DEPARTMENT OF THE NAVY

TECHNICAL GUIDELINES FOR EVALUATING MONITORED NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS AND CHLORINATED SOLVENTS IN GROUND WATER AT NAVAL AND MARINE CORPS FACILITIES

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EXECUTIVE SUMMARY

This document provides guidance for Navy and Marine Corps Remedial Project Managers (RPMs) and their contractors on how to assess natural attenuation as a remedial strategy for ground-water systems contaminated with petroleum hydrocarbons and/or chlorinated solvents. Common natural attenuation processes include dispersion, dilution, sorption, hydrolysis and biodegradation. Of these processes, biodegradation is the most common mechanism causing the transformation of contaminants to nontoxic products such as carbon dioxide. Because of this, this document places more emphasis on biodegradation than other natural attenuation processes.

Natural attenuation processes act to decrease concentrations of dissolved petroleum hydrocarbon and chlorinated solvent contaminants as they are transported by flowing ground water. The efficiency of natural attenuation processes, as defined in this document, refers to a quantitative comparison of contaminant transport rates to rates of biodegradation. If rates of biodegradation are fast relative to rates of transport, contaminant migration will be highly restricted, and the efficiency of natural attenuation will be relatively high. Conversely, if rates of biodegradation are slow relative to transport rates, contaminants will not be as restricted, and the efficiency of natural attenuation will be relatively low. When natural attenuation efficiency is high, contaminant transport to sensitive receptor exposure points may be prevented, and natural attenuation can be an effective part of overall site remediation. Conversely, when natural attenuation efficiency is low, contaminants may move freely and reach receptor exposure points. In this case, natural attenuation may not be the sole remedy but could be an appropriate component of a remedial strategy. Because the conditions that affect biodegradation of petroleum hydrocarbons and chlorinated solvents are well-known, it is possible to assess the efficiency of natural attenuation with a high degree of confidence.

Assessing the efficiency of natural attenuation requires information on (1) concentrations of contaminants and daughter products in space and/or time; (2) ambient geochemical conditions such as the reduction/oxidation (redox) state of ground water; (3) rates and directions of ground-water flow; (4) rates of contaminant biodegradation; and (5) demographic considerations such as presence of nearby receptor exposure points. This document outlines the chemical, hydrologic, and biologic data needed to assess the efficiency of natural attenuation, and provides guidance on how to use these data to determine if natural attenuation would be a viable component of site remediation. It is recognized that natural attenuation often will be used in conjunction with engineered actions to remove a non-aqueous-phase source of dissolved contamination.

Long-term monitoring is always part of a remediation system that includes natural attenuation as a component (USEPA, 1997). This document also provides guidance for establishing ground-water monitoring networks to document the long-term performance of remedial systems that include natural attenuation as part of the overall site remediation strategy.

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Glossary of Terms

Aerobe: Bacteria that use oxygen as an electron acceptor.

Anaerobe: Organisms that can use electron acceptors other than molecular oxygen to support their metabolism.

Anoxic ground water: Ground water that contains oxygen in concentrations less than about 0.5 mg/L. This term is synonymous with the term anaerobic.

Anthropogenic: Man-made.

Cometabolism: The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound.

Daughter Product: A compound that results directly from the biodegradation of another. For example *cis*-1,2-dichloroethene (*cis*-1,2-DCE) is commonly a daughter product of trichloroethene (TCE).

Diffusion: The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion.

Dispersion: The tendency for a solute to spread from the path that it would be expected to follow under advective transport.

Dispersivity: A property that quantifies the physical dispersion of a solute being transported in a porous medium.

Effective Porosity: The percentage of void space that is available for fluid flow.

Electron Acceptor: A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, Fe(III), Mn(IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride.

Electron Donor: A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

Facultative Anaerobes: Microorganisms that use (and prefer) oxygen when it is available, but can also use alternate electron acceptors such as nitrate under anoxic conditions when necessary.

Fermentation: Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidized and reduced daughter products.

Heterotroph: An organism that uses organic carbon as an external energy source and as a carbon source.

Hydraulic Conductivity: The relative ability of a unit cube of soil, sediment, or rock to transmit water.

Hydraulic Head: The height above a datum plane of the surface of a column of water. In the ground-water environment, it is composed dominantly of elevation head and pressure head.

Hydraulic Gradient: The maximum change in head per unit distance.

Mechanical Dispersion: A physical process of mixing along a flow path in an aquifer resulting from differences in path length and flow velocity. This is in contrast to mixing due to diffusion.

Metabolic Byproduct: A product of the reaction between an electron donor and an electron acceptor. Metabolic byproducts include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, and chloride.

Obligate Aerobe: Microorganisms that can use only oxygen as an electron acceptor. Thus, the presence of molecular oxygen is a requirement for survival and growth of these microbes.

Obligate Anaerobes: Microorganisms that grow only in the absence of oxygen; the presence of molecular oxygen either inhibits growth or kills the organism. For example, methanogens are very sensitive to oxygen and can live only under strictly anoxic conditions. Sulfate reducers, on the other hand, can tolerate exposure to oxygen, but cannot grow in its presence (Chapelle, 1993).

Oxic ground water: Ground water that contains oxygen in concentrations greater than about 0.5 milligram per liter (mg/L).

Reduction/Oxidation Reactions: A chemical or biological reaction wherein an electron is transferred from and electron donor to an electron acceptor.

Porosity: The ratio of void volume to total volume of a rock or sediment.

Predominant Terminal Electron-Accepting Process: The electron-accepting process (oxygen reduction, nitrate reduction, Fe(III) reduction, etc.) that sequesters the majority of the electron flow in a given system.

Reductive Dechlorination: Reduction of a chlorine-containing organic compound via the replacement of chlorine with hydrogen.

Respiration: The process of coupling the oxidation of organic compounds with the reduction of inorganic compounds, such as oxygen, nitrate, Fe(III), Mn(IV), and sulfate.

Seepage Velocity: The average velocity of ground water in a porous medium.

Substrate: A compound used by microorganisms to obtain energy for growth. The term can refer to either an electron acceptor or an electron donor.

List of Acronyms and Abbreviations

AFB: Air Force Base

ASTM: American Society for Testing and Materials

BTEX: benzene, toluene, ethylbenzene, and xylenes

cm^2: square centimeter(s)

CO_2: carbon dioxide

CT: carbon tetrachloride

DCE: dichloroethene, dichloroethylene

DOC: dissolved organic carbon

DQO: data quality objective

Fe(II): ferrous iron

Fe(III): ferric iron

ft/d: feet per day

ft^2/d: square feet per day

IC: ion chromatography

L: liter(s)

LLNL: Lawrence Livermore National Laboratory

μg: microgram(s)

μS: microsiemen(s)

MCL: maximum contaminant level

mg: milligram(s)

Mn(II): soluble manganese

Mn(IV): manganese oxide

MTBE: methyl tert-butyl ether

mV: millivolt(s)

NAPL: nonaqueous phase liquid

ORP: oxidation/reduction potential

PCE: perchloroethene, perchloroethylene, tetrachloroethene

POC: particulate organic carbon

Redox: reduction/oxidation

RPM: remedial project manager

SW: solid waste

TCA: trichloroethane

TCE: trichloroethene, trichloroethylene

TOC: total organic carbon

USEPA: United States Environmental Protection Agency

VC: vinyl chloride

VOC: volatile organic compound

SECTION 1

PURPOSE AND SCOPE

Monitored natural attenuation is the use of naturally occurring, contaminant degrading and dispersing processes combined with environmental monitoring to remediate contaminated ground water. Natural attenuation processes occur in all ground-water systems, but their effectiveness varies considerably from site to site and among different kinds of contaminants. It often is difficult to identify those sites where monitored natural attenuation is appropriate, and just as importantly, those sites where natural attenuation is not appropriate, as a remedial strategy. The purpose of this document is to:

1) Provide a concise overview of natural attenuation;

2) Describe how the efficiency of natural attenuation of petroleum hydrocarbons and chlorinated solvents can be assessed ;

3) Identify the hydrologic and geochemical data needed to make these assessments; and

4) Summarize the monitoring requirements needed to verify the effectiveness of natural attenuation.

The efficiency of natural attenuation depends on particular hydrologic and geochemical characteristics of the ground-water system into which the contaminants have been introduced. This makes it possible to assess the efficiency of natural attenuation using a few general hydrologic, geochemical, and biological principles. It is not possible to assess natural attenuation at all sites using exactly the same procedures. It is possible, however, to identify guidelines that can be applied to a wide variety of hydrologic conditions. This document is intended to provide this general guidance. Ultimately, the accurate assessment of natural attenuation will rely as much on the sound professional judgment of the practitioner responsible for the assessment as on the guidelines being followed.

