ecosystems.
- The rate of degradation balances the rate of migration and the potential for exposure, considering the likely nature and timing of potential exposures. For example, if a plume will degrade within 10 years and the ground water is not likely to be used for 20 years, intrinsic bioremediation should be seriously considered.

The Data Needed for an Intrinsic Remediation Determination

Determination of the appropriateness of an intrinsic remediation demonstration considers the extent of the data-gathering effort and the cost of the resources required. DuPont has developed the following list of minimum data to be gathered at all potential intrinsic remediation sites:

- VOCs, including isomers.
- Dissolved oxygen, redox potential, and conductivity.
- Methane, ethane, ethylene, and propane.
- Total organic carbon (TOC).
- Major anions and cations (sodium, potassium, calcium, chloride, iron, magnesium, manganese, nitrate, sulfate, and alkalinity).

DuPont recommends a tiered approach to intrinsic site assessment, based on the complexity of the site, to better understand what will be needed for a credible intrinsic remediation demonstration. Table 1 characterizes the three tiers of sites. For further information on requirements for demonstrations, consult the newly issued Remediation Technology Development Forum (RTDF) guidelines (1).

The Economics of Intrinsic Remediation

Those who have been involved in selecting the "best" remedy for a site know that this is a time-consuming task, which typically requires expensive sampling and analysis; the more parameters, the greater the analytical cost. Therefore, there is often a reluctance to evaluate a large number of remedial alternatives. DuPont has found, however, that the incremental cost of evaluating intrinsic bioremediation along with other options is relatively small. This incremental cost may be more than offset if intrinsic remediation is chosen over a technology

Table 1. Tiered Site Characteristics

Tier 1 (Easy Sites)	Tier 2 (Intermediate Sites)	Tier 3 (Difficult Sites)
Simple hydrogeology	Moderately complex hydrogeology	Hydrogeology complex
Single parent compound	Few contaminants	Confusing mixture
Size known (areal extent)	Plume size questionable	Large plume
Source and mass known	Source and mass not well defined	Very large or inaccessible source
Highest ground-water concentration < 10 mg/L	Highest ground-water concentration < 100 mg/L	Mobil DNAPLs
Static or shrinking plume	Plume-size trend not known	Growing plume or trend not known
Bioindicators obvious	Some bioindicators	No bioindicators
Receptors very far away	Receptors are "not too far"	Receptors close or affected
Analytical model sufficient	Flow-and-transport model needed	Needs a detailed fate-and-transport model

that would be more expensive to implement. This conclusion is based on using a "template" site to perform an engineering cost estimate. The template site has the following characteristics:

- 10-acre site
- Contaminant: tetrachloroethene (PCE)
- Concentration: 10 mg/L
- 20 monitoring wells, sampled twice a year for 30 years
- Completed remedial investigation
- Long-term monitoring costs are brought to present costs using an inflation rate of 3 percent and a discount rate of 12 percent, the corporate cost of capital

Much of the investigation cost is the same regardless of the remedy chosen. Therefore, only incremental costs are considered in this analysis. The incremental present cost of an intrinsic remediation demonstration above that of a standard investigation and long-term monitoring is approximately $100,000 over 30 years. The simplest pump-and-treat remedy (air stripping and vapor-phase granulated activated carbon) has a present cost of $2.1 million over 30 years. A comparable intrinsic remediation remedy has a present cost of $900,000. (See Table 2 for cost details.) If intrinsic remediation is protective, the saving is $1.2 million.

The Average Plume

DuPont recently surveyed over 50 sites and plumes to get a statistical picture of how and where intrinsic biodegradation is operating. The survey looked for evidence of reductive dehalogenation at these sites, which were primarily DuPont Resource Conservation and Recovery Act and Comprehensive Environmental Response, Compensation, and Liability Act sites. Some outside sites were included where data were available, as well as several sites clearly described in the scientific literature. To be included, the sites needed to have either SW846 Method 8240 analyses for VOCs, good geological delineation, and credible isoconcentration maps, or to be thoroughly described in the technical literature.

Biodegradation

The sites selected for analysis were ones at which the original contaminants could be identified; thus, field data could be examined for the biodegradation byproducts of those contaminants. The presence of these byproducts indicates activity by naturally occurring bacteria. For example, if most of the dichloroethene (DCE) present in ground water is the *cis*-1,2-DCE isomer, that is conclusive evidence of the biological degradation of trichloroethene (TCE). The biodegradation results are presented in Table 3. The data showed that:

- 88 percent of the sites have bacteria that can biodegrade PCE and TCE to DCE.

Table 2. Present Cost of Intrinsic Remediation Versus Investigation and Long-Term Monitoring

Cost Element	Investigation and Long-Term Monitoring Cost	Intrinsic Remedy Cost	Incremental Cost—Intrinsic Versus Investigation and Monitoring	Simple Pump-and-Treat Cost	Incremental Cost—Pump-and-Treat Versus Intrinsic
Up front	$95,000	$35,000	$40,000	$650,000	$515,000
Annual	$62,000	$68,000	$6,000	$35,000	$67,000
Present cost (30 years)	$800,000	$900,000	$100,000	$2,100,000	$1,200,000

Note: 12 percent discount rate, 3 percent annual inflation

Table 3. Biodegradation Results at Survey Sites

Reaction	Number of Sites Present	Total Sites	Percentage
PCE to TCE	27	31	87
TCE to DCE	39	44	88
DCE to VC	28	37	75
VC to ethane	18	31	58[a]

[a] Ethane data often are unavailable.

- 75 percent of the sites have bacteria that can biodegrade DCE to vinyl chloride (VC) or ethylene.

Some sites may not have enough bioavailable substrate to complete the degradation reactions. Insufficient substrate should always be suspected at sites where biodegradation stops at either TCE or VC. Sites without the full bacterial population needed for complete degradation would be expected to show either no degradation or degradation that stops at DCE.

Half-Lives

Two simple methods were used to estimate half-lives. The first method, developed by Buscheck et al. (2), is a semilog plot of individual well analyses versus time of transport. The second method is a simple graphical extrapolation. The graphical extraction method assumes that the plume is at steady state so that dilution, dispersion, and sorption factors are constant; measures concentration declines along the centerline of plumes on high-quality isoconcentration maps; and calculates the time for the water package to move each of those distances. The results of the two methods show good agreement, with the graphical extraction method giving somewhat longer half-lives. These data suggest that the key factor in evaluating intrinsic remediation should be the time of residence of contaminants in a plume before it reaches a potential receptor, if it ever does. The average solvent half-lives are shown in Table 4.

Table 4. Half-Lives Calculated by Graphical Extraction

Reaction	Average Half-Life (years)	Number of Sites
PCE to TCE	1.20	7
TCE to DCE	1.19	15
DCE to VC	1.05	12
VC to ethane	1.22	9

Intrinsic Remediation Capacity

As a further criteria, it may be advantageous to calculate the assimilative capacity of the aquifer, which is defined as its capacity to biodegrade a contaminant. At many sites, there appears to be no synthetic source of substrate. This implies that natural organic material in the aquifer is supplying electrons to drive the biodegradation reactions. Based on this assumption, one can calculate the amount of chlorinated solvent that an aquifer can biodegrade, although this estimate can only apply to sites at which the soils contain bacteria that can degrade chlorinated solvents.

Here is an example calculation. Typical aquifers contain between 0.3 percent and 1 percent natural organic carbon. This equals 8 to 28 pounds of organic carbon per cubic yard of soil at 2,800 pounds of soil per cubic yard. A conservative assumption is that the aquifer contains only 0.1 percent TOC and only 10 percent of the natural organic carbon is bioavailable. If bacteria can use only 10 percent of the bioavailable organic carbon as food for biodegrading chlorinated solvents, 0.03 pounds of organic carbon per cubic yard (1 percent of the total carbon present) is used as food in chlorocarbon degradation. Electron balance indicates that bacteria use 0.25 to 0.50 pounds of organic carbon to degrade 1 pound of solvents (3). Therefore, each cubic yard of this hypothetical aquifer has the capacity to biodegrade at least 0.06 pounds of chlorinated solvent.

The plume that the RTDF is studying at Dover Air Force Base in Delaware involves approximately 7.5 million cubic yards of aquifer. Using the previous estimate, bacteria in this aquifer should be able to biodegrade a minimum of 450,000 pounds of solvents—the equivalent of 820 drums of DNAPL. It is very unlikely that there are 820 drums of DNAPL at Dover. Therefore, the bacteria in this aquifer have an adequate supply of organic carbon to biodegrade all the contaminants that are currently in it.

What About Existing Pump-and-Treat Systems?

Shutting down a pump-and-treat system to let intrinsic processes complete the restoration is now regarded as acceptable during hydrocarbon remediation. Benzene is the main component of concern in most hydrocarbon plumes and is regulated at levels similar to those required for VC. Why shouldn't chlorinated solvent pump-and-treat systems be shut down at some logical point and intrinsic remediation be allowed to finish their work as well? Many chlorinated solvent pump-and-treat systems have already reached their useful lifetime for contaminant removal.

All of the following criteria should be met before intrinsic remediation can replace an existing, operating pump-and-treat system that treats chlorinated solvents:

- It can be demonstrated that intrinsic activity is already occurring in the aquifer.
- It is possible to predict how far the plume might extend if the pump-and-treat system was not operating, and it can be shown that no receptor will be affected.

- Intrinsic remediation is protective of human health and the environment.

Conclusions

- Intrinsic remediation is real. It is protective when properly employed.
- Intrinsic biodegradation occurs at many sites. Each biodegradation step has an average half-life of 1 to 2 years.
- The most important factors in determining the effectiveness of intrinsic remediation are plume residence time and the half-lives of the sequential biodegradation reactions.
- Most aquifers contain much more organic carbon than necessary to support intrinsic bioremediation. While anthropogenic carbon may help support intrinsic degradation, it is not essential.
- Intrinsic remediation is not a "do nothing" approach, and there is a moderate cost associated with it. The present cost of an intrinsic remediation remedy is approximately $900,000, compared with $2.1 million for the cheapest pump-and-treat system.

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Environmental Chemistry and the Kinetics of Biotransformation of Chlorinated Organic Compounds in Ground Water

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Introduction

Responsible management of the risk associated with chlorinated solvents in ground water involves a realistic assessment of the natural attenuation of these compounds in the subsurface before they are captured by ground-water production wells or before they discharge to sensitive ecological receptors. The reduction in risk is largely controlled by the rate of the biotransformation of the chlorinated solvents and their metabolic daughter products. These rates of biotransformation are sensitive parameters in mathematical models describing the transport of these compounds to environmental receptors.

Environmental Chemistry of Biodegradation of Chlorinated Solvents

[This section is designed specifically for engineers and mathematical modelers who have little or no chemistry background; other readers may wish to proceed directly to the next section.]

The initial metabolism of chlorinated solvents such as tetrachloroethylene, trichloroethylene, and carbon tetrachloride in ground water usually involves a biochemical process described as sequential reductive dechlorination. This process only occurs in the absence of oxygen, and the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process.

The chemical term "reduction" was originally derived from the chemistry of smelting metal ores. Ores are chemical compounds of metal atoms coupled with other materials. As the ores are smelted to the pure element, the weight of the pure metal are reduced compared with the weight of the ore. Chemically, the positively charged metal ions receive electrons to become the electrically neutral pure metal. Chemists generalized the term "reduction" to any chemical reaction that added electrons to an element. In a similar manner, the chemical reaction of pure metals with oxygen results in the removal of electrons from the neutral metal to produce an oxide. Chemists have generalized the term "oxidation" to refer to any chemical reaction that removes electrons from a material. For a material to be reduced, some other material must be oxidized.

The electrons required for microbial reduction of chlorinated solvents in ground water are extracted from native organic matter, from other contaminants such as the benzene, toluene, ethylene, and xylene compounds released from fuel spills, from volatile fatty acids in landfill leachate, or from hydrogen produced by the fermentation of these materials. The electrons pass through a complex series of biochemical reactions that support the growth and function of the microorganisms that carry out the process.

To function, the microorganisms must pass the electrons used in their metabolism to some electron acceptor. This ultimate electron acceptor can be dissolved oxygen, dissolved nitrate, oxidized minerals in the aquifer, dissolved sulfate, a dissolved chlorinated solvent, or carbon dioxide. Important oxidized minerals used as electron acceptors include iron and manganese. Oxygen is reduced to water, nitrate to nitrogen gas or ammonia, iron(III) or ferric iron to iron(II) or ferrous iron, manganese(IV) to manganese(II), sulfate to sulfide ion, chlorinated solvents to a compound with one less chlorine atom, and carbon dioxide to methane. These processes are referred to as aerobic respiration, nitrate reduction, iron and manganese reduction, sulfate reduction, reductive dechlorination, and methanogenesis, respectively.

The energy gained by the microorganisms follows the sequence listed above: oxygen and nitrate reduction provide a good deal of energy, iron and manganese

reduction somewhat less energy, sulfate reduction and dechlorination a good deal less energy, and methanogenesis a marginal amount of energy. The organisms carrying out the more energetic reactions have a competitive advantage; as a result, they proliferate and exhaust the ultimate electron acceptors in a sequence. Oxygen and then nitrate are removed first. When their supply is exhausted, then other organisms are able to proliferate, and manganese and iron reduction begins. If electron donor supply is adequate, then sulfate reduction begins, usually with concomitant iron reduction, followed ultimately by methanogenesis. Ground water where oxygen and nitrate are being consumed is usually referred to as an oxidized environment. Water where sulfate is being consumed and methane is being produced is generally referred to as a reduced environment.

Reductive dechlorination usually occurs under sulfate-reducing and methanogenic conditions. Two electrons are transferred to the chlorinated compound being reduced. A chlorine atom bonded with a carbon receives one of the electrons to become a negatively charged chloride ion. The second electron combines with a proton (hydrogen ion) to become a hydrogen atom that replaces the chlorine atom in the daughter compound. One chlorine at a time is replaced with hydrogen; as a result, each transfer occurs in sequence. As an example, tetrachloroethylene is reduced to trichlorethylene, then any of the three dichloroethylenes, then to monochloroethylene (commonly called vinyl chloride), then to the chlorine-free carbon skeleton ethylene, then finally to ethane.

Kinetics of Transformation in Ground Water

Table 1 lists rate constants for biotransformation of tetrachloroethylene (P.E.), trichloroethylene (TCE), cis-dichloroethylene (cis-DCE), and vinyl chloride extrapolated from field-scale investigations. In some cases, a mathematical model was used to extract a rate constant from field data; however, many of the rate constants were calculated by John Wilson from published raw data. In several cases, the primary authors did not choose to calculate a rate constant or felt that their data could not distinguish degradation from dilution or dispersion.

The data were collected or estimated to build a statistical picture of the distribution of rate constants, in support of a sensitivity analysis of a preliminary assessment using published rate constants. They serve as a point of reference for "reasonable" rates of attenuation; applying them to other sites without proper site-specific validation is inappropriate.

Table 1. Apparent Attenuation Rate Constants (Field Scale Estimates)

Location	Reference	Distance From Source	Time From Source	Residence Time	TCE	cis-DCE	Vinyl Chloride
		(meters)	(years)	(years)	Apparent Loss Coefficient (1/year)		
St. Joseph, MI	1-3	130 to 390	3.2 to 9.7	6.5	0.38	0.50	0.18
		390 to 550	9.7 to 12.5	2.8	1.3	0.83	0.88
		550 to 855	12.5 to 17.9	5.4	0.93	3.1	2.2
		240 to 460	2.2 to 4.2	2.0	1.4	Produced	Produced
Picatinny Arsenal, NJ	4, 5	320 to 460	2.9 to 4.2	1.3	1.2	Produced	Produced
		240 to 320	2.2 to 2.9	0.7		1.6	
		0 to 250	0.0 to 2.3			0.5	
Sacramento,CA	6	70 to 300	0.5 to 2 3	1.8	1.1	0.86	3.1
Necco Park, NY	7	0 to 570	0.0 to 1.6	1.6	0.7		
		0 to 660	0.0 to 1.8	1.8	0.7		
Plattsburgh AFB, NY	Weidemeider, this volume	0 to 300	0.0 to 6.7	6.7	1.3	Produced	Produced
		300 to 380	6.7 to 8.6	1.9	0.23	0.6	1.16
		380 to 780	8.6 to 17.7	9.1	Absent	0.07	0.47
Tibbitt's Road, NH	B. Wilson, this volume	0 to 24	0.0 to 2.4	2.4		0.21	Produced
		0 to 40	0.0 to 6.4	6.4		0.42	0.68
		0 to 55	0.0 to 10	10		0.73	> 0.73
San Francisco Bay Area, CA	8				4.4	5.11	
Perth, Australia	9	0 to 600	0.0 to 14			0.32	
Eielson AFB, AK	10					0.73	
						2.3	
Not identified	11				0.8	0.8	0.8
Cecil Field NAS, FL	Chapelle, this volume	0 to 140	0.0 to 1.2	1.2	3.3 to 7.3		3.3 to 7.3

The estimates of rates of attenuation tend to cluster within an order of magnitude. Figure 1 compares the rates of removal of TCE in those plumes that demonstrated evidence of biodegradation. Most of the first-order rates are very close to 1.0 per year, equivalent to a half life of 8 months. Table 1 also reveals that the rate of removal of P.E., TCE, and cis-DCE, and vinyl chloride are similar; they vary by little more than one order of magnitude.

Table 2 lists first-order and zero-order rate constants determined in laboratory microcosm studies. The rates of removal in the laboratory microcosm studies are similar to estimates of removal at field scale for TCE, cis-DCE, and vinyl chloride. Rates of removal of 1,1,1-trichloroethane (1,1,1-TCA) are similar to the rates of removal of the chlorinated alkenes.

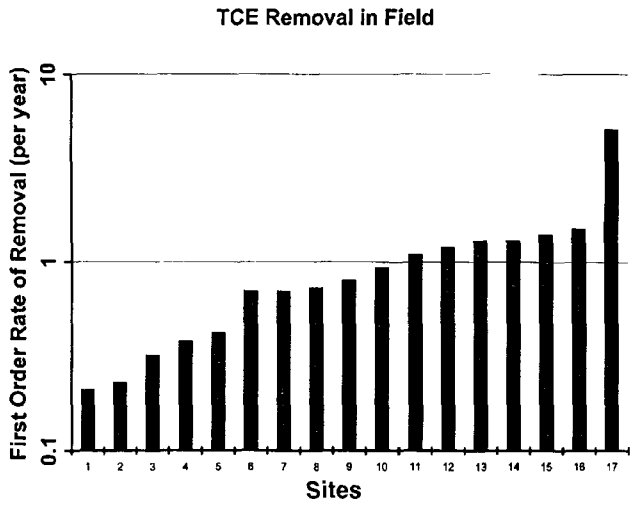

Figure 1. The first-order rate constant for biotransformation of TCE in a variety of plumes of contamination in ground water.

Summary

The rates of attenuation of chlorinated solvents and their less chlorinated daughter products in ground water are slow as humans experience time. If concentrations of chlorinated organic compounds near the source are in the range of 10,000 to 100,000 micrograms per liter, then a residence time in the plume on the order of a decade or more will be required to bring initial concentrations to current maximum contaminant levels for drinking water. Biodegradation as a component of natural attenuation can be protective of ground-water quality in those circumstances where the travel time of a plume to a receptor is long. In many cases, it will be necessary to supplement the benefit of natural attenuation with some sort of source control or plume management.

Table 2. Apparent Attenuation Rate Constants From Laboratory Microcosm Studies

Location of Material	Reference	Distance From Source	Time From Source	Incubation Time	TCE	cis-DCE	Vinyl Chloride	1,1,1-TCA
		(meters)	(years)	(years)	Apparent First-Order Loss (1/year) *Apparent Zero OrderLoss (µg/L*day)*			
Laboratory Microcosm Studies Done on Material From Field-Scale Plumes								
Picatinny Arsenal, NJ	12	240	2.2	0.5	0.64	0.52		
	13	320	2.9	0.5	0.42	9.4		
		460	4.2	0.5	0.21	3.1		
St. Joseph, MI	14			0.12, 0.077	1.8, 1.2			
Traverse City, MI	15	300		1.8	1.8			
Tibbitts Road, NH	16	At Source			4.8			
Laboratory Microcosm Studies Done on Material Not Previously Exposed to the Chlorinated Organic Compound								
Norman Landfill, OK	17	Aerobic material					4.2 *10*	
	18	Sulfate reducing						1.28 *1.62 1.75*
		Methan-ogenic						1.20 *1.65 1.42*
FL	16	Reducing						3.6
	19	Reducing					0.012	

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Future Vision: Compounds With Potential for Natural Attenuation

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Introduction

Attenuation of natural organic compounds, such as those present in hydrocarbon fuels, is predictable because the responsible microorganisms are ubiquitous in soil and the subsurface. Bacteria able to use hydrocarbons as their source of carbon and energy under either aerobic or anaerobic conditions have a tremendous selective advantage over other members of the microbial community. Therefore, the process can be self-sustaining and is limited only by the presence of electron acceptors or inorganic nutrients.

Bacteria able to grow at the expense of chlorinated aliphatic compounds are not widely distributed; natural attenuation of such compounds is consequently less predictable. The use of a chlorinated compound as a terminal electron acceptor (chlororespiration or dehalorespiration) can yield energy and thus provides a selective advantage to a limited range of anaerobic bacteria (1). Many of the transformations of chloroaliphatic compounds, such as trichloroethylene, are co-metabolic and yield no advantage to the bacteria that catalyze the reactions. In fact, co-metabolism can select against the organism because of the wasting of energy and production of toxic metabolites.

Between the extremes of readily degradable hydrocarbons and chlorinated aliphatic compounds that serve only as electron acceptors are many other synthetic organic compounds that can provide sources of carbon and energy for bacteria. This paper describes compounds that are known to be biodegradable and have the potential for natural attenuation in the field. Some synthetic chemicals are expected to be readily susceptible to natural attenuation, others are degraded at a limited number of sites, and some show only a limited potential. Where possible, recent review articles rather than primary literature will be cited. More detailed information on many of the compounds is also available in a recent book that provides an excellent analysis of the potential for biodegradation (2).

The first question to be asked when considering the potential for natural attenuation is whether biodegradation of the chemical contaminant has been reported. The question could be phrased, "Does the biology exist?" Biodegradation of some of the compounds has been studied extensively under field conditions. Transformation of others has only recently been discovered in laboratory systems or waste streams. Such laboratory studies should not be ignored because the processes discovered in such systems are catalyzed by bacteria obtained from the field. Laboratory studies are essential for revealing the mechanisms of the reactions and the conditions required for the process. They can also determine whether the process provides energy or nutrients—and thus a selective advantage—to the bacteria that catalyze the reactions.

The second question is whether the activity of the necessary specific organisms is present at the site under consideration. A considerable amount of effort has been spent on enumerating and identifying bacteria at hydrocarbon-contaminated sites under consideration for bioremediation. Because such bacteria are ubiquitous, it is much more useful to assess their activity as revealed by degradation of the hydrocarbons or transformation of electron acceptors. The biology can be assumed to be present but limited by other factors. In contrast, bacteria able to degrade specific synthetic chemicals cannot be assumed to be widely distributed in the field. Detection of bacteria able to grow on specific compounds in contaminated sites and failure to detect them in nearby uncontaminated areas can be taken as strong evidence for natural attenuation. Absence of bacteria able to catalyze the degradation of compounds known to be biodegradable could provide an opportunity for bioaugmentation, a strategy that has earned a poor reputation because of misapplication in the past.

The third question is whether conditions appropriate for natural attenuation exist or can be created at the site. Issues of electron donors and acceptors, bioavailability, mass transfer, contaminant mixtures, and concentration

must be resolved. A good understanding of the biodegradation process, including reaction stoichiometry and kinetics, is essential for evaluation of the potential for natural attenuation. Fortunately, such understanding exists for a wide range of synthetic chemical contaminants.

Chloroaromatic Compounds

Bacteria able to degrade all but the most complex chloroaromatic compounds have been discovered during the past 20 years. Polychlorobenzenes, including hexachlorobenzene, can be sequentially dehalogenated to monochlorobenzene under methanogenic conditions in soil slurries (3). Reductive dehalogenation of chlorobenzene has not been reported, but chlorotoluenes are dehalogenated to toluene in the above methanogenic systems, and it seems likely that chlorobenzene could serve as a substrate for reductive dehalogenation.

Chlorobenzenes up to and including tetrachlorobenzene are readily biodegraded under aerobic conditions. Bacteria able to grow on chlorobenzene (4), 1,4-dichlorobenzene (4-6), 1,3-dichlorobenzene (7), 1,2-dichlorobenzene (8), 1,2,4-trichlorobenzene (9), and 1,2,4,5-tetrachlorobenzene (10) have been isolated and their metabolic pathways determined. The pathways for aerobic degradation are remarkably similar and lead to the release of the halogens as hydrochloride (HCl).

Chlorobenzenes are very good candidates for natural attenuation under either aerobic or anaerobic conditions. Aerobic bacteria able to grow on chlorobenzene have been detected at a variety of chlorobenzene-contaminated sites but not at uncontaminated sites (11). This provides strong evidence that the bacteria are selected for their ability to derive carbon and energy from chlorobenzene degradation in situ. Removal of multiple halogens as HCl consumes a large amount of alkalinity and produces a considerable drop in the pH of unbuffered systems, which could lead to a loss of microbial activity at some sites.

Chlorophenols and chlorobenzoates are dehalogenated under anaerobic conditions in sediments and subsurface material (12-13). In some instances, the dehalogenation clearly yields energy for the growth of specific bacteria. In other examples, the dehalogenation is specific and enriched in the community but has not been rigorously linked to energy production. The addition of small fatty acids or alcohols as either electron donors or sources of carbon can enhance the process of reductive dehalogenation. Aerobic pathways for the degradation of chlorophenols and chlorobenzoates are initiated by an oxygenase catalyzed attack on the aromatic ring and the subsequent removal of the halogen after ring fission or hydrolytic replacement of the halogen with a hydroxyl group. Bacteria able to grow on chlorophenols and chlorobenzoates are widely distributed and are readily enriched from a variety of sources, which indicates a high potential for natural attenuation. The chlorophenols are unusual among the synthetic compounds discussed here, however, as they can be very toxic to microorganisms. They are often used as biocides, and, therefore, high concentrations can dramatically inhibit biodegradation. Inoculation with specific bacteria has been helpful in overcoming toxicity and stimulating degradation of chlorophenols (12).

Pentachlorophenol deserves special consideration because it has been widely used as a wood preservative and has been released into the environment throughout the world. Reductive dehalogenation of pentachlorophenol under methanogenic conditions can lead to mineralization (12). Aerobic bacteria catalyze the replacement of the chlorine in the 4 position by a hydroxyl group to form tetrachlorohydroquinone, and subsequent reductive dehalogenations lead to the formation of ring fission substrates. Bacteria able to degrade pentachlorophenol are widely distributed, and both experimental and full-scale bioremediation projects have been successful in field applications (12). In some instances, the addition of selected strains has been helpful, whereas in others indigenous strains have been used. Wood treatment facilities are typically contaminated with complex mixtures of organic compounds, so investigations of toxicity must be conducted for each site under consideration. Natural attenuation of pentachlorophenol seems to be possible because specific bacteria able to use it as a growth substrate are enriched at contaminated sites. Rates seem to be low at the sites investigated to date, however, due to the toxicity and bioavailability of the pentachlorophenol.