SECTION 2

OVERVIEW OF NATURAL ATTENUATION

Natural attenuation processes (biodegradation, dispersion, dilution, sorption, volatilization, and abiotic degradation mechanisms) affect the fate and transport of petroleum hydrocarbons and chlorinated solvents in all hydrologic systems. When these processes are shown to be protective of human health and the environment, and when an adequate monitoring program is in place to document the effectiveness of these processes, they can be used as an exclusive remedy or as a component of an engineered remedy at a site. Monitored natural attenuation is a term that refers specifically to the use of natural attenuation processes as part of overall site remediation. The United States Environmental Protection Agency (USEPA, 1997) defines monitored natural attenuation as follows:

> *The term "monitored natural attenuation," as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; and chemical or biological stabilization, transformation, or destruction of contaminants.*

In practice, natural attenuation also is referred to by several other names, such as intrinsic remediation, intrinsic bioremediation, natural restoration, or passive bioremediation. Natural attenuation processes are dominant factors in the fate and transport of contaminants. Biodegradation processes are of special importance in natural attenuation because they reduce the mass of contaminants and generally transform toxic contaminants to nontoxic byproducts. Therefore, biodegradation mechanisms are the principal focus of this document. Additional useful guidance documents for evaluating natural attenuation include McCallister and Chiang (1994), Buscheck and O'Reilly (1995), Wiedemeier *et al*., (1995a and 1996a), and Chapelle *et al*. (1996b).

2.1 BIODEGRADATION OF PETROLEUM HYDROCARBONS

Over the past two decades, numerous laboratory and field studies have shown that hydrocarbon-degrading microorganisms are ubiquitous in the subsurface environment, and that these microorganisms can degrade a variety of organic compounds, including components of gasoline, kerosene, diesel, jet fuel, and many other petroleum hydrocarbons. Recent research conducted by the Lawrence Livermore National Laboratory (LLNL, Rice *et al.*, 1995) and the

Texas Bureau of Economic Geology (Mace *et al.*, 1997) shows that about 85 to 90 percent or more of the dissolved fuel hydrocarbon plumes present in the shallow subsurface of the United States are at steady-state equilibrium, or are receding.

Petroleum hydrocarbons are biodegraded via biological oxidation when electron donors and electron acceptors are combined to produce energy for microbial growth (and metabolic byproducts). In general, fuel hydrocarbon biodegradation proceeds via the following generalized equation:

$$\text{Electron Donor} + \text{Electron Acceptor} \rightarrow \text{Metabolic Byproducts} + \text{Energy}$$
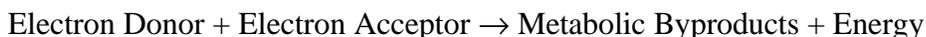
Petroleum hydrocarbons serve as electron donors in microbial metabolism. Electron acceptors include oxygen, nitrate, Mn(IV), Fe(III), sulfate, and carbon dioxide. Carbon dioxide, water, nitrogen gas, Mn(II), Fe(II), hydrogen sulfide, and methane are some of the metabolic byproducts typically produced from the biodegradation of petroleum hydrocarbons. The biodegradation of petroleum hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and generally will proceed until all of the contaminants that are biochemically accessible to the microbes are oxidized. It is generally observed that an adequate supply of electron acceptors is present in most, if not all, hydrogeologic environments (Wiedemeier *et al*., 1995b and 1998).

Methyl tert-butyl ether (MTBE), a fuel oxygenate that has been added to gasoline since the early 1970s, also is susceptible to microbially mediated degradation processes. However, because MTBE is a relatively oxidized compound, it is an inefficient electron donor in microbial metabolism. Field studies have shown that while MTBE biodegrades in ground-water systems, its degradation is less efficient than degradation of BTEX compounds (Borden *et al*., 1997; Landmeyer *et al*., 1998).

2.2 BIODEGRADATION OF CHLORINATED SOLVENTS

In contrast to the simple biological oxidation of petroleum hydrocarbons, where contaminants are used exclusively as electron donors, the common chlorinated solvents such as perchloroethene, (PCE), trichloroethene (TCE), trichloroethane (TCA), and carbon tetrachloride (CT) are biodegrade by predominantly reductive processes. Reductive dechlorination, which is typically the initial step in biodegradation, requires an adequate supply of electron donors. These electron donors can include petroleum hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate) as well as natural organic carbon. Furthermore, the organic carbon driving reductive dechlorination can be either dissolved or particulate. Once degradation has commenced via reductive dechlorination, reduced daughter products such as dichloroethene (DCE) or vinyl chloride (VC) can be further degraded by direct oxidation. In addition to direct oxidation and reduction, chlorinated ethenes can be degraded by cometabolic processes. Specific cometabolic processes, such as in the methane monoxygenase system (McCarty and Semprini, 1994), can be important in some natural environments. It is more common, however, for growth-supporting oxidation or reduction to dominate in natural systems. In general, the efficient degradation of chlorinated solvents is facilitated by initial reducing conditions, followed by oxidizing conditions as contaminants are transported along ground-water flowpaths.

Because of the complex nature of these reductive/oxidative degradation pathways, the behavior of chlorinated solvents in ground-water systems is more variable than that of petroleum hydrocarbons. Thus, it is important to have a good understanding of the interactions among chlorinated aliphatic hydrocarbons, anthropogenic or natural carbon, dissolved and/or particulate organic carbon, and inorganic electron acceptors at the site. Site-specific characterization is the only way to adequately document and understand these processes.

SECTION 3

ASSESSING THE EFFICIENCY OF NATURAL ATTENUATION

The efficiency of natural attenuation can be defined in terms of rates of contaminant attenuation relative to rates of contaminant transport. If rates of contaminant attenuation are fast relative to rates of contaminant transport, the efficiency of natural attenuation is relatively high. Conversely, if rates of attenuation are slow relative to rates of transport, the efficiency of natural attenuation is relatively low.

The two most practical lines of evidence for assessing the efficiency of natural attenuation are (Wiedemeier et al., 1996a):

1) Historical ground-water chemistry data showing plume stabilization and/or loss of contaminant mass over time.

2) Ground-water chemistry data showing that geochemical conditions are suitable for biodegradation, and that active biodegradation has occurred as indicated by the consumption of electron acceptors and/or the production of final products. These chemical and geochemical analytical data can include evidence of

- depletion of electron acceptors and donors
- increasing metabolic byproduct concentrations
- decreasing parent compound concentrations
- increasing daughter compound concentrations.

The first line of evidence involves using historical ground-water-chemistry data to show that the contaminant plume is shrinking, stable, or growing at a rate slower than predicted by ground-water seepage velocity calculations. In some cases a biologically recalcitrant (nonreactive or conservative) tracer commingled within the contaminant plume (e.g., trimethylbenzene) can be used to show that a reduction in contaminant mass is occurring and to estimate biodegradation rate constants (Wiedemeier *et al*., 1996b).

When microorganisms degrade organic contaminants in the subsurface they cause measurable changes in soil and ground-water chemistry. The second line of evidence involves documenting these biochemical and geochemical changes. The first line of evidence shows that the contaminant plume is being attenuated, and in some cases can show that contaminant mass is being destroyed. The second line of evidence can show that the geochemical conditions are either favorable or unfavorable for biodegradation to occur.

3.1 DOCUMENTED LOSS OF CONTAMINANT MASS - TIME VERSUS SPACE

An historical database showing plume stabilization and/or loss of contaminant mass over time can be used to show that natural attenuation is occurring at a site. This is perhaps the best line of evidence to support selection of monitored natural attenuation as a remediation approach. Database adequacy is determined on a site by site basis.

A useful method for presenting historical data is to prepare isopleth maps of contaminant concentrations in space and/or time. It is important to consider that incomplete site characterization may bias the interpretation of these isopleth maps. Figure 3.1 shows isopleth maps of total VOC concentrations in ground water at the depth of highest contaminant concentrations. Note that the multi-year contaminant data were collected during approximately the same seasonal time period. This is important because seasonal variations in aquifer recharge can cause significant changes in contaminant concentrations and ground-water geochemistry. Thus, an apparent reduction in plume size and/or contaminant concentrations could be the result of a seasonal phenomenon, and may not reflect a significant overall trend in contaminant concentrations. Also plotted on Figure 3.1 is the projected extent of contamination if biodegradation were not occurring. These projections were made using a fate and transport model that incorporated the effects of advection, dispersion, and sorption only; biodegradation was assumed not to occur in these simulations. Model predictions suggest that if biodegradation were not occurring at this site, the plume would advance approximately 1,500 feet per year. Because chemical data show that this is not the case, plume stabilization is likely the result of biodegradation. Such an analysis provides credible evidence for the occurrence of ongoing biodegradation.

3.2 GEOCHEMICAL CONDITIONS

The efficiency of petroleum hydrocarbon and chlorinated solvent biodegradation varies under different geochemical conditions (Chapelle, 1996; Wiedemeier et al., 1998). Biodegradation of petroleum hydrocarbons, for example, occurs more rapidly under oxic (aerobic) conditions than under anoxic (anaerobic) conditions. In contrast, some chlorinated solvents (such as PCE) degrade more efficiently under anoxic conditions, while others (such as VC) degrade more efficiently under oxic conditions. Documenting the geochemical conditions present at a site, specifically the sequence of redox processes along ground-water flowpaths, provides important information about the occurrence or non-occurrence of biodegradation processes.