Polychlorinated biphenyls (PCB) have been studied extensively because of their stability, toxicity, and bioaccumulation potential (14). Anaerobic transformation of PCB is catalyzed by bacteria in aquatic sediment from a wide range of both contaminated and uncontaminated sites. Higher activity in contaminated sites suggests that the dehalogenation reactions provide a selective advantage to the microbial population, which indicates the potential for significant natural attenuation. Studies have clearly demonstrated that natural attenuation of PCB is taking place in anaerobic sediments at significant rates, with methanogenic conditions in freshwater sediments apparently providing the highest rates of reductive dehalogenation. Dehalogenation converts the more highly chlorinated congeners to less chlorinated products containing one to four chlorine. Complete dehalogenation does not occur, but the depletion of the more highly chlorinated congeners dramatically reduces not only the toxicity and carcinogenicity, but also the bioaccumulation of the mixture.

A variety of different dechlorination patterns have been identified as a function of the microbial community involved. The patterns are constant within a given microbial

community or enrichment, which supports the premise that dehalogenation provides a selective advantage to the organisms involved. The results also suggest that a wide range of different bacteria have the ability to dehalogenate PCB. The electron donors for the dehalogenation in sediment are unknown. The addition of exogenous carbon sources does not stimulate the reaction. In contrast, "priming" the mixtures with low levels of bromobiphenyl or specific isomers of tetrachlorobiphenyl (15) seems to selectively enrich a population of PCB-dechlorinating bacteria and dramatically stimulate the dechlorination of the other congeners.

The lower chlorinated PCB congeners, whether part of the original Arochlor mixture or derived from reductive dehalogenation, are biodegraded by aerobic bacteria (16). The initial attack is catalyzed by a 2,3- or 3,4-dioxygenase, followed by a sequence of reactions that lead to ring cleavage and the accumulation of chlorobenzoates which are readily degraded by a variety of bacteria. The enzymes that oxidize PCB are produced by bacteria grown on biphenyl, and adding biphenyl to slurry-phase reactors stimulates the growth and activity of PCB degraders. Such stimulation has been shown to be effective in the field (17). There is also good evidence that aerobic PCB degradation is taking place in contaminated river sediments (18).

Clearly, reductive dechlorination is ongoing at a wide range of PCB contaminated sites. The strategy of anaerobic dehalogenation followed by aerobic degradation seems to be particularly effective with PCB whether in an engineered system or in natural systems (e.g., during resuspension of anaerobic sediments). To date the complete biodegradation of PCB is slow and difficult to predict or control in the field. Several new strategies, including construction of novel strains, may increase the potential for effective PCB biodegradation.

Chloroaliphatic Compounds

Several good reviews have recently appeared on the biodegradation of small (one- and two-carbon) chloroaliphatic compounds (19-21); therefore, this paper briefly mentions only some aspects that might otherwise be overlooked. Among the one- and two-carbon chlorinated compounds, the more highly chlorinated molecules are subject to reductive dehalogenation under a variety of conditions. Thus, carbon tetrachloride can be sequentially reduced to chloroform and dichloromethane. Similarly, perchloroethylene can be reduced to ethylene via trichloroethylene, dichloroethylene, and vinyl chloride. The degradation of chloroethylenes is discussed in considerable detail by Gossett and Zinder (this volume). Most of the work to date has focused on mixed microbial cultures that use chlorinated solvents fortuitously as electron acceptors. Such activity is very widely distributed in anaerobic ecosystems and catalyzes the slow and often partial reduction of chlorinated contaminants. In contrast, some microbial communities and a few isolated strains can derive energy from the use of chlorinated compounds as terminal electron acceptors (Gossett and Zinder, this volume). Such processes are much faster than the co-metabolic processes because they provide a selective advantage for the bacteria and are self-sustaining.

Several chloroaliphatic compounds can serve as growth substrates for aerobic bacteria. The more chlorinated compounds such as trichloroethylene and chloroform do not provide energy and carbon for aerobic growth, although they can be degraded co-metabolically. In contrast, methylene chloride can support the growth of both anaerobes (22) and aerobes (20). 1,2-Dichloroethane (23) and vinyl chloride (20) similarly can be readily degraded by aerobic bacteria. Any of these compounds that serve as growth substrates would be excellent candidates for natural attenuation where oxygen is present. Aerobic mineralization of the related molecule, ethylene dibromide, has been reported in soil, but the distribution of the responsible bacteria and the corresponding ability to predict degradation are not well understood.

Nitroaromatic Compounds

The literature on biodegradation of nitroaromatic compounds has been reviewed recently (25). Nitroaromatic compounds are subject to reduction of the nitro groups in the environment under either aerobic or anaerobic conditions. Co-metabolic reduction does not lead to complete degradation in most instances and could be considered nonproductive for purposes of natural attenuation. In contrast, aerobic bacteria able to grow on nitrobenzene, nitrotoluenes, dinitrotoluenes, dinitrobenzene, nitrobenzoates, and nitrophenols have been isolated from a variety of contaminated sites, which suggests that natural attenuation is taking place at such sites. The simple nitroaromatic compounds (not including trinitrotoluene) can be considered excellent candidates for natural attenuation. Some of the compounds, including 3-nitrophenol, nitrobenzene, 4-nitrotoluene, and 4-nitrobenzoate, are degraded via catabolic pathways that involve a partial reduction of the molecule prior to oxygenative ring fission. The pathways minimize the use of molecular oxygen and are particularly well suited for operation in the subsurface, where oxygen is limiting.

Mixtures of the isomeric nitro compounds can be problematic for microbial degradation. For example, the industrial synthesis of polyurethane produces large amounts of 2,4- and 2,6-dinitrotoluene in a ratio of four to one. Bacteria able to grow on 2,4-dinitrotoluene have been studied extensively. Unfortunately, 2,6-dinitrotoluene inhibits the degradation of 2,4-dinitrotoluene and may prevent natural attenuation. Bacteria able to grow on 2,6-dinitrotoluene have been isolated recently (26),

and insight about the metabolic pathway might allow better prediction of the mixture's degradation.

Ketones

Acetone and other ketones are not xenobiotic compounds, but most of the current production is via synthetic routes. They are readily biodegraded by both aerobic and anaerobic (27) bacteria in soil and have a very high potential for natural attenuation.

Methyl-*tert*-butyl Ether

Gasoline oxygenates such as ethanol, methyl-*tert*-butyl ether (MTBE), and *tert*-butyl alcohol are used extensively as octane enhancers in unleaded gasoline. The ether bond of MTBE makes it particularly resistant to biodegradation. Its water solubility, low volatility, and high concentrations in gasoline (up to 15 percent) create concerns about its behavior in the subsurface.

Preliminary studies indicate that it behaves almost as a conservative tracer in gasoline-contaminated sites.[1] Mixed cultures able to grow on MTBE have been enriched from refinery and chemical plant waste treatment systems (24),[2] so bacteria clearly can successfully attack the ether bond. The degradation rates are slow, however, and there is no evidence that the bacteria are widely distributed in soil. MTBE and other oxygenates containing ether bonds biodegrade very slowly, if at all, under anaerobic conditions (28). At present, even though the biological capability for MTBE degradation is known to exist, the potential for natural attenuation of MTBE seems low. The problem is sufficiently important to merit additional study, perhaps involving extensive acclimation of soil communities or bioaugmentation. The available evidence indicates that *tert*-butyl alcohol is much more readily degradable than MTBE under aerobic or anaerobic conditions.

Nitrate Esters

A variety of nitrate esters, including glycerol trinitrate, pentaerythritol tetranitrate, and nitrocellulose, have been used extensively as explosives. Recent studies indicate that the nitrate esters can be degraded by bacteria from a variety of sources (29, 30). Bacterial metabolism releases nitrite, which can serve as a nitrogen source and yield a selective advantage for the organisms. The biodegradation of nitrate esters has only recently been studied extensively, and little is known about degradation in the environment. Recent laboratory results strongly suggest that natural attenuation is possible, but more information is needed on the bioavailability, toxicity, and kinetics of the process.

[1] Weaver, J. 1996. Personal communication with the author.

[2] Cowan, R. 1996. Personal communication with the author.

Pesticides

Most pesticides used in the past 20 years in the United States have been formulated to degrade in the environment, and a considerable amount of information is available on degradation kinetics in soil and water. The U.S. Environmental Protection Agency Risk Reduction Engineering Laboratory in Cincinnati, Ohio, has developed an extensive Pesticide Treatability Database that contains information on a variety of compounds. Many pesticides hydrolyze and yield compounds that serve as growth substrates for bacteria. For example, carbamates, chlorophenoxyacetates, dinitrocresol, coumaphos, atrazines, and some organophosphates serve as growth substrates for bacteria and would be good candidates for natural attenuation. A variety of other pesticides are hydrolyzed by extracellular enzymes derived from soil bacteria but provide no advantage to the organisms that produce the enzymes. Similarly, some of the organohalogen insecticides can be reductively dehalogenated but provide no advantage to specific organisms. Their biodegradation rates are proportional to the biomass and activity in the soil.

Conclusion

To date, the focus of natural attenuation has been on hydrocarbon fuels and chlorinated aliphatic solvents. A wide range of synthetic chemicals released in the environment are known to be biodegradable by bacteria, and much is known about the processes and their requirements. The potential for natural attenuation of biodegradable contaminants should be considered before more costly and disruptive treatment options.

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Natural Attenuation of Chlorinated Compounds in Matrices Other Than Ground Water: The Future of Natural Attenuation

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Introduction

To date, natural attenuation study and application have focused on the dissolved phase in ground water in unconsolidated sediments. There are good reasons for this. Ground-water transport is the primary pathway of concern at many sites, our understanding of aqueous-phase processes with relatively short half-lives (1 year or less) in ground water is relatively well developed, and we have a better understanding of ground-water processes in unconsolidated media than in rock. This paper addresses the potential importance of both natural attenuation in other media and of slower processes. Specifically, natural attenuation in fractured rock, of nonaqueous-phase liquids (NAPLs), and in the vadose zone, as well as low-rate processes, will be discussed.

Fractured Rock

Ground water in fractured rock presents a special problem. In most rock formations, surface area is limited and flow paths tend to be complex when compared with unconsolidated sediments. Many of the same processes occur, but they tend to be more difficult to monitor. The Test Area North (TAN) site, located at the Idaho National Engineering Laboratory (INEL), contains a trichloroethene (TCE) ground-water plume approximately 9,000 feet long. The geology is characterized by basalt flows with sedimentary interbeds that consist primarily of low permeability, fine-grained sediments. The basalt flows are highly variable, and ground-water flow appears to occur primarily in the fractured basalt. The basalt varies from massive to highly fractured. The source of contamination appears to be an abandoned waste disposal well. In addition to chlorinated solvents, the well received a variety of wastes including nonchlorinated sludges and some radioactive materials. TCE appears to be the only significant chlorinated solvent in the source material, yet in ground water near the source, dichloroethene (DCE) concentrations are in the same range as TCE. The DCE:TCE ratio then declines downgradient to a distance of about 6,000 feet beyond which only TCE is found. All the TAN site data can be found in INEL (1).

What appears to be happening is anaerobic dechlorination near the source, very likely driven by the carbon source in the nonchlorinated sludge. Downgradient conditions appear to be aerobic, and no evidence of dechlorination is seen more then a few hundred feet from the source well. One possible explanation for the smaller DCE plume is aerobic degradation. This site also has a tritium plume originating from the same source. If we assume that all of the plumes are of the same age, we can estimate the kinetics of the aerobic degradation of DCE and make some inferences concerning the TCE.

The DCE plume is approximately 6,000 feet, the tritium plume 7,500 feet, and the TCE plume 9,000 feet long. Ignoring retardation and assuming a 12 year half-life for tritium, the DCE half-life would be approximately 10 years. If the TCE is degrading aerobically, its half-life is probably greater than 14 years. Based on these field observations, it appears that the same processes that have been observed at many sites in consolidated sediments are occurring in the fractured basalt at the TAN site. Therefore, anaerobic dechlorination and aerobic oxidation of the less chlorinated solvents should occur in fractured rock. The significant challenge presented by fractured rock will be the accurate determination of flow paths, the same as for any ground-water investigation.

Nonaqueous-Phase Liquid

When NAPL is present on a site, the mass of contaminant in the NAPL is typically orders of magnitude greater than that dissolved in ground water. With the exception of dissolution (and evaporation in the vadose zone), little is known about natural attenuation processes that occur in or near the NAPL phase. While evaporation can be a significant attenuation mechanism and should certainly be considered whenever vadose-zone contamination is of concern, the NAPL below the water table is normally the greatest concern. Dissolution is the mechanism by which the ground water is initially contaminated, and although rates are high enough to create a ground-water

problem at many sites, dissolution is often quite slow when compared with the mass of contaminant present.

At the Hill Air Force Base (AFB) OU-2 site, thousands of gallons of NAPL (primarily TCE) have been recovered and many thousands of gallons remain below the water table, yet the rate of dissolution (based on mass of dissolved contaminant migrating off site) is tens of gallons per year.1 This is not unusual. It is difficult based on our current understanding of the fate and behavior of chlorinated solvents to postulate mechanisms for the biotic or biotic degradation of NAPLs, but a few years ago the same would have been concluded about dissolved TCE or even benzene. The rates of any such degradation would not have to be high to be significant.

In the fractured rock discussion above, aerobic DCE degradation with a half life on the order of 9 years is noted. This phenomenon is rarely observed in laboratories or in short-term field studies, yet such a process could be quite important. It is conceivable that an as yet unidentified process exists that degrades NAPL in situ with a half life of 10 years, which could result in a much more significant mass removal than the dissolution process followed by degradation in ground water. This is an area which has been largely overlooked, and the research needed to evaluate these mechanisms will require a longer-term and significantly different approach than is current practice; however, to achieve a reasonable understanding of the long-term effects of natural attenuation, it should not be overlooked.