3.3 CHEMICAL DATA NEEDED TO ASSESS NATURAL ATTENUATION

In order to assess the second line of evidence for evaluating natural attenuation it is necessary to characterize the ground-water chemistry, both within and outside the contaminant plume. The first line of evidence is collected by directly measuring contaminant concentrations over space and- time. But the biodegradation of organic compounds also brings about distinct and measurable changes in ground-water geochemistry. Documenting these changes can provide the information necessary to assess the occurrence and efficiency of specific biodegradation processes. Table 3.1 presents ground-water analytical parameters that can be used to assess and quantify natural attenuation, including biodegradation, for petroleum hydrocarbons and chlorinated solvents. The data collection process should be conducted in accordance with the data quality objectives process outlined by USEPA (1994) and summarized in Table 3.2. Conforming with this process will ensure that the data collected are appropriate for evaluating natural attenuation at individual sites.

August 1993

July 1994

September 1995

Source Area

Ground-Water Flow Direction

8,000

4,000

ND

20,000

8,000

4,000

ND

8,000

4,000

ND

4,000

Projected Maximum Extent of Plume with Advection, Dispersion, and Sorption Accounted For and Biodegradation Omitted

4,000 — Line of Equal Total BTEX Concentration (µg/L)

Ground-Water Flow Velocity = 1,600 feet per year

N

0   300   600
FEET
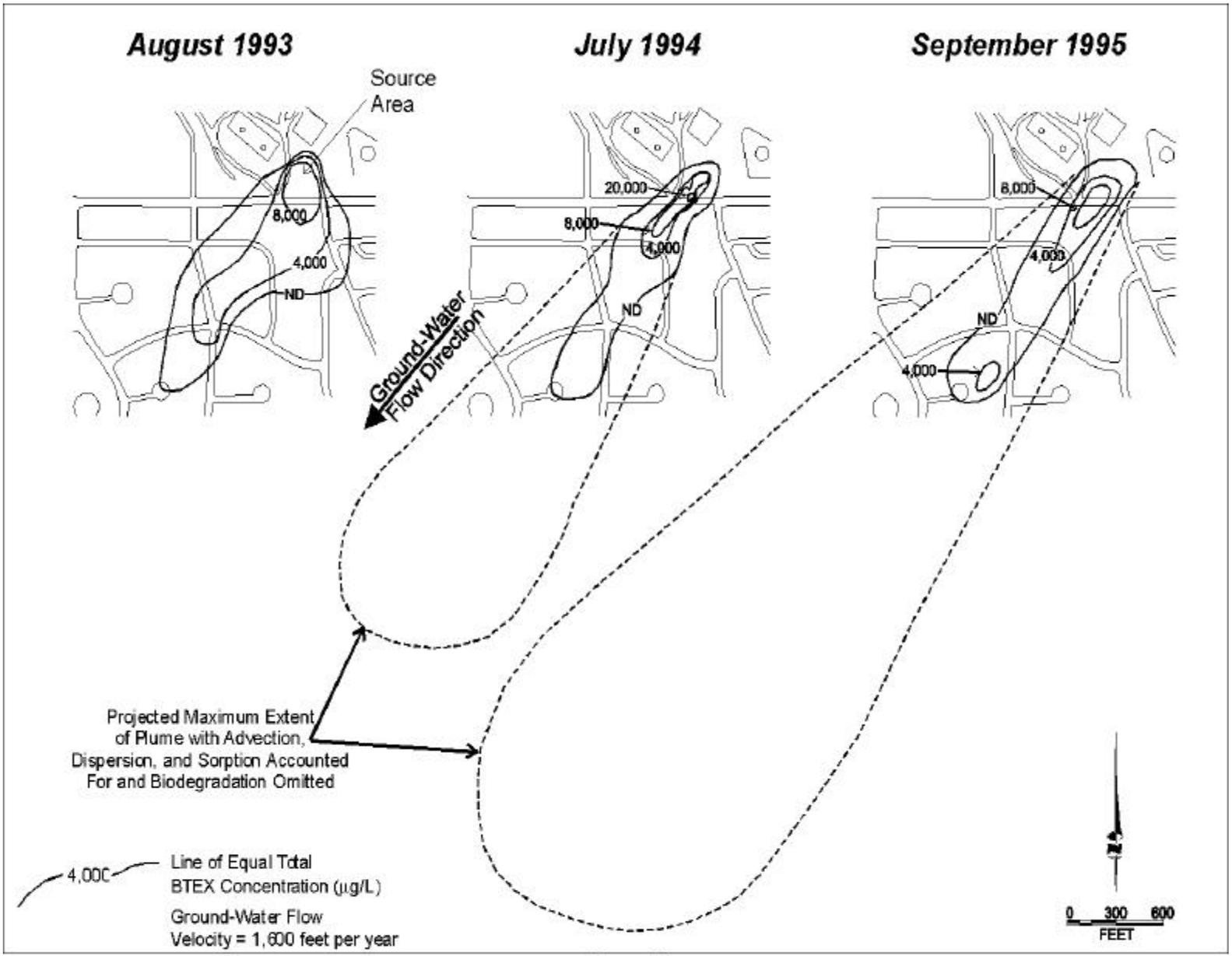
Figure 3.1

Isopleth Maps Showing Dissolved Contaminant Distribution Over Time

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3-3

Table 3.1

Ground-Water Analyses for Assessing Natural Attenuation
(From Wiedemeier *et al.*, 1996a)*

Analysis	Method/Reference	Comments	Data Use	Field or Fixed-Base Laboratory
Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds) and MTBE	SW-846 Method 8020 (sites with petroleum hydrocarbons only) SW-846 Method 8260B (sites with chlorinated solvents or mixed solvents/petroleum hydrocarbons)	Analysis may be extended to higher-molecular-weight alkyl benzenes.	Method of analysis for BTEX, MTBE, and chlorinated solvents/byproducts, which are the primary target analytes for monitoring natural attenuation; method can be extended to higher molecular weight alkylbenzenes; trimethylbenzenes are used to monitor plume dilution if degradation is primarily anoxic.	Fixed-base
Oxygen (O_2)	Dissolved oxygen meter calibrated in the field according to the supplier's specifications	Refer to American Society for Testing and Materials (ASTM) Method A4500 for a comparable laboratory procedure.	Concentrations generally <0.5 mg/L generally indicate an anoxic pathway.	Field
Nitrate (NO_3^-)	Ion chromatography (IC) method E300	Can be done in the field, but analysis by a fixed-base laboratory is recommended.	Substrate for microbial respiration if oxygen is depleted.	Fixed-base
Soluble Manganese [Mn(II)]	Colorimetric Hach® Company Method 8149	Filter if turbidity interferes with analysis.	May indicate an anoxic degradation process due to depletion of oxygen and nitrate.	Field
Ferrous Iron [Fe(II)]	Colorimetric Hach® Company Method 8146	Filter if turbidity interferes with analysis.	May indicate an anoxic degradation process due to depletion of oxygen, nitrate, and manganese.	Field
Sulfate (SO_4^{2-})	IC method E300	Do not use the field method if this method is used.	Substrate for anoxic microbial respiration.	Fixed-base
Sulfate (SO_4^{2-})	Hach® Company Method 8051	Colorimetric, do not use the fixed-base laboratory method if this method is used.	Substrate for anoxic microbial respiration.	Field
Hydrogen Sulfide (H_2S)	Color Disk Methylene Blue Method	Hach® Catalog Number 2238-01.	The presence of H_2S suggests biodegradation via sulfate reduction.	Field
Methane (CH_4), ethane[a/], and ethene[a/]	Kampbell *et al.* (1989) or SW-846 Method 3810 Modified	Method published by researchers at the USEPA. Limited to few commercial labs.	The presence of CH_4 suggests biodegradation via methanogenesis. Ethane and ethene data are used where chlorinated solvents are suspected of undergoing biological transformation.	Fixed-base
Dissolved Inorganic Carbon	Can be estimated from alkalinity and pH (Hach® alkalinity test kit model AL AP MG-L)	Phenolphthalein method.	Dissolved inorganic carbon is a byproduct of organic carbon oxidation and indicates the difference in microbial oxidation processes inside versus outside a contaminant plume.	Field

Table 3.1 (Concluded)

Ground-Water Analyses for Assessing Natural Attenuation
(From Wiedemeier et al., 1996a)

Analysis	Method/Reference	Comments	Data Use	Field or Fixed-Base Laboratory
Total Organic Carbon	SW-846 Method 9060		To determine the potential for reductive dechlorination.	Fixed-base
Oxidation/reduction potential (ORP)	ASTM Method A2580B	Measurements made with electrodes and meter; protect samples from oxygen. Report results against the hydrogen electrode (Eh) by adding a correction factor specific to the electrode used.	The ORP of ground water reflects the relative oxidizing or reducing nature of the ground-water system. ORP is influenced by the nature of the biologically mediated degradation of contaminants, and may range from 800 millivolts (mV) (oxygenated) to less than -400 mV (strongly reducing).	Field
Chloride (Cl^-)	IC method E300	SW-846 Method 9050 may also be used.	Chloride is released during reductive dechlorination.	Fixed-base
pH	Field probe with direct-reading meter calibrated in the field according to the supplier's specifications	Field.	Aerobic and anoxic processes are pH-sensitive.	Field
Temperature	Field probe with direct-reading meter	Field only.	Well purging.	Field
Conductivity	E120.1/SW-846 Method 9050, direct reading meter		General water quality parameter used as a marker to verify that site samples are obtained from the same ground-water system.	Field
Hydrogen (H_2)[a]	Equilibration with gas in the field; determined with a reduction gas detector. (Chapelle *et al.*, 1997)	Optional specialized analysis.	Determine terminal electron accepting process. Predicts the possibility for reductive dechlorination.	Field

NOTES:

*   These methods are commonly used for these analyses. Other analytical methods may be required to meet site-specific data quality objectives.