Vadose and Discharge Processes

One of the primary practical values of natural attenuation is plume stability. In many plumes, at some point the rate of degradation of dissolved contaminants is more or less equal to the rate of dissolution, and the plume achieves a quasi-steady state. To date, most of the work on natural attenuation has focused on degradation in the aqueous-phase in the aquifer. Little attention has been given to the vadose zone or discharge points. Any attenuation mechanism that contributes to plume stability is important, and it appears that other mechanisms such as volatilization to the vadose zone and ground-water discharge can be important mechanisms in creating plume stability, although volatilization from ground water to the vadose zone is probably only important where net evaporation exceeds infiltration to ground water. The process of contaminant diffusion to the water table and through the capillary fringe into ground water is likely too slow to be of much significance at most sites.

There are sites in the western United States, however, at which net ground-water evaporation occurs. The obvious manifestation of this is the caliche found in many western soils. This appears to be happening at Hill AFB. For example, there is a TCE plume approximately 5,000 feet long at the OU-6 site. In the first several thousand feet of plume, the depth to ground water is about 100 feet, and net infiltration appears to be occurring. Near the downgradient extreme of the plume, ground water is much shallower (10 feet or less), and net evaporation appears to be occurring. Significant TCE concentrations have been observed in soil gas above the downgradient end of the plume, possible evidence of volatilization to the vadose zone.

Discharge is an obvious attenuation mechanism, and the nature of the discharge will determine its usefulness. For example, if the discharge is to a surface-water stream where the result is unacceptably high contaminant concentrations, this would not be a helpful mechanism. Frequently, however, discharge may not result in unacceptable exposure. At Hill AFB there are six plumes that vary in length, but all are in the thousands of feet. In five of the plumes, TCE is the predominant contaminant; in one DCE predominates. Although the plumes are miles apart and their source elevations vary, all of the plumes end at approximately the same elevation, and most of these plumes appear stable.

One reason for the stability is discharge. An old, low-permeability deposit from Lake Bonneville occurs just below this depth that causes the ground water to discharge. This discharge takes several forms: evaporation, evaportranspiration, discharge into field drains which in turn discharge to ditches, and discharge into seeps or springs. To the author's knowledge, no contamination reaches a water supply, a permanent surface-water body, or a stream. At the Hill AFB sites, plume stability appears to have been achieved by a combination of mechanisms. There is certainly evidence of conventional degradation in ground water, and at all of the sites some anaerobic dechlorination is occurring. Plume stability appears to have been achieved as a result of this degradation, coupled with volatilization and discharge.

Summary

Natural attenuation of chlorinated compounds is an important process, and a full understanding will require looking beyond the conventional aqueous-phase processes at many sites. This will probably include both very slow mechanisms we do not yet understand and a more careful consideration of physical, chemical, and evapotransporative processes we have not often quantified in natural attenuation studies.

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Poster Session

Degradation of Chloroform Under Anaerobic Soil Conditions

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This study was designed to determine the rate of chloroform biodegradation under anaerobic conditions. Subsurface soil samples were taken from leachate plumes downgradient from two different bleached kraft mill landfills chosen to represent a northern climate soil and a southern climate soil. Anaerobic subsurface soil conditions were modeled by assembly of the sample soils into microcosms, with care taken throughout the study to ensure that the soils and microcosms were maintained and handled anaerobically. Following assembly, the microcosms were spiked with chloroform at either a 10, 60, or 160 micrograms per liter spike level. (Spiked sterilized soils and unspiked soil blanks were included as controls.) The microcosms were incubated at the year-round average ambient soil temperature and were analyzed for chloroform over a period up to 64 weeks following their preparation.

Data from these experiments showed that in accordance with the literature, chloroform degraded at a rapid rate under anaerobic conditions. For the southern site microcosms, an 8-week adaptation period was noted, followed by rapid degradation ($t_{1/2}$ = 4-16 weeks). For the northern site soil microcosms, the chloroform concentration was reduced to 5 percent of the initial concentration in a total of 4 weeks or less ($t_{1/2}$ = 0.4 to 3 weeks), with no adaptation period noted. The absence of chloroform degradation in sterilized control microcosms and the absence of degradation intermediates (methylene chloride and chloromethane) suggest that chloroform was degraded completely by a microbial pathway. The data generated in these experiments were incorporated into an attenuation fate-and-transport model for organic substrates in subsurface soils. This model demonstrated that at the rates determined in this study and at the most conservative rate estimates, several orders of magnitude higher, the biodegradation process is a significant factor in the rapid removal of organics from subsurface soils. Modeling runs resulted in receptor well concentrations for chloroform that were predominantly orders of magnitude below current analytical capabilities.

Anaerobic Mineralization of Vinyl Chloride in Iron(III)-Reducing Aquifer Sediments

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In anaerobic aquifer systems, intrinsic bioremediation of chlorinated ethenes is considered problematic because of both the production of vinyl chloride during microbial reductive dechlorination of higher chlorinated contaminants and the apparent poor biodegradability of vinyl chloride under anaerobic conditions. Previous investigations have suggested that reductive dechlorination of vinyl chloride to ethene may represent an environmentally significant pathway for in situ bioremediation of vinyl chloride contamination. This poster provides laboratory evidence for an alternative mechanism of vinyl chloride degradation: anaerobic oxidation of vinyl chloride under iron(III)-reducing conditions.

Microcosm experiments conducted with material collected from two geographically isolated, chlorinated-ethene-contaminated aquifers demonstrated oxidation of [1,2-^{14}C]vinyl chloride to $^{14}CO_2$ by indigenous microorganisms under iron(III)-reducing conditions. Addition of chelated iron(III) (as Fe-EDTA) to aquifer microcosms resulted in mineralization of up to 34 percent of [1,2-^{14}C]vinyl chloride within 84 hours. The results indicate that vinyl chloride can be mineralized under iron(III)-reducing conditions, and that the bioavailability of iron(III) is an important factor affecting the rates of mineralization. The microcosm results are consistent with the attenuation of vinyl chloride concentrations observed in the field and suggest that contaminant oxidation coupled to microbial iron(III) reduction may be an environmentally significant mechanism contributing to intrinsic bioremediation of vinyl chloride in anaerobic ground-water systems.

Intrinsic Biodegradation of Chlorinated Aliphatics Under Sequential Anaerobic/Co-metabolic Conditions

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Tetrachloroethene (PCE) and trichloroethene (TCE) are being biodegraded under naturally occurring sequential anaerobic/co-metabolic conditions in ground water at an inactive landfill in New Hampshire. Ground water in the vicinity of the landfill is predominantly aerobic, with the exception of an anaerobic zone that has developed at the landfill source area where significant historical biodegradation of dichloromethane, ketones, and aromatic hydrocarbons has occurred. Acetogenesis, methanogenesis, sulphate reduction, and iron reduction are the dominant microbial processes occurring in the anaerobic zone. PCE and TCE have been sequentially dechlorinated to cis-1,2-dichloroethene (cis-1,2-DCE) in the anaerobic zone, to the extent that PCE and TCE are no longer present at significant concentrations in the site ground water. Cis-1,2-DCE concentrations attenuate more rapidly (e.g., from 20 to less than 1 milligrams per liter) than can be predicted based on physical processes (i.e., advection, dispersion, retardation) alone. Vinyl chloride (VC) and ethene concentrations do not account for the extent of cis-1,2-DCE attenuation occurring. Degradation of VC and ethene to carbon dioxide under aerobic conditions (1) or anaerobic iron-reducing conditions (2) may result in an underestimation of cis-1,2-DCE reductive dechlorination. Toluene and methane are present in the downgradient aerobic ground water, however, and are likely promoting co-metabolic biodegradation of cis-1,2-DCE. Preliminary laboratory microcosm studies have confirmed that the indigenous microorganisms can co-metabolize cis-1,2-DCE (and VC) in the presence of toluene and methane at the concentrations found in the site ground-water.

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Analysis of Methane and Ethylene Dissolved in Ground Water

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A headspace equilibrium technique and gas chromatography can be used to measure dissolved methane and ethylene in water. A water sample is collected in a 50-milliliter (mL) glass serum bottle. Several drops of 1:1 diluted sulfuric acid are added. The bottles are then capped using Teflon-lined butyl rubber septa. Later at the analytical laboratory, a headspace is prepared by replacing 10 percent of the water sample by helium. The bottle is then shaken for 5 minutes. Aliquots of headspace, usually 300 microliters, are removed using a gas-tight syringe. The subsample is injected into a gas chromatograph with a Porapak Q stainless-steel column and a flame ionization detector. The gaseous components are separated, and chromatogram peak retention times and areas are compared with calibration standards. The concentration of the aqueous gas components can be calculated using sample temperature, bottle volume, headspace concentrations, and Henry's Law.

Limits of detection for methane and ethylene are 0.001 and 0.003 milligrams per liter (mg/L), respectively. Determination of precision and accuracy for a 19.8 mg/L methane prepared sample using six replicates was a standard deviation of 0.6 mg/L, risk-specific dose (RSD) = 3.2 percent, and average recovery of 87 percent. Similar statistics for 118 mg/L ethylene using three replicates was a standard deviation of 8.8 mg/L, RSD=7.5 percent, and an average recovery of 90 percent. Typical dissolved methane and ethene concentrations at natural attenuation field sites have been less than 1 and less than 0.1 mg/L, respectively. Methane levels have always been higher.

The method can also be adapted to determine ethane, nitrous oxide, vinyl chloride, carbon dioxide, and possibly other dissolved gases in ground water.

Estimation of Laboratory and In Situ Degradation Rates for Trichloroethene and cis-1,2-Dichloroethene in a Contaminated Aquifer at Picatinny Arsenal, New Jersey

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Natural attenuation of chlorinated organic compounds in aquifers includes apparent loss mechanisms, such as biodegradation, advective transport, volatilization, sorption, and diffusion. Determination of quantitative degradation rates for the different processes is an important step in planning cost-effective site remediation. Soil and ground water at Picatinny Arsenal, New Jersey, have been studied by the U.S. Geological Survey since 1986 to determine fate and transport of chlorinated ethenes in a shallow unconfined aquifer. This poster describes the methods used to quantify the major processes affecting fate and transport of trichloroethene (TCE) and cis-1,2-dichloroethene (cis-DCE) in the aquifer.

Analyses of water and soil core samples, collected at a series of locations within and outside a contaminant plume, were used to identify the lateral and vertical distribution of organic contaminants in the aquifer, major electron acceptors, background geochemistry, and dissolved chemicals that affect biodegradation of chlorinated ethenes within the plume. Results indicated that ground water within the plume contained TCE concentrations ranging up to 20 mg/L^{-1}, methane concentrations generally less than 85 mg/L^{-1}, and dissolved oxygen and nitrate concentrations of less than 0.5 mg/L^{-1}, the major terminal electron accepting processes were sulfate and iron(III) reduction; and anaerobic in situ biodegradation of TCE and cis-DCE was occurring. Following initial site characterization, soil cores were collected from a series of locations along the major ground-water flow path within the plume for determination of TCE and cis-DCE biodegradation rates in a laboratory study.

Static batch microcosms were constructed under anaerobic conditions to determine the rates of TCE and cis-DCE biodegradation. Sterilized 50-milliliter serum vials were filled to the base of the neck with composited core materials and amended with a 2-milliliter sterile aqueous solution of TCE or cis-DCE to bring the pore-water chlorinated ethene concentration to 1,100 mg/L^{-1}. Pore-water samples from duplicate serum vials were periodically assayed by gas chromatography to quantify the chlorinated ethene concentrations. The results were used to determine the first-order biodegradation rate constants for TCE and cis-DCE, after compensation for abiotic losses. First-order biodegradation rate constants for TCE ranged from -0.004 wk^{-1} to -0.035 wk^{-1} and were greater near the plume origin and the discharge point (Green Pond Brook) than in the plume center. Geochemical results indicated that natural organic acids leached from shallow peat deposits in the vadose zone probably were a major electron donor for biodegradation of chlorinated ethenes in situ. In general, cis-DCE was degraded more slowly than TCE. First-order biodegradation rate constants for cis-DCE ranged from less than -0.01 wk^{-1} to -0.05 wk^{-1}. Biodegradation of cis-DCE was most rapid in soils underlying a peat layer near the plume discharge point.

Degradation of TCE in situ also was estimated using the concentrations of chlorinated ethenes determined for a series of monitoring wells along the major ground-water flow path within the plume. Chlorinated ethene concentrations in ground water at up- and downgradient wells measured at time intervals corresponding to the estimated TCE solute transport time between sites were used to estimate first-order TCE removal rate constants in the aquifer. In situ first-order rate constants for TCE removal generally ranged from -0.012 wk^{-1} to -0.02 wk^{-1}. The close approximation of these in situ removal estimates to laboratory biodegradation rates indicated that biodegradation in situ probably was a major removal process for TCE at Picatinny Arsenal.

Results of in situ geochemistry and ground-water modeling were used to quantify the removal of TCE by major processes in the unconfined aquifer at Picatinny Arsenal.

Diffusive, sorptive, and volatilization losses were estimated separately and used to correct for apparent in situ TCE removal. Biodegradation is probably the major removal process for chlorinated ethenes in the aquifer, removing about 400 kg/y^{-1} of TCE from the contaminant plume. Advective transport removes about 47 kg/y^{-1} of TCE in ground water, discharging to Green Pond Brook. Volatilization and lateral diffusive losses of TCE from the plume are estimated to total 10 to 50 kg/y^{-1}. Sorptive losses of TCE to aquifer soils are minor because of the low organic carbon concentration of sediments in the saturated zone.

Measurement of Dissolved Hydrogen in Ground Water

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A gas stripping procedure and reduction gas detector can be used to measure aqueous concentrations of hydrogen in ground water. Polyethylene tubing is placed near the center of the screen in a well casing with the other end connected to a peristaltic pump. After purging several well volumes, a 250-milliliter (mL) glass sampling bulb is placed in the water sampling line. The bulb is completely filled with water. Then the pump is stopped, and nitrogen gas is injected into the bulb to create a 20-mL headspace. The bulb outlet is placed at a lower level then the inlet, and the pump is turned on. A water flow of 200 mL per minute is maintained for 20 minutes to equilibrate the dissolved hydrogen with the nitrogen gas phase. Duplicate 2-mL gas samples are then removed with a gas-tight syringe for analysis by the hydrogen detector. The hydrogen analyzer operates on the reaction principle of $X + HgO$ (solid) $\rightarrow XO + Hg$ (vapor), where X represents any reducing gas. An ultraviolet photometer quantitatively measures the resultant mercury vapor. Reduction gas species are identified as chromatograph peaks at different retention times. Retention time for hydrogen is less than 1 minute. The limit of detection is 0.01 parts per million (ppm) hydrogen. A standard calibration curve over the range of 0.01 to 1.26 ppm hydrogen has a linear correlation coefficient of R^2=1.00. A 1.0-ppm hydrogen in the gas phase corresponds to 0.8 nanomoles per liter of dissolved hydrogen for fresh water in equilibrium with a gas phase at 1 atmosphere. Typical dissolved hydrogen concentrations detected at four different natural attenuation sites were less than 10 nanomoles and most frequently less than 1 nanomole.

Successful sample assays depend on careful following of procedure detail and overnight stabilization of the detector.

Evidence of Natural Attenuation of Chlorinated Organics at Ft. McCoy, Wisconsin

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Ft. McCoy is a Resource Conservation and Recovery Act regulated U.S. Army facility located in western Wisconsin. Fire Training Burn Pit 1 (FTBP1) on the site was operated from approximately 1973 to 1987. Operations at the pit consisted of filling the pit with a layer of water and fuel, then repeatedly igniting and extinguishing the contents until the fuel was consumed. The soil beneath the 3-foot deep and 30-foot diameter pit is a well sorted sand (low organic content) with an average hydraulic conductivity of 0.0048 centimeters per second. The water table is generally 12 feet below the ground surface.

Sampling activities conducted in 1993 and 1994 indicated significant concentrations of chlorinated organics (1,2-dichloroethene [1,2-DCE], trichloroethene, and perchloroethene) in the soil and ground water. Chlorinated organic contamination in the soil was limited to the area under the former fire pit. Based on the local hydraulic gradient and hydraulic conductivity, ground water present under FTBP1 when operations were initiated in 1973 has traveled an estimated 7,000 feet. Evidence of natural attenuation of ground-water contamination is provided by the short travel distance (approximately 600 feet) of the leading edge (1 microgram per liter) of the chlorinated organics relative to the ground water over the 20-year period and the decrease in size and concentration of the chlorinated organic contaminant plume during the period of sampling (e.g., peak 1,2-DCE concentrations decreased from 2,100 to 700 micrograms per liter during the sampling period).

Natural attenuation mechanisms potentially active on ground-water contamination at the site include dispersion, sorption, volatilization, and biological degradation. The bulk of the ground-water contamination was recently remediated using air sparging/soil vapor extraction. Based on the evidence of natural attenuation present at the site and information in the U.S. Air Force technical protocol on intrinsic remediation (1), natural attenuation will be included as a component of the recommended remedial alternative for remaining ground-water contamination at this site.

Reference

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Challenges in Using Conventional Site Characterization Data To Observe Co-metabolism of Chlorinated Organic Compounds in the Presence of an Intermingling Primary Substrate

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Site characterization data from a leaking underground storage tank (LUST) site and adjacent dry cleaners were retrospectively analyzed for evidence of chlorinated solvent biodegradation. The sites are in the path of a wide chlorinated solvent ground-water plume emanating from the Dover Air Force Base (DAFB) in Dover, Delaware. Discrete hydrocarbon and tetrachlorethene plumes originate from the aforementioned LUST and dry cleaner sources and mingle with the DAFB plume (1, 2). From the chlorinated organics natural attenuation program at DAFB (3) and our own laboratory studies using DAFB sediment (4), evidence abounds regarding the potential for natural biodegradation of chlorinated compounds in the shallow Columbia aquifer.

We hypothesized that the subsurface, containing gasoline product, gasoline vapors, and high levels of dissolved hydrocarbons, was a likely area for co-metabolism of chlorinated compounds derived from either DAFB or the dry cleaners. In this case, the hydrocarbons would serve as the primary substrate for co-metabolism of chlorinated compounds mixing within the hydrocarbon-contaminated zone. Soil vapor, multilevel hydropunch, and monitoring well data from the LUST and dry cleaner investigations were reviewed, looking specifically for relationships between concentrations of hydrocarbons (the presumed primary substrate), chlorinated solvents (e.g., tetrachloroethene [PCE], trichloroethene [TCE], and carbon tetrachloride), and chlorinated solvent breakdown products (e.g., vinyl chloride, dichloroethene [DCE], TCE, and chloroform).

Although some patterns of intrinsic biodegradation were evident, the data did not make a compelling case for co-metabolism in or near the hydrocarbon plume. The most promising data were the soil gas concentrations, which generally showed a decrease in the PCE:TCE ratio with increase in hydrocarbon concentration, implying degradation of PCE to TCE in the presence of hydrocarbon vapors. Even though numerous ground-water samples were obtained for the site characterization studies, no relationships could be established for the ground-water regime.

We conclude that the data from this conventional site characterization effort were either too limited in quality (e.g., not enough analytes) or quantity to adequately discern patterns, or that co-metabolism was not occurring in the saturated zone. Perhaps vapor diffusion in the unsaturated zone promotes better substrate mixing than in the saturated zone, where slow dispersion may limit the effects of co-metabolism. This retrospective analysis points out the need for careful development of a natural attenuation conceptual model while planning site characterization efforts. Sampling and analysis not conventionally used in contaminant site assessments, particularly for chlorinated natural attenuation assessments, may be required to test the hypothesized conceptual model.

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Development of an Intrinsic Bioremediation Program for Chlorinated Solvents at an Electronics Facility

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From 1963 to 1978, an area on a manufacturing facility for electronic components was used to dispose of residual sludge from cleaning baths. The sludge contained chlorinated solvents, including trichloroethylene (TCE), tetrachloroethylene (PCE) and 1,1,1-trichloroethane (TCA). An initial investigation of the site during the mid to late 1980s revealed substantial levels of TCE (up to 5,700 micrograms per liter) and TCA (up to 6,900 micrograms per liter) in the ground water. A corrective measures study was performed, and corrective action was implemented in the form of standard pump-and-treat activities.

After 5 years of pumping, it was evident that this method was removing very little chlorinated solvent mass, and alternative remediation methods were assessed. During a review of the historical data, it was determined that the concentration of chlorinated solvents had greatly decreased before implementation of the pump-and-treat program and that site soils were likely to be anaerobic, potentially allowing natural biodegradation of TCE and related solvents. Discussions held with the regulatory agencies, the U.S. Environmental Protection Agency and the Oregon Department of Environmental Quality, resulted in a program designed to investigate intrinsic bioremediation as a viable remedial option for the site.

Information was obtained using Geoprobe sampling techniques; evidence of anaerobic conditions and of the anaerobic breakdown products of the contaminants was sought. The results indicated anaerobic conditions; this was based on low to nondetectable dissolved oxygen, dissolved nitrogen predominantly as ammonia, high levels of ferrous iron (up to 85 milligrams per liter), and significant levels of methane (up to 1.2 milligrams per liter). The results also indicated that TCE was being biodegraded by sequential, reductive dechlorination to nonchlorinated products prior to reaching the site boundary. Both *cis*-1,2-dichloroethylene and vinyl chloride were detected near the source area at maximum concentrations of 130 and 12 micrograms per liter, respectively, then decreased to near or below the detection level at the site boundary. Low levels of the nonchlorinated product, ethylene, were detected downgradient of the source area.

Subsequent discussions with the agencies led to an agreement that intrinsic bioremediation was a viable remedial alternative for contaminant containment and eventual cleanup. The ground-water pump-and-treat system is being decommissioned, and a monitoring program is being implemented to track and ensure that adequate remediation of the site continues by intrinsic bioremediation. Implementation of this program is allowing redevelopment of this site.

Overview of the U.S. Air Force Protocol for Remediation of Chlorinated Solvents by Natural Attenuation

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The U.S. Air Force Center for Environmental Excellence, Technology Transfer Division (AFCEE/ERT), in conjunction with personnel from the U.S. Environmental Protection Agency's National Risk Management Research Laboratory (NRMRL) and Parsons Engineering Science, Inc. (Parsons ES), has developed a technical protocol to document the effects of natural attenuation of fuel hydrocarbons dissolved in ground water. This same group is currently developing a similar protocol for confirming and quantifying natural attenuation of chlorinated solvents. The intended audience for the new protocol is U.S. Air Force personnel and their contractors, scientists, and consultants, as well as regulatory personnel and others charged with remediating ground water contaminated with chlorinated solvents.

Mechanisms of natural attenuation of chlorinated solvents include biodegradation, hydrolysis, volatilization, advection, dispersion, dilution from recharge, and sorption. Patterns and rates of natural attenuation can vary markedly from site to site depending on governing physical and chemical processes. The proposed protocol presents a straightforward approach based on state-of-the-art scientific principles that will allow quantification of the mechanisms of natural attenuation. In this way, the effectiveness of each mechanism can be evaluated in a cost-effective manner, allowing a decision to be made regarding the effectiveness of natural attenuation as a remedial approach.

Incorporation of Biodegradability Concerns Into a Site Evaluation Protocol for Intrinsic Remediation

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A project is being conducted to develop a site evaluation protocol for determining the potential applicability of intrinsic remediation at industrial sites with soil and ground-water contamination. The project is sponsored by an industry-supported research center because the sponsor industries are interested in extending the applicability of currently available intrinsic remediation protocols (e.g., the U.S. Air Force guidance document by Wiedemeier et al. [1]) to include any biodegradable contaminant, not just benzene, toluene, ethylbenzene, and xylenes and related (fuel-derived) compounds. To extend the protocol in this manner, the biodegradability of any contaminants that may exist at these sites must be addressed because the knowledge of contaminant biodegradability can be an absolute requirement for application of intrinsic remediation. How to go about this is the focus of the work.

Progress on the project to date has been the development of a preliminary site screening document and a draft of the protocol to determine biodegradability. In addition, information has been collected concerning contamination at several industrial sites, and one site has been selected for more detailed study. The site selected contains a contaminated fractured bedrock aquifer so we are experiencing difficulty concerning the predictability of contaminant transport in addition to the contaminant biodegradability issues that were initially the focus of the project.

This poster will:

- Present an overview of intrinsic remediation technology and definitions for related terminology.
- Discuss preliminary site screening using existing data to make an initial determination as to whether intrinsic bioremediation is likely to be suitable for a given site; the goal is to decide whether a more detailed look at the site should be taken.
- Describe the biodegradability assessment protocol, which contains two sections: assessment of biodegradability through a search of existing databases and the literature, and experimental methods for the determination of in situ biodegradability.
- Depict a flow chart, based on biodegradability concerns, that can be used to select and implement the appropriate approach for making a detailed assessment of the potential for intrinsic remediation.
- Give the current status of the industrial site study.

Reference

1. Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. U.S. Air Force Center for Environmental Excellence, San Antonio, TX.

Intrinsic Remediation of Chlorinated Solvents as an Effective Containment Strategy

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At a site in California, a tetrachloroethene (PCE) plume over 1,300 feet long was discovered within the capture zone of two municipal supply wells. Fortunately, the plume was restricted to an upper water-bearing unit that was separated from the drinking water aquifer by a continuous clay zone. Nevertheless, the concentrations of PCE in this shallow zone exceeded 1,000 parts per billion (ppb) and represented a potential threat to human health and the environment. After 3 years of investigation, pilot-scale air sparging in the release areas, and significant regulatory negotiation, a full-scale air sparging system was installed and operated for 2 years. PCE concentrations within the source areas declined by an order of magnitude during this time. Despite operation of the remedial system, PCE concentrations in the source areas stabilized at 100 ppb, 20 times higher than the closure criteria specified in the state cleanup order. Remedial efforts outside the source areas were not required by the approved plan unless PCE concentrations rose above unacceptable levels, signaling plume migration.

Outside the source area "hot spots," PCE concentrations remained constant over the 5-year period at concentration levels ranging from 20 to 50 ppb; these monitoring data demonstrated that the plume was not expanding. The stability of the plume and the documented inefficiency of the pump-and-treat/air-sparging remedial system permitted establishment of a risk-based plume management plan that called upon institutional controls rather than hydraulic manipulation and ground-water treatment. The containment strategy was permitted based on the empirical evidence of 5 years of ground-water monitoring and the acceptance by the regulatory agency that intrinsic remediation was active at the site.

Based on 6 years of data monitoring concentrations of halogenated solvents (HVOC), pH, conductivity, temperature, turbidity, dissolved oxygen, and salinity, intrinsic remediation now appears to be occurring. In June 1995, the first chemical samples were obtained to specifically document intrinsic remediation processes occurring at this site (HVOC, total hydrocarbons, volatile hydrocarbons, dissolved oxygen, nitrate, sulfate, methane, ethane, ethene, redox potential, pH, temperature, conductivity, and chloride). These data were used to validate our hypothesis of effective intrinsic remediation at this site, using the protocol developed by the U.S. Air Force Center for Environmental Excellence for fuel hydrocarbon intrinsic remediation as a guide but modeling for the important parameters of chlorinated solvent intrinsic attenuation/remediation.