[a]   For use at sites with chlorinated solvents; not widely available at this time, but is expected to become more available in the future.

Table 3.2
Data Quality Objectives to Implement the Natural Attenuation Guidelines
(From Wiedemeier *et al*., 1996a)

Analysis	Minimum Limit of Quantification	Precision	Potential Data Quality Problems
Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds) and MTBE	Lesser of maximum contaminant levels (MCLs) or risk-based screening levels	Coefficient of variation ≤ 10 percent.	Volatilization during shipment and biodegradation due to improper packaging/preservation.
Oxygen	0.2 mg/L	+/- 0.2 mg/L.	Improperly calibrated electrodes or bubbles behind the membrane, a fouled membrane, or introduction of atmospheric oxygen during sampling.
Nitrate	0.1 mg/L	+/- 0.1 mg/L.	Must be preserved.
Mn(II)	0.1 mg/L	Coefficient of variation ≤ 20 percent.	Possible interference from turbidity (must filter if turbid). Protect from sunlight and analyze within minutes of collection.
Fe(II)	0.5 mg/L	Coefficient of variation ≤ 20 percent.	Possible interference from turbidity (must filter if turbid). Protect from sunlight and analyze within minutes of collection.
Sulfate	5 mg/L	Coefficient of variation ≤ 20 percent.	Fixed-base.
Hydrogen Sulfide	0.5 mg/L	Coefficient of variation ≤ 20 percent.	Possible interference from turbidity (must filter if turbid). Keep sample cool.
Methane, ethane, and ethene	1 μg/L.	Coefficient of variation ≤ 20 percent.	Method standard operating procedure must be thoroughly understood by the laboratory before sample submittal. Sample must be preserved against biodegradation and collected without headspace (to minimize volatilization).

Table 3.2 (Concluded)
Data Quality Objectives to Implement the Natural Attenuation Guidelines
(From Wiedemeier et al., 1996a)

Analysis	Minimum Limit of Quantification	Precision	Potential Data Quality Problems
Dissolved inorganic carbon	1 mg/L	Standard deviation ≤ 20 percent	Analyze sample within 1 hour of collection.
Oxidation/reduction potential	+/- 300 mV	+/-+/- 50 mV	Improperly calibrated electrodes or introduction of atmospheric oxygen during sampling.
Total organic carbon	0.1 percent	Coefficient of variation ≤ 20 percent	Samples must be collected from contaminant-transporting (i.e., transmissive) intervals.
pH	0.1 standard units	0.1 standard units	Improperly calibrated instrument; time sensitive.
Temperature	0 degrees Celsius	+/- 1 degree Celsius	Improperly calibrated instrument; time sensitive.
Conductivity	50 microsiemens per square centimeter ($\mu S/cm^2$)	+/- 50 $\mu S/cm^2$	Improperly calibrated instrument.
Chloride	1 mg/L	Coefficient of variation ≤ 20 percent	May be hard to discern trends due to background conditions.
Hydrogen[a]	0.1 nanomole (nM)	+/- 0.1 nM.	Several, see Chapelle *et al.*, (1997).

[a] Required for chlorinated solvents; not required for petroleum hydrocarbons.

There are numerous technical difficulties involved in collecting the chemical data used for assessing natural attenuation that can lead to sampling or analysis errors. Perhaps the most common error is inadvertently oxygenating water samples collected for dissolved oxygen measurements. Because of these potential difficulties, it is important to review the data for potential inconsistencies. For example, it would be highly unusual to find ground water containing significant concentrations of dissolved oxygen (>2 milligrams per liter, mg/L) that also contain high concentrations of Fe(II) (>5 mg/L) or high concentrations of dissolved methane (>1 mg/L). Such inconsistencies should be carefully screened to identify possible analytical errors, to avoid data misinterpretation, and to identify highly heterogeneous geochemical conditions.

3.4 KINETIC EVALUATION OF INTRINSIC BIODEGRADATION

The natural attenuation of contaminants in ground-water systems depends largely on ambient rates of microbial biodegradation. One approach to measuring biodegradation rates is to collect aquifer material, construct either static or flow-through microcosms in the laboratory, and measure the decrease in concentrations of particular compounds, or the production of $^{14}CO_2$ from radiolabeled compounds (Chapelle *et al.*, 1996a). These methods are advantageous in that they can be applied to a wide range of hydrologic systems and because abiotic controls can be used to separate biotic from abiotic effects. However, the laboratory approach introduces uncertainties due to sediment disturbance and difficulties in reproducing *in situ* conditions.

Another approach to measuring biodegradation rates is to track the loss of contaminants along ground-water flowpaths. This approach also is subject to various uncertainties, particularly in separating the effects of microbial processes from abiotic processes such as hydrodynamic dispersion, advection, and sorption. Uncertainty is associated with estimating contaminant mass from a limited number of data points in a heterogeneous medium.

Microbial utilization of substrates (contaminants) conforms to enzyme saturation (Monod) kinetics according to the Michaelis-Menton equation:

$$V = [v_{max}/K_s + S] (SB) \qquad \text{eq. 3.1}$$

Where V is the rate of substrate uptake (moles per time), v_{max} is the maximum rate of substrate uptake (moles of substrate per time per gram of cells), K_s is the substrate concentration at which $v = \frac{1}{2} v_{max}$ (moles of substrate per liter), S is substrate concentration (moles per liter), and B is the amount of cells (grams). At low substrate concentrations where $S \sim K$ (i.e., substrate uptake is not limited by enzyme availability), and when the microbial population is neither increasing or decreasing with time, the Michaelis-Menton equation is approximated by first-order kinetics:

$$V \sim kS \qquad \text{eq. 3.2}$$

Where k is a rate constant (units of 1/time). In many substrate-limited ground-water systems, first-order kinetics are a adequate approximation of contaminant degradation, and this approach has been widely used to simulate solute-transport of organic contaminants. It is recognized, however, that this simplification is not appropriate for sites with (1) high contaminant concentrations (> 1 mg/L, Beakins *et al.*, 1998) where the availability of degradation enzymes is significantly less than the availability of the contaminant; (2) contaminant concentrations that are toxic to microorganisms; (3) more than one substrate that limit microbial degradation rates; and/or (4) microbial populations that are increasing or decreasing.

Two methods for estimating biodegradation rates from field data are a dispersion-model approach (Chapelle *et al.*, 1996a), and a conservative-tracer approach (Wiedemeier *et al.*, 1996b). Both of these methods were originally developed for dissolved BTEX compounds, but can be applied to dissolved chlorinated solvents as well.

The dispersion-model approach assumes that the dispersion, advection, and biodegradation of a soluble contaminant in flowing ground water may be described by the equation:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - SC^n - kC$$

eq. 3.3

Where C is the solute concentration (µg/L), D is the coefficient of hydrodynamic dispersion (square feet per day, ft^2/d), v_x is ground-water seepage velocity (feet per day, ft/d), S and n are Freundlich adsorption isotherm parameters, and k is a first-order rate constant for biodegradation of solute C (1/day). Solutions to this equation can be obtained by analytical or numerical methods, depending on the complexity of the problem at hand. Assuming that the plume has reached approximate steady-state conditions (i.e., the plume is not expanding or contracting with time and ($\partial C/\partial t=0$), the solute-transport equation simplifies to the ordinary differential equation:

$$0 = D\frac{d^2 C}{dx^2} - v_x \frac{dC}{dx} - kC$$

eq. 3.4

Which for boundary conditions of C = C_0 at x=0, and C=0 as $x \rightarrow \infty$ has the solution:

$$C(x) = C_o \exp - \left[\frac{v_x + \sqrt{v_x^2 - 4Dk}}{2D} \right] x$$

eq. 3.5

Equation 3.5 describes the exponential decrease in solute concentrations away from a constant source. The decrease is proportional to ground-water velocity (v_x), the coefficient of hydrodynamic dispersion (D), and the biodegradation rate constant (k). This solution does not take into account transverse dispersion.