The purpose of this poster is to present another case history of intrinsic remediation of chlorinated solvents. We maintain that case histories such as this will enhance the acceptance of intrinsic remediation as an effective containment strategy, obviating the need for extensive regulatory negotiations and, possibly, operation of mechanical remedial systems at source areas.

A Field Evaluation of Natural Attenuation of Chlorinated Ethenes in a Fractured Bedrock Environment

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Before a long-term ground-water monitoring program was conducted in support of natural attenuation as a remedial remedy for halogenated organic contamination, a focused evaluation of ground-water chemistry provided valuable insight into attenuative mechanisms in areas where remedial options were being evaluated. This poster describes a field investigation and data analysis at Loring Air Force Base, Limestone, Maine, and presents the results of the evaluation of natural attenuation.

Chemical data collected prior to this evaluation indicated the presence of chlorinated ethenes (tetrachloroethene [PCE] and trichloroethene [TCE], cis-1,2-dichloroethene [cis-1,2-DCE] and vinyl chloride [VC]) in the fractured bedrock ground-water environment at several locations on site. Samples representative of the interior and exterior of the chlorinated hydrocarbon plumes were collected at pre-existing basewide remedial investigation locations. The analytical protocol included hydrocarbon target compounds, ground-water quality parameters, indicator parameters, electron acceptors, and microbial community evaluations. Several of the contaminant plumes demonstrated characteristics of reductive dehalogenation, indicating a potential for natural degradation of PCE and TCE to cis-1,2-DCE and VC in a fractured bedrock environment. Dissolved oxygen and nitrate concentrations were depleted, oxidation/reduction potential values and sulfate concentrations decreased, and methane concentrations were observed at locations where chlorinated ethenes were detected.

Intrinsic Bioattenuation of Chlorinated Solvents in a Fractured Bedrock System

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Spent chlorinated solvents were released from two underground storage tanks at the Colorado Department of Transportations materials testing laboratory in Denver, Colorado. An estimated 5,000 to 15,000 liters of trichloroethene, 1,1,1-trichloroacetic acid (TCA), 1,1,2-TCA, dichloromethane, benzene, toluene, ethylbenzene, xylene, and asphaltic compounds were released into a highly fractured bedrock consisting of interbedded claystone, siltstone, and fine-grained sandstone. The resulting dense, nonaqueous-phase liquid resides between 20 and 30 feet below ground surface (bgs). Downward migration has been impeded by a relatively massive claystone at 30 to 40 feet bgs, although some solvents are present at a depth of more than 50 feet in a siltstone. The ground-water plume, consisting of source compounds and products of reductive dechlorination (e.g., 1,1-DCE, 1,2-DCE, 1,1-DCA and 1,2-DCA), has migrated in excess of 4,500 feet off site.

This site is being characterized for intrinsic bioattenuation to establish baseline conditions prior to the potential implementation of a source removal action, recognizing that substantial residuals would likely remain. An anaerobic core in the source area has been characterized on the basis of water chemistry differences between the plume and inflowing upgradient ground water. Downwell probe sondes were used to measure dissolved oxygen, pH, redox potential, and temperature. Zero headspace ground-water samples were collected into 160 milliliter serum bottles using a Grundfos submersible pump and were immediately capped with Teflon lined caps. Analysis for methane, ethane, ethene, and hydrogen was performed by headspace analysis after displacing a fixed volume of water by nitrogen gas displacement. Aqueous samples were analyzed for NO_3-, PO_4-3, SO_4-2, Cl^-, S^{-2}, and Fe^{+2} using Hach methodologies; total organic carbon, chemical oxygen demand, and bicarbonate were analyzed using standard methods. An evaluation of microbial populations in ground water was performed using the phospholipid fatty acid procedure.

Low levels of dissolved oxygen, in conjunction with the identification of elevated methane, ferrous iron, and chloride levels in the source area of the plume, indicate the presence of anaerobic activity. Significant reductions in the levels of inflowing nitrate within the source area of the plume have been observed and appear to be coincident with the reductions in the levels of aromatic hydrocarbon constituents within and downgradient of the source area. Intrinsic bioattenuation of dichloromethane (DCM) appears to be occurring based on contaminant transport model predictions (MT3D) and actual field measurements of the DCM plume dimensions. Further indication of intrinsic bioattenuation has been the identification of low levels (15 parts per billion) of vinyl chloride immediately downgradient of the source area.

Modeling Natural Attenuation of Selected Explosive Chemicals at a Department of Defense Site

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Natural attenuation of explosives in the subsurface has received considerable attention during recent years. The idea behind natural attenuation is that within a reasonable time natural processes can degrade effectively some explosive chemicals. One site selected to evaluate natural attenuation is located at the Louisiana Army Ammunition Plant (LAAP) in northwest Louisiana approximately 22 miles east of Shreveport. The study site is the area including the former Area P lagoons, 16 unlined lagoons covering approximately 25 acres. The Area P lagoons were used sporadically between 1940 and 1981. Untreated, explosive-laden wastewater from munition packing operations within LAAP was collected in concrete sumps at each of several facilities and hauled by tanker to Area P. The site also was used as a burning ground for many years.

LAAP was placed on the National Priority List (NPL) in March 1989 due to detection of measurable explosive chemicals in the soil and ground water and its proximity to water supply wells. As part of an interim remediation, the wastewaters at Area P were removed and the soil was excavated to a depth of 5 feet. The total explosives concentration in untreated soil was in excess of 100 milligrams per kilogram. Excavated soil was incinerated, and treated soil was used to backfill the area. The concentration of treated soil was below a detection limit (BDL). A natural cap of low permeability was placed over the site to inhibit infiltration and further migration of residual explosives below the excavation depth.

The monitoring wells at LAAP have been sampled and analyzed for explosives since 1982. The results of these analyses are maintained in the U.S. Army Environmental Center database (IRDMIS). A comparison between 1990 and 1994 data for trinitrotoluene (TNT) and RDX concentrations within and adjacent to Area P showed a general decrease during this period. The concentration of TNT in 1990 ranged from 16,000 to 55.6 micrograms per liter (µg/L); by 1994, the concentration ranged from 11,000 µg/L to BDL. The RDX concentration ranged from 7,600 to 33.8 µg/L in 1990 and from 8,400 to 14.4 µg/L in 1994. Although these two data sets indicated a general downward trend in contamination at Area P due to remedial measures and/or natural attenuation, a few monitoring wells showed the opposite trend. To clarify the conflicting results and provide a better understanding of explosives attenuation, eight additional monitoring wells have been installed at the site since 1995.

This poster discusses the feasibility of applying three-dimensional ground-water flow and transport to this heterogeneous aquifer. The capability of a comprehensive computer graphical system—Groundwater Modeling System (GMS)—which is used in the modeling of the site, also will be discussed and illustrated.

Long-Term Application of Natural Attenuation at Sierra Army Depot

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A record of decision (ROD) for Sierra Army Depot selecting natural attenuation and degradation for treatment of ground water was signed by the state of California and the Army on September 8, 1995—the first approved ROD in the United States selecting natural attenuation as a primary remedial alternative for trichloroethene (TCE) and explosives in ground water. The natural attenuation alternative consists of institutional controls to eliminate future use of ground water in the area surrounding the site, long-term ground-water monitoring, and evaluation of contaminant migration and degradation rates.

Explosives and volatile organic compounds (VOCs) are present in shallow ground water over a 26-acre area of Sierra Army Depot, which is located approximately 50 miles northwest of Reno, Nevada. No surface water features or water supply wells exist within the area of the site. A ground-water plume of explosive compounds originates from the TNT Leaching Beds, a facility used during the 1940s for percolation of waste water from a shell washout facility. Dissolved explosive compounds in the ground water include RDX, 1,3,5-trinitrobenzene, HMX, and minor concentrations of numerous other explosive compounds. The highest concentration of total explosive compounds detected is 1,200 micrograms per liter within the vicinity of the former leaching beds. A VOC plume originates from a former paint shop used during the 1940s and 1950s for the renovation of ammunition. Dissolved VOCs present in the highest concentrations are TCE, chloroform, and carbon tetrachloride. The highest concentration of trichloroethene detected is 1,000 micrograms per liter in a monitoring well 175 feet downgradient from the former paint shop.

Under current conditions, the plumes appear to migrate at slow rates. Estimated ground-water flow velocities across the site range from 1 to 140 feet per year, with average estimated ground-water velocities of 2 to 6 feet per year. The shallow aquifer is highly stratified, with numerous fine-grained layers in the upper 25 feet. Because contaminants have diffused into the fine-grained layers over approximately a 50-year period, restoration of ground water to background or drinking-water quality by pump-and-treat or other active remediation does not appear feasible. Long-term ground-water monitoring of the plumes is expected to provide data on degradation reactions that may occur at slow rates over extended periods. In addition to providing these data, this action could save the Army up to $10 million in ground-water remediation costs at Sierra Army Depot.

When Is Intrinsic Bioremediation Cost-Effective? Financial-Risk Cost-Benefit Analysis at Two Chlorinated Solvent Sites

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Interest in intrinsic bioremediation and natural attenuation as remediation alternatives for chlorinated solvent sites is rapidly growing because the methods are significantly more cost-effective than conventional remediation alternatives (e.g., pump-and-treat). When evaluating the long-term cost-effectiveness of intrinsic bioremediation and natural attenuation alternatives, however, many analysts and decision-makers consider direct engineering costs, such as capital, operation and maintenance, and monitoring costs, but fail to adequately assess the potential legal and corporate costs that may arise from choosing an intrinsic-based remediation alternative. If the alternative fails, for example, additional costs would be incurred to address remediation with a new method or to deal with the land's decrease in value or marketability or possible legal action. Financial-risk cost-benefit analysis, which incorporates a more comprehensive set of costs in the cost-effectiveness analysis, is a tool that analysts and decision-makers can use to evaluate objectively whether intrinsic bioremediation and natural attenuation are in fact the most cost-effective remediation alternatives in the long run.

This poster presents the results of using financial-risk cost-benefit analysis to examine the impact of cost factors other than engineering costs on the long-term cost-effectiveness of intrinsic bioremediation versus other remediation alternatives under various scenarios at two chlorinated solvent sites. At both sites, chlorinated volatile organic compounds are currently being intrinsically bioremediated to environmentally acceptable end products (e.g., ethene and ethane).

Natural Attenuation as a Cleanup Alternative for Tetrachloroethylene-Affected Ground Water

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A chlorinated solvent storage and transfer facility operated in an industrial area of Seattle, Washington, from the mid-1940s to the mid-1970s. Historical releases of tetrachloroethylene (PCE) at fill pipes and underground storage tanks have migrated into a shallow sand aquifer underlying the site. A recently completed field screening and ground-water sampling investigation characterized the nature and extent of a local PCE ground-water plume and a more extensive plume of cis-1,2-dichloroethylene and vinyl chloride. Additional ground-water chemistry data, including nitrogen, phosphorus, iron, sulfur, dissolved oxygen, and permanent gas (methane, ethane, ethene) concentrations, were collected. Elevated concentrations of ferrous iron (11 parts per million [ppm]), sulfide (0.39 ppm), and ammonia (14 ppm), and low concentrations of dissolved oxygen (0.25 ppm) indicate anaerobic conditions in the source area that are conducive to natural attenuation of PCE. Methane, ethane, ethene, cis-1,2-dichloroethylene, and vinyl chloride concentrations increase by one to two orders of magnitude 150 feet downgradient of the source area. Near-saturation concentrations of PCE decrease by several orders of magnitude over the same distance. Preliminary estimates indicate a half-life of 150 to 200 days for PCE degradation.

There are no beneficial uses of ground water in the industrial area, and ground-water discharges to a surface-water body 2,500 feet from the site. Concentrations of the contaminants of concern at the property boundary are lower than Washington State surface-water quality criteria. Because natural attenuation appears to effectively remediate the chlorinated hydrocarbons, the proposed remedial action for the site will be limited to ground-water monitoring.

Natural Attenuation of Trichloroethene in a Sandy Unconfined Aquifer

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The natural attenuation of dissolved-phase trichloroethene (TCE) in ground water was evaluated at a state-regulated, operating chemical plant in South Carolina. Natural attenuation was documented via the observed attenuation and loss of TCE within a sandy unconfined aquifer (approximately 25 feet thick with $K_h=10^{-3}$ centimeters per second), 8 years of ground-water monitoring data, and modeling with site-specific retardation coefficients.

The evaluation and demonstration of natural attenuation of TCE was part of a successful technical argument that considered the natural microbial and/or geochemical attenuation processes in the establishment of downgradient ground-water quality compliance points, obviating the need for containment or other remedial actions. The recently promulgated South Carolina Groundwater Mixing Zone Regulations require that, under very specific and stringent attenuation conditions, alternate ground-water protection standards are addressed in zones where attenuation of dissolved-phase chemicals is demonstrated.

No relationship between TCE, electron acceptors, and biodegradation byproduct isopleth maps was observed, suggesting that TCE was not degrading via aerobic or anaerobic pathways. Elevated microtoxicity levels were observed, and minimal quantities of both aerobic and anaerobic TCE degraders were identified. The empirically calculated K_d (using soil total organic carbon [TOC]) was estimated to be 0.4 liters per kilogram. The resulting empirically calculated retardation factor did not correlate with the observed attenuation of TCE at the site, indicating that non-TOC related mechanisms were contributing to TCE attenuation. Consequently, a site-specific K_d was estimated via batch adsorption tests employing toxicity characteristic leaching procedure extraction techniques, using ground water and soils from the site area of interest. A site-specific K_d of 10 liters per kilogram was estimated through these tests. The site-specific retardation factor correlated with the observed natural attenuation of TCE. Differences in the site-specific retardation factor and the empirically calculated estimate may be attributed to soil/ground-water geochemical interactions, such as low pH-induced bonding of the TCE to the soil matrix, which are unrelated to TOC.