The seepage velocity of ground water can be estimated by applying a modification of Darcy's equation, and the coefficient of hydrodynamic dispersion can be estimated from the scale of the plume. Given these estimates, k can be estimated by curve-fitting solutions of equation 3.5 to field data.

For chlorinated ethenes, this procedure is complicated by the fact that TCE, DCE, and VC are produced as daughter products from PCE as well as being degraded. TCE, DCE, and VC concentration changes along a flowpath segment reflect the difference between production and degradation. Thus, for TCE, *cis*-1,2-DCE, and VC, this procedure yields apparent degradation rate constants that underestimate actual degradation rate constants. In addition to underestimating degradation rate constants for daughter products, this method introduces several other sources of uncertainty, including those related to (1) source concentrations, (2) ground-water flow rates, (3) adequately sampling within the plume, and (4) deviations from steady-state conditions within the plume. While these sources of uncertainty can be reduced by extensive data collection and the use of more sophisticated models, they cannot be entirely eliminated. Because of these uncertainties, it is clear that degradation rate constants obtained with these methods should be regarded as rough estimates.

The conservative-tracer approach (Wiedemeier *et al.*, 1996b) corrects for dispersion and advection by using biologically conservative tracers such as chloride or trimethylbenzenes that are present in many contaminant plumes. If the decrease in contaminant concentration along a flowpath (which is affected by dispersion, dilution, and biodegradation) is a first-order relationship then it can be described by the equation:

$$C = C_o e^{-k_{tot}t}$$

eq. 3.6

Where C is contaminant concentration at some point downgradient along the flowpath, C_o is the initial contaminant concentration, k_{tot} is the total contaminant decay rate constant, and t is time. Then, the decrease in concentration of the conservative tracer (which is affected only by dispersion and dilution) is fit to the equation:

$$C_{TD} = C_o e^{-lt}$$

eq. 3.7

Where C_{TD} is the tracer-normalized contaminant concentration at some point downgradient along the flowpath, C_o is the initial contaminant concentration, λ is the biodegradation decay rate constant, and t is time. The first-order degradation rate constant λ is the biodegradation rate constant because the effects of dispersion, dilution, and volatilization have been removed by using the ratio of the conservative tracer concentration at the upgradient and downgradient points. The tracer-normalized contaminant concentration at some point downgradient along the flowpath is given by:

$$C_{TD} = C_D \left(\frac{T_A}{T_B} \right)$$

eq. 3.8

Where C_D is the measured concentration of the compound of interest at the downgradient point along the flowpath, T_A is the measured concentration of the tracer at the upgradient point, and T_B is the measured concentration of the tracer at the downgradient point. The reader is referred to Wiedemeier *et al.* (1996b) for an example of how to complete these calculations.

Biodegradation rates calculated by the mass-balance approach are subject to the same assumptions made in applying the dispersion-model approach. Therefore, it is clear that degradation rate constants obtained with these methods should be regarded as rough estimates In addition, the mass-balance approach assumes that a conservative tracer is present in the plume and can be used to correct for dilution and dispersion.

3.5 THE USE OF LABORATORY STUDIES

Caution should be exercised when using laboratory studies to assess the efficiency of natural attenuation processes at particular sites. Biodegradation processes are often specific to ambient redox conditions (i.e., oxic vs. anoxic conditions), the availability of electron donors and acceptors, and the availability of nutrients. All of these factors can be changed significantly, either intentionally or unintentionally, when sediments or ground water from a particular site are brought to the laboratory. For example, if anoxic sediments are collected and incubated under oxic conditions in the laboratory, these experimental results may greatly overestimate *in situ* rates of petroleum hydrocarbon biodegradation, or greatly underestimate rates of *in situ* chlorinated solvent biodegradation. It is difficult to verify that experimental conditions in the laboratory match ambient *in situ* conditions. Thus, conclusions from such studies are often difficult to interpret.

There are some circumstances, however, when laboratory studies are necessary. When specific questions are raised concerning conditions under which biodegradation processes occur or do not occur, controlled laboratory studies may be required (Bradley and Chapelle, 1996). For example, if concentrations of a particular compound are observed to decrease in the field, it may not be clear whether this decrease is due to sorption, dilution, or biodegradation. Laboratory studies in which the effects of each process can be isolated and controlled (they usually cannot be controlled in the field) are the only available method for answering these questions.

3.6 A WEIGHT-OF-EVIDENCE APPROACH FOR DEALING WITH UNCERTAINTY

The terrestrial subsurface varies in complexity from relatively straightforward "sand box" systems to extremely complex systems. In addition, the bio- and geochemical fate of dissolved organic compounds, especially the chlorinated solvents, can be quite complicated, and will vary depending on site conditions. To reduce the uncertainty associated with sampling and analyzing sediment and ground water from complicated systems, care should be taken when collecting samples, and independent and converging lines of evidence should be used to evaluate the efficiency of natural attenuation. 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 the ground water.

For example, methane data may suggest that redox conditions are sufficiently reducing to allow reductive dechlorination, but this piece of evidence alone is insufficient to show that reductive dechlorination is occurring. Additional evidence that could be used to document reductive dechlorination includes hydrogen concentrations in the range of sulfate reduction or methanogenesis; depleted dissolved oxygen, nitrate, and sulfate concentrations; lowered oxidation/reduction potential (ORP), the presence of daughter products that were not released at the site, and a stable contaminant plume. In total, the weight of this evidence strongly supports the inferred occurrence of reductive dechlorination.
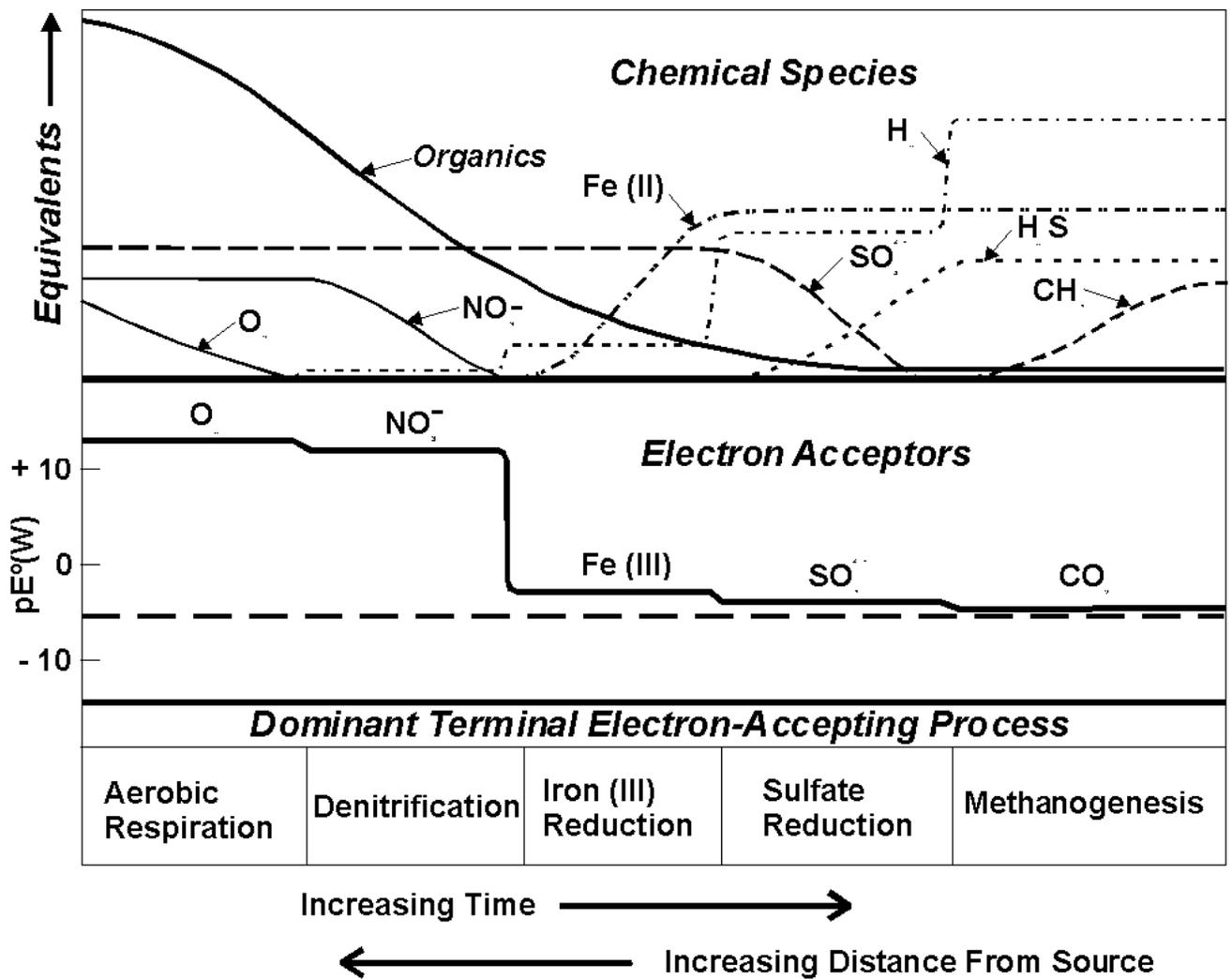
SECTION 4

NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS

4.1 INTRODUCTION

Field and laboratory studies conducted in the last twenty years have demonstrated that petroleum hydrocarbons, including aliphatic and aromatic compounds, are subject to a variety of biodegradation processes. More recent studies have shown that fuel oxygenates, such as MTBE, also are subject to microbial degradation processes. However, available data indicate that MTBE degrades less efficiently than BTEX. These processes are most commonly oxidative and can transform petroleum contaminants into carbon dioxide (CO_2) and water. Petroleum hydrocarbon degradation occurs in all shallow hydrologic systems under both oxic and anoxic conditions. These processes can effectively remediate contaminated ground water without human intervention. If it can be reliably shown that natural attenuation processes are sufficient to protect receptors from contamination, then they should be included in remedial action plans.