Subsequent ground-water modeling using the site-specific retardation factor (and K_d) indicates that dissolved-phase TCE would not migrate to the downgradient receptor for a minimum period of 100 years. The final natural attenuation remedy for the site, recommended in the mixing zone application submitted to South Carolina, included a time-weighted "monitoring only" component with no active remediation. This application is currently under review.

Analysis of Intrinsic Bioremediation of Trichloroethene-Contaminated Ground Water at Eielson Air Force Base, Alaska

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A simple ground-water model was used to determine the apparent rate of trichloroethene (TCE) transformation, to estimate the mass of TCE and its transformation products, and to predict the effects of active treatment options, such as source removal, at Eielson Air Force Base, Alaska.

A modification of the three-dimensional solution to the advection-dispersion-reaction equation (ADRE) proposed by Domenico (1) was used to estimate the rate of TCE transformation. The model was calibrated using the spatial distribution of TCE observed during a field sampling event conducted in July 1995. TCE concentrations as high as 90,000 micrograms per liter were observed at the site and utilized in the model calibration effort. The calibrated model showed that intrinsic remediation of TCE is occurring at the site. The estimated first-order degradation rate for TCE ranged from 0.0020 to 0.0064 day^{-1}.

TCE mass and apparent mass degraded were also estimated using the calibrated model. TCE mass predictions using the model closely matched TCE mass calculated from observed ground-water data. The TCE mass degraded was used to estimate the mass of TCE products that would be present in the system, assuming these products are accumulating. A comparison of observed product mass to the estimated mass of these compounds showed that the mass of these compounds present was significantly less than estimated, suggesting rapid transformation of the compounds to nonchlorinated compounds.

The calibrated model was also used to predict the effects of source removal on the lifetime of the dissolved TCE plume. These predictions, along with source lifetime estimations, suggest that source removal activities may not significantly reduce the time required to meet cleanup goals for the site.

Reference

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

Involvement of Dichloromethane in the Intrinsic Biodegradation of Chlorinated Ethenes and Ethanes

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The metabolism of dichloromethane (DCM) by acetogenic microorganisms has resulted in the production of an electron donor (acetic acid) that is stimulating reductive dechlorination of tetrachloroethene (PCE), trichloroethene (TCE), and 1,1,1-trichloroethane (TCA) to ethene and ethane in a shallow aquifer beneath a bulk chemical transfer facility in Oregon. DCM, TCE, and toluene releases as well as *de minimis* losses of PCE, TCA, ethylbenzene, and xylene have occurred at the site. DCM concentrations in the source area decreased by an order of magnitude (from 2,300 milligrams per liter [mg/L] to 190 mg/L) between 1990 and 1995, with corresponding production of acetic acid. The distribution of DCM attenuates two orders of magnitude to less than 1 mg/L within 100 meters from the source area, far more rapidly than predicted by its mobility in the site ground water. PCE, TCE, and TCA concentrations also attenuate more rapidly downgradient from the source area than would be predicted by their mobilities relative to the ground-water velocity at the site. The distributions of 1,2-dichloroethene, vinyl chloride (VC), 1,1-dichloroethane, and chloroethane (CA) increase downgradient from the source area. Ethene and ethane are present in the ground water downgradient from the source area, in association with VC and CA, indicating that the chlorinated volatile organic compounds are being dechlorinated to environmentally acceptable end products. Intrinsic bioremediation is being considered as a remediation alternative for this site.

Intrinsic Bioremediation of 1,2-Dichloroethane

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Spills of 1,2-dichloroethane, also known as ethylene dichloride (EDC), resulted in free- phase contamination of a Gulf Coast site. There are two aquifers beneath the site, as well as peat, clay, and silt layers. An ongoing recovery and hydraulic containment program in the shallow aquifer is recovering nonaqueous-phase liquid (NAPL) and dissolved-phase EDC. Degradation products of EDC, including 2-chloroethanol, ethanol, ethene, and ethane, were detected in both the highly contaminated upper aquifer as well as in the deeper, less contaminated aquifer. Possibly as a result of cross contamination during drilling operations, low concentrations (less than 1.0 parts per million) of dissolved EDC were detected in the deeper aquifer.

EDC concentrations in wells in the deeper aquifer have decreased greatly over the last year, to between less than 0.005 parts per million (the detection limit) and 0.05 parts per million. First-order decay half-lives for loss of EDC from wells in this aquifer range from 64 to 165 days. Laboratory microcosm studies demonstrated that microbes from the deeper aquifer can transform EDC under anaerobic conditions. A geochemical evaluation demonstrated that microbes at the site are capable of using oxygen, nitrate, sulfate, iron, manganese, and carbon dioxide as electron acceptors; elevated methane concentrations indicate carbon dioxide is the major electron acceptor.

Modeling efforts with DuPonts comprehensive multiphase NAPL model revealed that free-phase EDC will not reach the underlying aquifer because of retention of the free-phase EDC in the overlying silt and clay zones and ongoing intrinsic biodegradation of the dissolved-phase EDC. The three-dimensional, three-phase finite difference model includes simultaneous flow of water, gas, and organic phases; energy transport; temperature-, pressure-, and composition-dependent interphase partitioning; and dispersive transport within phases. The model was originally developed by Sleep and Sykes (1, 2) and modified by Sehayek. The modified model is not commercially available.

References

1. Sleep, B.E., and J.F. Sykes. 1993. Compositional simulation of groundwater contamination by organic compounds, 1. Model development and verification. Water Resour. Res. 29(6):1697-1708.
2. Sleep, B.E., and J.F. Sykes. 1993. Compositional simulation of groundwater contamination by organic compounds, 2. Model applications. Water Resour. Res. 29(6):1709-1718.

A Practical Evaluation of Intrinsic Biodegradation of Chlorinated Volatile Organic Compounds

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At a former industrial site, intrinsic bioremediation was evaluated to address low levels (less than 100 micrograms per liter [µg/L]) of chlorinated volatile organic compounds (VOCs) in ground water. The VOCs detected in ground water include chlorinated ethanes, 1,1-dichloroethene, vinyl chloride, chlorobenzene, benzene, toluene, and ethylbenzene. Total VOC concentrations ranged from not detected to 530 µg/L. Historically, the site was mined for rock and subsequently used for the disposal of tailing sands and clay waste from ore processing. As a result, a complicated ground-water system consisting of at least five water-bearing units exists at the site. Although current remedial activities at the site, including a ground-water pump-and-treat system, have been effective at reducing VOC levels to their present concentrations, continued pumping does not appear to be effective at further concentration reduction.

To reevaluate remedial options, an assessment of naturally occurring transformation processes was performed. Initially, the assessment included VOC data over time, collected to monitor the ground-water pump-and-treat system. Long-term ground-water monitoring results indicate that concentrations of parent VOC compounds have been reduced in all water-bearing units; after an associated temporary increase, a reduction in concentrations of reduction dehalogenation breakdown products was observed.

To further determine whether the natural attenuation observed at the site is a result of intrinsic bioremediation, a study was implemented involving field monitoring and ground-water sampling and analysis for select geochemical indicator compounds and dissolved permanent gases. The geochemical indicator compounds included NO_3/N, total and dissolved iron, and SO_4/S. Dissolved permanent gases include oxygen, CH_4, and CO_2. Redox potential and pH were field measured. Concentrations of organic compounds were evaluated over time, and trends in inorganic indicator compound and dissolved permanent gas concentrations were evaluated spatially. Results of this study strongly suggest that intrinsic bioremediation is responsible for transformation of the VOCs present in site ground water. This poster discusses the study and provides results for evaluating bioremediation of chlorinated VOCs in ground water.

Using Evidence of Natural Attenuation To Locate the Source of a Chlorinated Volatile Organic Compound Plume

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An upper Midwest manufacturing plant has been the site of recent subsurface investigations because of past mishandling practices associated with degreasing solvents, namely trichloroethene (TCE) and 1,1,1-trichloroethane (TCA), during the early 1970s. The site is situated on a well-graded sandy silt aquifer, with limestone bedrock located from 30 to 45 feet below grade.

Initial investigations focused on a solvent storage area adjacent to the building. Results of these investigations revealed significant concentrations of TCE and TCA breakdown products—cis-1,2-dichloroethene (cis-DCE), 1,1-dicloroethane (1,1-DCA), and vinyl chloride—ranging in concentration from 100 to 12,000 micrograms per liter. Since this was the only known source area for these chemicals, the absence of parent compounds was puzzling, especially given the low hydraulic conductivity of the overburden aquifer (10^{-5} centimeters per second range). Ground water was tested for the general water quality parameters of hardness, sulfate, chemical oxygen demand, phosphate, and nitrates. In addition, methane, ethane, and ethene were analyzed in the ground water. These data revealed that in areas of high breakdown product concentrations, there were corresponding decreases in sulfate, nitrate, and phosphate concentrations and increases in the formation of byproduct gases. Conversely, in uncontaminated areas, sulfate (greater than or equal to 200 milligrams per liter) and nitrate (greater than or equal to 10 milligrams per liter) were present and the gases were absent. This evidence of natural attenuation did not explain the absence of parent compounds. Contouring concentrations of electron donors and acceptors, nutrients, and breakdown products, combined with ground-water contour overlays and plume prediction models, indicated that the actual source of contamination may be under the building. Latest investigations resulted in isolating source areas from unknown solvent disposal areas through a series of borings inside the plant.

To the best of our knowledge, this represents one of the first instances in which evidence of natural attenuation, instead of historical information, has been used to locate the source of contamination.

New Jersey's Natural Remediation Compliance Program: Practical Experience at a Site Containing Chlorinated Solvents and Aromatic Hydrocarbons

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In recent years, regulatory agencies have begun to place increasing emphasis on understanding the natural mechanisms of contaminant degradation/attenuation in ground-water at sites undergoing remediation. Guidelines and criteria for natural remediation assessments have been established at both the state and federal level, providing the regulated community with an improved ability to determine site conditions under which a natural remediation approach is feasible and will be acceptable to regulators. These initiatives reflect transition from conventional remedy selection to consideration and appropriate implementation of alternate remedies that incorporate considerations of risk and cost-effectiveness.

One good example of this evolving regulatory process is the Natural Remediation Compliance Program (NRCP), developed by the New Jersey Department of Environmental Protection (NJDEP). General guidelines (termed "minimum requirements") for natural remediation proposals were defined concurrent with NJDEP's establishment of the NRCP in 1994 and have been augmented recently by detailed technical suggestions for screening of sites (1).

In late 1994, McLaren/Hart Environmental Engineering Corporation conducted investigative and remedial activities that led to a proposal to implement the NRCP at a New Jersey industrial site with soil and ground-water affected by chlorinated solvents and aromatic hydrocarbons. The NRCP proposal, submitted as part of a remedial action workplan for site ground water and concurrent with a remedial action report for source area soils, addressed the following NJDEP prerequisite conditions ("minimum requirements") for natural remediation proposals: delineation and remediation of sources; contaminant migration assessment to confirm receptors not at risk; documentation of degradibility and/or attenuation capacity; identification of site-specific characteristics favorable to natural degradation and/or attenuation; establishment of a sentinel well system; development of a ground-water monitoring program; documentation regarding current and potential future ground-water uses; and written notification to potentially affected downgradient property owners.

Specific activities conducted to address the requirements included delineation of source area soils using a Geoprobe, source area soil excavation/disposal, postexcavation sampling, ground-water sampling, in situ measurement of ground-water field parameters, a well search, and an evaluation of potential receptor impacts through modeling. The results of these investigations suggested that "steady state" conditions of contaminant influx and attenuation were in effect, and that, even in the absence of the source remediation conducted, receptor impacts were not expected. Accordingly, the NRCP proposal was submitted, requesting approval to implement the monitoring program outlined therein.

This program could save the property owner significant remediation costs. Given NJDEP's rigorous minimum requirements for NRCP implementation, the costs to demonstrate applicability of the NRCP should be compared with costs for active ground-water plume management. This cost evaluation will allow a property owner to make informed decisions regarding remedial options and cash flow management.

Reference

1. New Jersey Department of Environmental Protection. 1996. Site remediation news. March.

Field and Laboratory Evaluations of Natural Attenuation of Chlorinated Organics at a Complex Industrial Site

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Natural attenuation of tetrachloroethene (PCE), trichloroethene (TCE), carbon tetrachloride, and hexachlorobenzene (HCB) is under investigation at a large industrial site. The site has a number of complexities due to past manufacturing activities, topography, hydrology, and the presence of several surface water bodies that are connected to shallow ground water. Perched ground water, shallow and deep aquifers, creeks, rivers, and a manufactured impoundment all contribute to site hydrology and affect ground-water flow direction and velocity. Regions of high ground-water pH (pH 10 to 14) are found beneath settling ponds that contain high pH waste liquors from past manufacturing processes. Ground-water microbes have been shown to be inactive when the pH exceeds 9.5. The aquifer apparently has significant buffering capacity to neutralize the ground water as it migrates away from the impoundments.

Contaminant concentration varies across the site, with dense nonaqueous-phase liquid contributing a high concentration of dissolved contaminants in a few locations. Contaminant concentration changes and the occurrence of anaerobic biodegradation products of PCE and TCE support the conclusion that intrinsic biodegradation is occurring. Attenuation rates for PCE, TCE, and cis-1,2-dichloroethene indicate a half-life of approximately 300 days for each. Preliminary evidence of intrinsic biodegradation has also been derived from ground-water geochemistry data. Increased concentrations of iron(II) and dissolved manganese correspond with neutral ground-water pH, chemicals of concern, and biodegradation products. Nitrate is found in very low concentrations in the general area, and this respiratory substrate does not significantly contribute to biodegradation. Ground-water alkalinity is affected by site activities and pH, which mask changes in alkalinity due to intrinsic biodegradation. Dissolved methane concentrations, oxidation reduction potential, sulfate concentrations, and dissolved oxygen in the ground water are currently being examined.