Biodegradation of petroleum hydrocarbons most commonly occurs by means of aerobic, nitrate-reducing, Fe(III)-reducing, sulfate-reducing, and methanogenic respiration. In addition Mn(IV) reduction can occur in some hydrologic environments, but is a minor component of electron flow compared to other electron acceptors. For this reason, Mn(IV) reduction is not explicitly discussed in this text but can be evaluated in the same manner as the other electron acceptors discussed in this document. Figure 4.1 illustrates the evolution of ground-water geochemistry in an initially pristine aquifer into which petroleum hydrocarbons are introduced. This hypothetical aquifer initially contains dissolved oxygen, nitrate, biologically available Fe(III), sulfate, all necessary nutrients, and has a positive ORP (oxidizing). Shortly after the introduction of petroleum hydrocarbons into an aquifer such as this, aerobic bacteria begin to biodegrade soluble organic compounds. Because of the low aqueous solubility of oxygen and the plethora of aerobic bacteria, the system soon becomes anoxic. After dissolved oxygen concentrations in an aquifer fall below about 0.5 mg/L, denitrification will begin if nitrate is present. During denitrification, nitrate concentrations typically decrease to the point where denitrification can no longer be supported. After the majority of the available nitrate is consumed, Fe(III) reducers will begin utilizing petroleum hydrocarbons if a suitable source of Fe(III) is available. During Fe(III) reduction, the amount of biologically available Fe(III) decreases, and Fe(II) concentrations increase. After the majority of the biologically available Fe(III) is consumed, sulfate reducers will begin utilizing petroleum hydrocarbons if sulfate is available. During sulfate reduction, sulfate concentrations decrease, typically to the point where this process can no longer be supported. After the majority of the available sulfate is consumed, methanogenesis becomes the dominant biodegradation mechanism. During methanogenesis, methane concentrations increase. Table 4.1 summarizes trends in contaminant, electron acceptor, metabolic byproduct during biodegradation of fuel hydrocarbons.

Chemical Species

Equivalents

Organics

Fe (II)

H

H S

O

NO⁻

SO

CH

Electron Acceptors

pE°(W)

O

NO⁻₃

+ 10

0

Fe (III)

SO

CO

- 10

Dominant Terminal Electron-Accepting Process

Aerobic Respiration	Denitrification	Iron (III) Reduction	Sulfate Reduction	Methanogenesis

Increasing Time →

← Increasing Distance From Source

After: Bouwer and McCarty, 1984

Figure 4.1

Geochemical Evolution of
Ground Water Contaminated
with Petroleum Hydrocarbons

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Table 4.1

**Trends in Contaminant, Electron Acceptor, and
Metabolic Byproduct Concentrations During Biodegradation**

Analyte	Trend in Analyte Concentrations During Biodegradation	Terminal Electron Accepting Processes Causing Trend
Petroleum hydrocarbons	Decrease	Aerobic Respiration, Denitrification, Mn(IV) Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis
Highly Chlorinated Solvents and Daughter Products	Parent Compound Concentrations Decrease, Daughter Products Increase Initially and Then May Decrease	Reductive Dechlorination and Cometabolic Oxidation
Lightly Chlorinated Solvents	Decrease	Aerobic Respiration and Fe(III) Reduction (Direct Oxidation) and Cometabolism (Indirect Oxidation)
Dissolved Oxygen	Decrease	Aerobic Respiration
Nitrate	Decrease	Denitrification
Mn(II)	Increase	Mn(IV) Reduction
Fe(II)	Increase	Fe(III) Reduction
Sulfate	Decrease	Sulfate Reduction
Methane	Increase	Methanogenesis
Chloride	Increase	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound
Oxidation/Reduction Potential	Decrease	Aerobic Respiration, Denitrification, Mn(IV) Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis, and Halorespiration
Dissolved Inorganic Carbon	Increase	Aerobic Respiration, Denitrification, Fe(III) Reduction, and Sulfate Reduction

4.2 METHODS FOR EVALUATING NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS

The precise methods for assessing the natural attenuation of petroleum hydrocarbons will vary from site to site depending on ambient conditions. Nevertheless, the following steps can be executed in sequence to evaluate the efficiency of natural attenuation processes in ground-water systems:

Step 1-- Install sufficient number of monitoring wells at the site to delineate the areal and vertical extent of ground-water contamination and determine the distribution of hydrostratigraphic units (see Section 6). Data quality objectives (DQOs) such as those presented in USEPA (1994) should be used when designing a sampling plan.

Step 2--Measure water levels in the wells, prepare a potentiometric map, determine hydraulic gradient, and perform slug tests or pumping tests to determine the distribution of hydraulic conductivity. Use measured hydraulic conductivity data, hydraulic gradient data, and estimates of aquifer porosity to determine the direction and velocity of ground-water flow using:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL}$$

<div align="right">eq. 4.1</div>

where v_x is the average ground-water seepage velocity (feet/day), dH/dL is the hydraulic gradient (dimensionless), K is the hydraulic conductivity (ft/d), and is n_e is the effective porosity (dimensionless).

Step 3--Measure concentrations of the indicator parameters listed in Table 3.1. The spatial relationships among contaminants, daughter products, inorganic electron acceptors, and metabolic byproducts can be used qualitatively to evaluate the occurrence of petroleum hydrocarbon degradation. Isopleth (isoconcentration) maps allow the investigator to map the relationships among these parameters in space. These maps portray graphically the first and second lines of evidence used to document natural attenuation. Figure 4.2 gives examples of completed isopleth maps for BTEX, dissolved oxygen, nitrate, Fe(II), sulfate, and methane. The patterns illustrated on Figure 4.2 show that there is a strong correlation among areas with elevated BTEX, depleted electron acceptor, and elevated metabolic byproduct concentrations. These relationships provide strong evidence that biodegradation is occurring via the processes of aerobic respiration, denitrification, Fe(III) reduction, sulfate reduction, and methanogenesis.

Step 4--Estimate Biodegradation Rates. Such estimates can be made by evaluating field or laboratory data (Buscheck and Alcantar 1995; Chapelle *et al*., 1996a; Wiedemeier *et al*., 1996b). Experience has shown that biodegradation kinetics for petroleum hydrocarbons are adequately described by a first-order rate law. In addition, experience has shown that there is a fairly narrow range (within an order of magnitude) of first-order rate constants for soluble petroleum hydrocarbons, as shown in Table 4.2.

Step 5--Using the Results of Steps 1, 2, and 4, Compare Rate of Contaminant Transport to Rate of Biodegradation. Such comparisons can be made using simple analytical solutions of the advection/dispersion equation such as that presented in the model BIOSCREEN (Newell *et al*., 1996). For complex problems (e.g., sites with a heterogeneous distribution of hydraulic conductivity), numerical solute transport models may be appropriate (Wiedemeier *et al*., 1995a; Chapelle *et al*., 1996).

Step 6--Evaluate Potential Receptor Impacts. If the efficiency of natural attenuation is sufficient to prevent contaminant transport to potential receptor exposure points (e.g., domestic wells or surface water bodies), then monitored natural attenuation may be a viable remedial option. If the efficiency of natural attenuation is insufficient to prevent contaminant transport to exposure points, then monitored natural attenuation may be ruled out as the sole remedial option, but may be used as a component of the overall cleanup strategy.
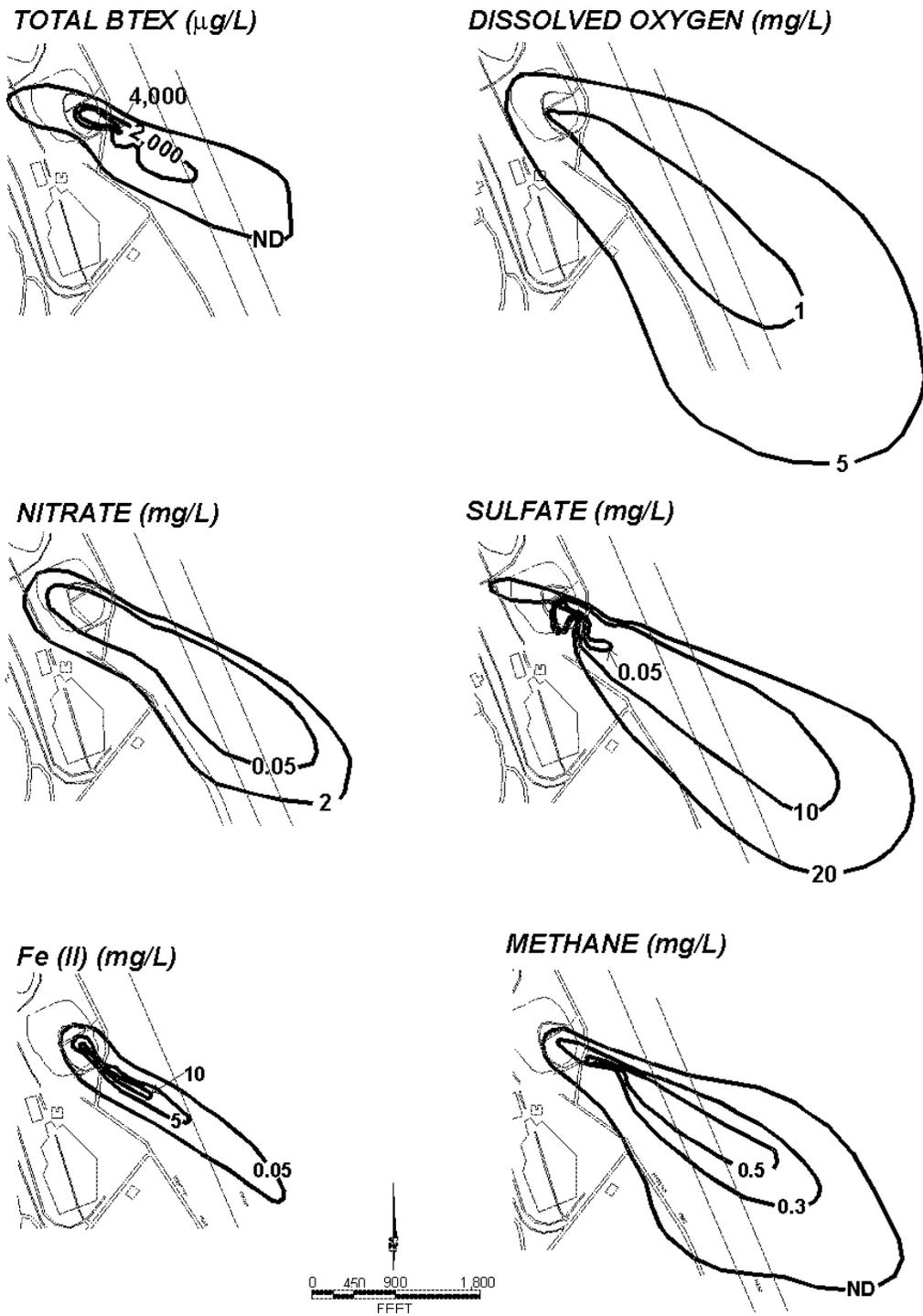
TOTAL BTEX (μg/L)

4,000

2,000

ND

DISSOLVED OXYGEN (mg/L)

1

5

NITRATE (mg/L)

0.05

2

SULFATE (mg/L)

0.05

10

20

Fe (II) (mg/L)

10

5

0.05

METHANE (mg/L)

0.5

0.3

ND

0   450   900   1,800

FEET

Figure 4.2

BTEX, Inorganic Electron Acceptor,
and Metabolic Byproduct Isopleth Maps

Table 4.2
Biodegradation Rate Constants

Site or Reference	Biodegradation Rate Constant				
	Benzene (1/day)	Toluene (1/day)	Ethylbenzene (1/day)	Xylenes (1/day)	Total BTEX (1/day)
Hill AFB, UT	0.025-0.028[a] 0.027-0.038[b]	0.023-0.026[a] 0.029-0.031[b]	0.009-0.02[a] 0.024-0.01[b]	0.006-0.027[a] 0.008-0.024[b]	0.01-0.02[a] 0.010.025[b]
Madison ANGB, WI					0.004[a]
Elmendorf AFB, AK – Hangar 10					0.01[a]
Elmendorf AFB, AK – ST-41					0.005[a]
MacDill AFB, FL – Pump House 75					0.0005[a]
Myrtle Beach, SC – POL facility					0.002[b]
Pope AFB, NC – FPTA #4					0.006[b]
Fairchild AFB, WA – Bldg 1212					0.007[b]
Eaker AFB, AR – Gas Station					0.006[b]
Dover AFB, DL – Site SS27/XYZ					0.003[a]
Bolling AFB, D.C. – Car Care Center					0.003[a]
Westover AFB, MA – Christmas Tree Fire Training Area					0.0034[b]
Columbus AFB, MS – ST-24					0.08[b]
Landmeyer *et al.* (1996)	0.00025	0.003			
Chapelle *et al.* (1996a)	0.003	0.01			
Chapelle *et al.*, (1996b)		0.001			
Stauffer *et al.* (1994)	0.07			0.13	
MacIntyre *et al.* (1993)	0.049 to 0.084			0.07 to 0.14	

a/ Biodegradation rate constant calculated using trimethylbenzene as a conservative tracer.
b/ Biodegradation rate constant calculated using the method of Buscheck and Alcantar (1995).
c/ Biodegradation rate constant from microcosm study.
d/ Biodegradation rate constant calculated using the method of Chapelle *et al*. (1996a).

SECTION 5

NATURAL ATTENUATION OF CHLORINATED SOLVENTS

5.1 INTRODUCTION

Field and laboratory studies conducted in the last ten years have demonstrated that chlorinated solvents, including chlorinated ethenes, ethanes, and benzenes, are subject to a variety of biodegradation processes. These biological processes include reductive and oxidative degradation pathways, and can ultimately transform these contaminants to environmentally innocuous carbon dioxide (CO_2) and chloride (Cl^-). In addition, abiotic mechanisms such as hydrolysis can work to degrade some of the common chlorinated solvents. For example, 1,1,1-trichloroethane can be degraded to 1,1-DCE via hydrolysis. Figure 5.1 summarizes the common biological and abiotic degradation reaction pathways for the chlorinated ethenes, ethanes, and methanes. If it can be reliably shown that natural attenuation processes are sufficient to protect receptors from contamination, then it is appropriate that they be included in remedial action plans. Conversely, if it can be reliably shown that natural attenuation processes are not sufficient to protect receptors, natural attenuation can be ruled out as a sole remedial option. Even when natural attenuation is not viable as the sole remedial action, it may be used as part of the overall site remediation strategy. It is less common for natural biodegradation to be efficient for chlorinated solvents than for petroleum hydrocarbons. This section provides technical guidelines for assessing the efficiency of natural attenuation processes for chlorinated solvents.

5.2 BACKGROUND INFORMATION

The microbial degradation of chlorinated solvents is complex. Under some redox conditions, these compounds can serve as electron donors in microbial metabolism; that is, microorganisms use them as a source of energy in the form of electrons. Under other redox conditions, chlorinated ethenes serve as electron acceptors, where microorganisms use them as a sink for electrons. In addition, these compounds can be degraded by various cometabolic processes .

Under anoxic conditions, chlorinated solvents can be reductively dechlorinated. For chlorinated ethenes (PCE, TCE, DCE, and VC) this process occurs in the following sequence:

$$PCE \Rightarrow TCE + Cl^- \Rightarrow DCE + Cl^- \Rightarrow VC + Cl^- \Rightarrow ethene + Cl^- \qquad eq.\ 5.1$$