This poster discusses the intrinsic remediation of PCE and TCE with respect to contaminant concentrations and ground-water geochemistry. Laboratory studies conducted to evaluate the rate of biodegradation are also described.

Assessment of Intrinsic Bioremediation of Chlorinated Aliphatic Hydrocarbons at Industrial Facilities

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Intrinsic bioremediation of chlorinated aliphatics at several industrial sites was evaluated to determine its significance and whether it could be used as a corrective action alternative for reducing potential environmental impact. The premise behind the implementation of an intrinsic bioremediation approach was that naturally occurring microorganisms present in subsurface environments of each site were capable of degrading the contaminants of interest and that the contaminant concentrations would be degraded to acceptable levels.

A variety of chlorinated aliphatic hydrocarbons were detected in ground water at the sites, including tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), vinyl chloride (VC), trichloroethane (TCA), and methylene chloride. Concentrations of individual chlorinated aliphatics typically ranged from nondetect to less than 500 micrograms per liter (mg/L), with the highest concentrations in the 1,000 to 3,000 mg/L range.

Ground-water data from each site were examined for indicators of intrinsic bioremediation and the existence of conditions favorable for bioremediation. Indicators of intrinsic bioremediation included changes in contaminant concentrations, detection of biodegradation metabolites, and changes in geochemical measurements. Indicators of conditions favorable for bioremediation that were evaluated included pH, oxidation-reduction potential, concentrations of electron acceptors, nutrients, primary substrates sufficient to support microbial activity, and the lack of inhibitory concentrations of toxicants.

The data from each site were collectively evaluated through a "weight-of-evidence" approach to determine whether intrinsic bioremediation was a viable remedial alternative for each site. Based on these evaluations, it was concluded that intrinsic bioremediation was occurring under anaerobic conditions at each site, nonchlorinated co-contaminants served as primary substrates, and microbial activity was limited by nutrient availability.

Although the data indicated that intrinsic bioremediation was occurring, the existing data were insufficient to support intrinsic bioremediation as the sole remedial alternative. Ground-water monitoring for indicator parameters continued to allow further evaluation of the potential application of intrinsic bioremediation as a remedial alternative for the sites.

Natural Attenuation as Remedial Action: A Case Study

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The subject site is an informative case study of factors leading to a decision by state regulators to acknowledge natural attenuation as the principal action to remediate trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride.

A team of hydrogeologists and engineers, under contract with the New York State Department of Environmental Conservation (NYSDEC), completed a remedial investigation and feasibility study for a site in Rockland County, New York. The site is in the glaciated northeast, with a 100-foot thick glacial till underlying the site. The till overlies Brunswick (Passaic) formation fractured silty sandstone bedrock, which comprises the principal aquifer system in the site vicinity. Heterogeneity in the till and fractured rock ground-water hydraulics have resulted in a complex array of potential contaminant migration pathways.

A lighting fixture manufacturing operation discharged an unknown volume of liquid waste containing TCE-dominated mixed volatile organic compounds (VOCs), in concentrations ranging from 1 to 1,000 parts per million total VOC, into a shallow, ephemeral stream/drainage ditch on site for an unknown period, ending in 1980. The remedial investigation was initiated in 1994, 14 years after the discharge was eliminated, and implemented in two phases over a 1.5-year period. The timing and duration of the investigation facilitated identification and characterization of natural degradation and attenuation of the chlorinated constituents (TCE, cis-1,2-DCE, and vinyl chloride) in the site subsurface.

Project personnel used conventional techniques, including soil gas survey and stream sediment, soil, surface water, and ground-water sampling and analysis, during the initial Phase I remedial investigation. The Phase I Remedial Investigation and Phase I and II Feasibility Study lasted 1 year. The investigation and study results suggested that concentrations of chlorinated constituents were naturally attenuating to levels below NYSDEC established cleanup standards (in the parts per billion range). Furthermore, the rates of natural attenuation appeared to be sufficient to preclude offsite migration via most of the potential pathways.

Due to the indications that natural attenuation was functioning on site, project personnel designed and implemented a focused Phase II remedial investigation that, in part, addressed natural attenuation related issues. The latter phase of the remedial investigation was implemented over a period of 6 months and included modified techniques and strategies for stream sediment, soil, surface water, and ground-water sampling and analysis, in addition to a treatability study at the field and laboratory scale. The remedial investigation/feasibility study RI/FS was completed in February 1996. The record of decision was signed in March 1996, and the selected remedy allows for limited (near-surface hot-spot removal) soils remedial action and continued ground-water monitoring to demonstrate the efficacy of natural attenuation in the subsurface as the principal ground-water remedial action for the site.

Patterns of Natural Attenuation of Chlorinated Aliphatic Hydrocarbons at Cape Canaveral Air Station, Florida

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Activities at a former fire training area (Site CCFTA-2 [FT-17]) at Cape Canaveral Air Station in Florida resulted in contamination of shallow soils and ground water with a mixture of chlorinated aliphatic hydrocarbons (CAHs) and fuel hydrocarbons. The dissolved contaminant plume, beneath and at least 1,200 feet downgradient from a body of mobile, light nonaqueous phase liquid (LNAPL) containing commingled petroleum and chlorinated solvents, consists of commingled benzene, toluene, ethylbenzene, and xylenes (BTEX) and CAHs. Before construction of a horizontal air sparging system, contaminated ground water discharged to surface water in a canal downgradient of the source area. The desire for a long-term approach to address the dissolved contaminant mass prompted an assessment of the potential for natural attenuation mechanisms to reduce the mass, toxicity, and mobility of trichloroethene (TCE), dichloroethene (DCE), vinyl chloride (VC), and BTEX dissolved in ground water at CCFTA-2 (FT-17).

Several lines of chemical and geochemical evidence indicate that dissolved CAHs at the site are undergoing reductive dehalogenation, facilitated by microbial oxidation of BTEX compounds and native organic matter. Data on the distributions of TCE, *cis*-1,2-DCE, VC, and ethene indicate that TCE dissolved from the LNAPL body is being sequentially dehalogenated, with VC accumulating near the terminus of the CAH plume. While the ground-water system outside of the plume is nearly anaerobic due to microbial degradation of native organic matter, petroleum hydrocarbons released at the site have fostered additional microbial activity and created conditions that favor reductive dehalogenation of CAHs. Distribution of electron acceptors and metabolic byproducts, along with dissolved hydrogen concentrations, indicate that biodegradation mechanisms operating at the site include aerobic respiration, iron reduction, sulfate reduction, and methanogenesis.

Approximation of field-scale biodegradation rates at the site suggests that TCE and *cis*-1,2-DCE have a half-life of approximately 2.4 to 3.2 years. Because reducing conditions persist from the source area to the canal, VC has accumulated and therefore affected surface water. Air sparging near the canal, however, will serve to both physically remove dissolved contaminants and foster more rapid (aerobic) biodegradation of VC.

Applying Natural Attenuation of Chlorinated Organics in Conjunction With Ground-Water Extraction for Aquifer Restoration

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Natural attenuation of dissolved chlorinated organics (primarily tetrachloroethene, trichloroethene, and 1,1,1-trichloroethane) via dilution is being successfully employed near the end of a 2,200-foot long plume at the South Municipal Water Supply Well Superfund site in Peterborough, New Hampshire. The U.S. Environmental Protection Agency's (EPA's) record of decision required that the entire plume be remediated through pumping a network of extraction wells. Installation and operation of an extraction well near the end of the plume was not practical, however, because of property access difficulties, the presence of a flood plain, and anticipated problems in conveying extracted water via a forcemain due to expected low flows and a large head differential.

Field measurements were supported by finite-difference, three-dimensional flow modeling and indicated that the aquifer at the end of the plume discharges into the Contoocook River. Furthermore, modeling indicated that discharge would occur, although at a lower rate, when the aquifer was pumped in upgradient portions of the plume. Modeled flux through the end of the plume was compared with projected removal rates by an extraction well and was found to be similar. Concentrations of water discharging into the river were conservatively estimated based on the highest concentration detected in a monitoring well within the proposed attenuation zone. Dilution factors were calculated based on the flux of contaminated water from the aquifer versus the river's 7-day low flow over a period of 10 years (7Q10). Dilution factors were applied to discharge concentrations, and results were compared with health-based water quality criteria (for water and fish ingestion) and found to be acceptable. Finally, a flushing model was used to determine that the attenuation zone would be reduced to cleanup levels within the time frame stated in the record of decision. EPA accepted the technical arguments for integrating natural attenuation into the ground-water remediation system, and the record of decision was modified accordingly through issuance of an explanation of significant difference.

Natural Attenuation of Chlorinated Organics in Ground Water Based on Studies Conducted at Naval Amphibious Base Little Creek Sites 12 and 13

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The Department of Defense (DOD) designed the U.S. Navy's Installation Restoration Program (IRP) to investigate past disposal sites according to the Comprehensive Environmental Response, Compensation, and Liability Act of 1983 and the Superfund Amendments and Reauthorization Act of 1986. The IRP has been under way at Naval Amphibious Base (NAB) Little Creek since 1984. As part of the program, multiple ground-water investigations have been conducted at several sites between 1986 and 1996. Chlorinated organics, namely trichloroethylene (TCE), perchloroethylene (PCE), and pentachlorophenol (PCP), have been the major constituents of concern at the following sites:

- *Site 12—Exchange Laundry Waste Disposal Area:* This site consists of an area surrounding a former storm drain used for disposal of soaps, sizing agents, dyes, and PCE sludges from a laundry operation between 1973 and 1978. A sewer line, which received dry cleaning waste from the former laundry facility, drained to a canal that eventually flows into Little Creek Cove. Remains of the laundry facility and the sewer line were removed by 1992. A new commissary building, covering a portion of the site, was constructed in 1993. Ground-water studies conducted from 1992 have indicated volatile organic compound levels as high as 18,200 parts per billion (ppb), mainly consisting of 1,2-dichloroethene, TCE, and PCE.
- *Site 13—Public Works Dip Tank and Wash Rack:* This site consists of an area surrounding a former dip tank used to treat wood with PCP. The tank reportedly contained 300 to 400 gallons of PCP during its use from early 1960s to 1974. All wood-treating operations were discontinued, and the equipment was dismantled by 1982. Ground-water and soil sampling has indicated PCP at levels as high as 890,000 ppb in subsurface soil and 1,700 ppb in ground water.

Slug tests have been conducted at both sites to characterize the hydrogeology, and the plumes have been delineated by sufficient perimeter sampling. In addition, step tests and an 8-hour pump test have been conducted at Site 12. The depth of the water table aquifer at these sites is between 20 and 24 feet below ground surface (bgs).

Remedial alternatives at these sites, including natural attenuation, will be evaluated to mitigate the human health and ecological risks as well as the impact on nearby surface water. The remedy selection process is expected to be complete by the end of 1996. Although no specific remedy has been selected, data collected over a 9-year span allow evaluation of natural attenuation occurring at these sites. This presentation identifies trends and makes projections for future attenuation periods. The two sites present an opportunity to compare natural attenuation of relatively mobile and volatile compounds (TCE and PCE) with that of immobile and semivolatile compounds (PCP) in almost identical hydrogeological settings.

A Modular Computer Model for Simulating Natural Attenuation of Chlorinated Organics in Saturated Ground-Water Aquifers

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Although several field-scale natural attenuation projects have already been considered for managing benzene, toluene, ethylbenzene, and xylene (BTEX) plumes, a rational basis for implementing natural attenuation technology has yet to be formulated for chlorinated solvent plumes. Successful validation of natural attenuation involves significant upfront and followup field characterization to ensure that intrinsic processes are indeed destroying contaminants of concern at reasonable rates. Given the extensive amount of data collected during this type of effort, computer-aided design and data analysis tools are needed. These tools must facilitate the interpretation of these data so that the design engineer can determine whether intrinsic remediation can achieve the cleanup objectives and assess the risks associated with the action. Computer models are also useful for forecasting the influence of natural attenuation processes over long periods.

To adequately analyze natural attenuation processes, models should also consider simultaneous multispecies transport and bio- and geochemical interactions. This poster describes a newly developed computational tool, designated RT3D (Reactive Transport in Three Dimensions). This tool can simulate natural attenuation of various subsurface contaminants and their decay products in saturated ground-water aquifers.

RT3D was developed from the U.S. Environmental Protection Agency's public domain computer code MT3D. The MT3D model simulates single-species transport with or without sorption and first-order reaction. Contaminant transport velocities are calculated from the head distribution computed by the U.S. Geological Survey's model MODFLOW.

We have extended MT3D to describe multispecies transport and reactions. The present version of RT3D can simulate three-dimensional transport of multiple aqueous-phase species and the fate of multiple solid-phase species, along with the physical, chemical, and biological interactions among them. The code is organized in a modular fashion to ensure flexibility. The reactive portion of the code is a separate module using an operator-split strategy; hence, any type of reaction kinetics can be accommodated through an appropriate reaction module. The present version has four separate reaction modules: aerobic, instantaneous BTEX reactions (similar to BIOPLUME II); multiple-electron acceptor, kinetic-limited BTEX reactions (similar to BIOPLUME III); denitrification-based carbon tetrachloride transformation reactions; and chlorinated ethene reactions.

This poster describes the numerical details of the RT3D code and the chlorinated ethene reaction module. An example problem is solved to illustrate the potential use of this code for planning natural attenuation of chlorinated organics in saturated ground-water aquifers.