However, the efficiency of dechlorination differs for particular compounds and for particular geochemical conditions. It is observed, for example, that dechlorination of PCE and TCE to DCE occurs under either mildly or strongly reducing conditions (Vogel *et al*., 1987), whereas the transformation of DCE to VC, and the transformation of VC to ethene, require the more strongly reducing conditions characteristic of methanogenesis (Friedman and Gossett, 1989; DeBrunin *et al*., 1992). Research indicates that reductive dechlorination is driven by molecular hydrogen, as shown on Figure 5.2 (DiStefano *et al*., 1991). As shown by this figure, a chlorine on the solvent molecule is removed and replaced with hydrogen during reductive dechlorination.
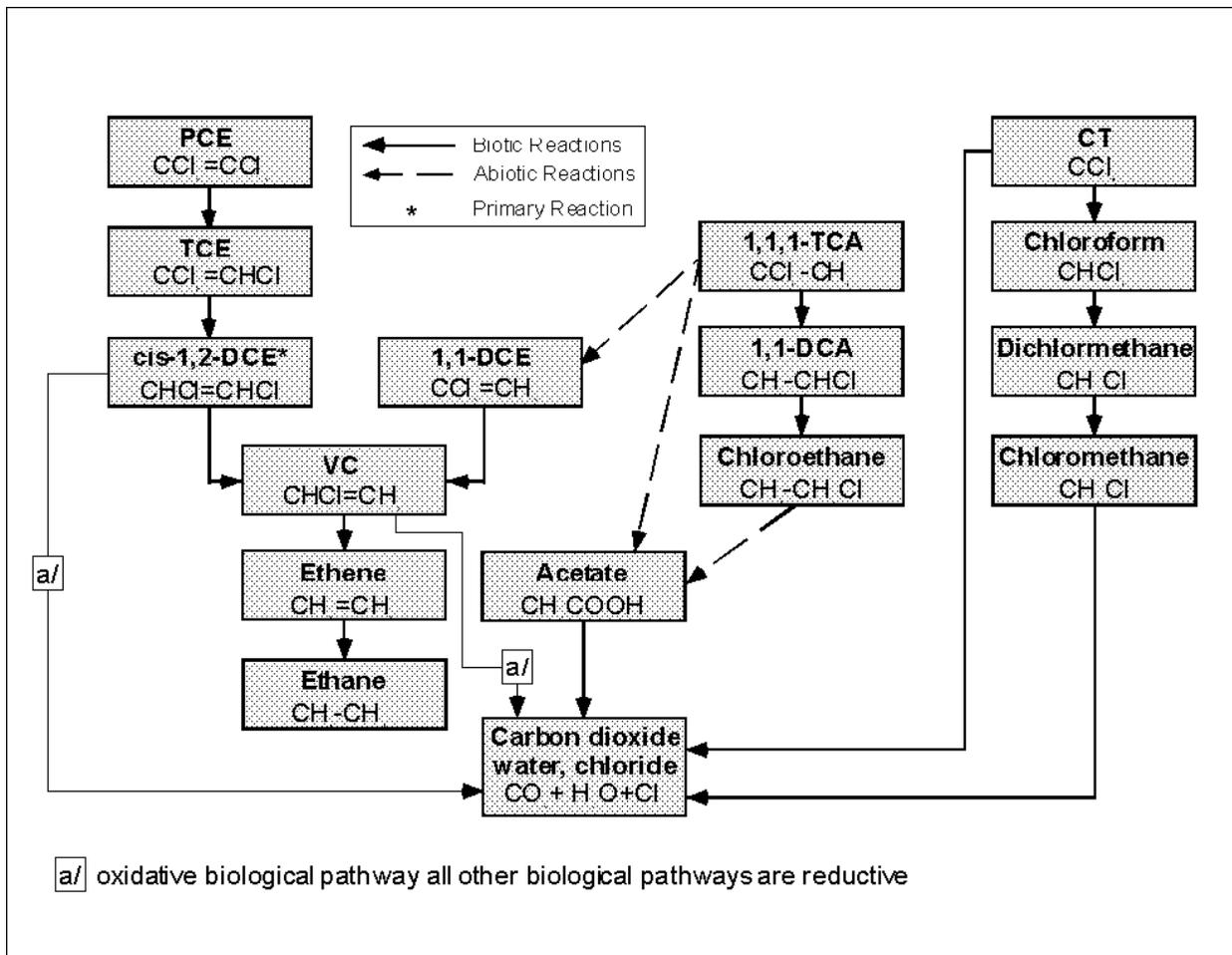
Figure 5.1

Abiotic and biological transformation pathways for selected
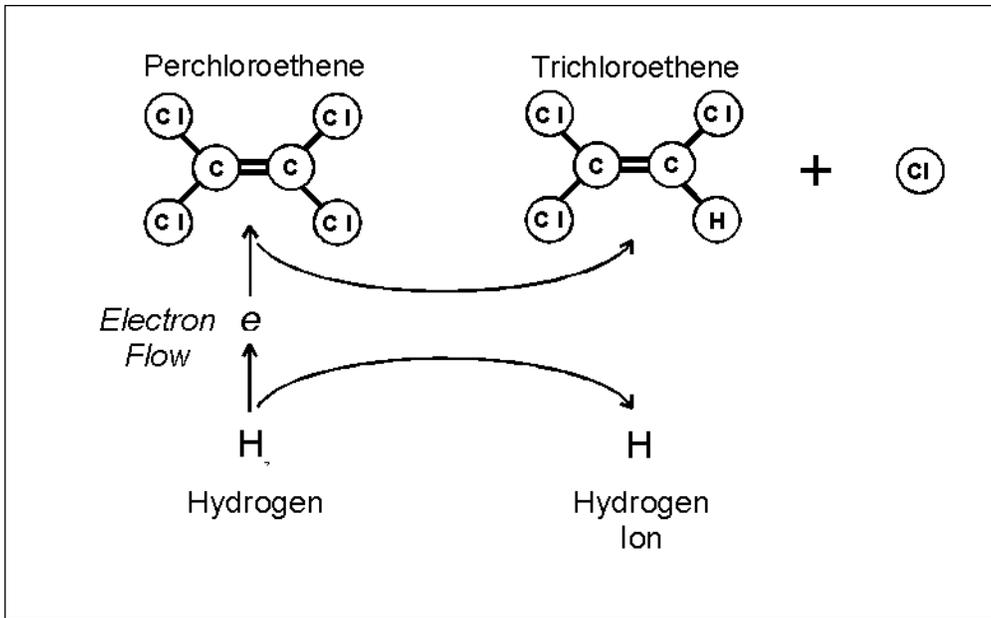chlorinated solvents (Modified from McCarty and Semprini, 1994; after Vogel et al., 1987)

Figure 5.2

Reductive Dechlorination of Perchloroethene to Trichloroethene

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This, in turn, shows why the efficiency of reductive dechlorination is sensitive to redox conditions. Hydrogen is continuously produced in anoxic systems by fermentation of organic matter. This is represented by the generalized relationship:

$$3CH_2O + H_2O \rightarrow CH_3COOH + CO_2 + 2H_2$$

The hydrogen produced by fermentation is then utilized by respirative microorganisms such as methanogens:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
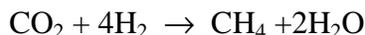
In microbial ecology, these coupled processes are known as interspecies hydrogen transfer. Because methanogenesis is a relatively inefficient hydrogen-consuming process, concentrations of molecular hydrogen are relatively high (Table 5.1). Hydrogen concentrations are progressively lower under sulfate-reducing, Fe(III)-reducing, and denitrifying conditions, which support successively more efficient hydrogen utilizers (Table 5.1).

Table 5.1

**Hydrogen Concentrations Characteristic of Different
Terminal Electron-Accepting Processes**

Terminal Electron-Accepting Process	Characteristic Hydrogen Concentration (nM)
Denitrification	<0.1
Fe(III) Reduction	0.2 – 0.8
Sulfate Reduction	1-4
Methanogenesis	>5

The efficiency of reductive dechlorination is directly linked to the availability of molecular hydrogen. Under denitrifying conditions, relatively little hydrogen is available, and reductive dechlorination is relatively inefficient. Conversely, significantly more hydrogen is available under methanogenic conditions and reductive dechlorination is proportionally more efficient.

While chlorinated solvents such as PCE and TCE are most commonly degraded by reductive dechlorination, the daughter products of reductive dechlorination can be directly oxidized (Davis and Carpenter, 1990; Bradley and Chapelle, 1996). For example, under oxic conditions, DCE and VC can be oxidized to carbon dioxide according to the equations:

for DCE $\quad\quad\quad Cl_2C_2H_2 + 2O_2 \Longrightarrow 2CO_2 + 2H^+ + 2Cl^-$ $\quad\quad\quad$ eq. 5.2

for VC $\quad\quad\quad ClC_2H_3 + 5/2\ O_2 \Longrightarrow 2CO_2 + H_2O + H^+ + Cl^-$ $\quad\quad\quad$ eq. 5.3

The complete degradation of chlorinated solvents is favored by sequential anoxic/oxic conditions (Chapelle, 1996):

anoxic (reductive dechlorination)   oxic (direct oxidation, cometabolism)

$$PCE, TCE \Rightarrow DCE \text{ and } VC \qquad \Rightarrow \qquad DCE, VC \Rightarrow 2CO_2 \text{ and } Cl^- \qquad \text{eq. 5.4}$$

The key to assessing the natural attenuation of chlorinated solvents, therefore, is an accurate delineation of redox conditions in ground-water systems.

5.3 DELINEATING TERMINAL ELECTRON-ACCEPTING PROCESSES IN GROUND-WATER SYSTEMS

The most common terminal electron-accepting processes (TEAPs) in ground-water systems are oxygen-, nitrate-, Fe(III)-, sulfate-, and carbon dioxide-reduction (methanogenesis). The stoichiometry of these processes can be represented by the generalized equations:

$$O_2 + CH_2O \Rightarrow CO_2 + H_2O \qquad \text{eq. 5.5}$$

$$4NO_3^- + 4H^+ + 5CH_2O \Rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{eq. 5.6}$$

$$4Fe(OH)_3 + CH_2O + 8H^+ \Rightarrow 4Fe^{2+} + CO_2 + 11H_2O \qquad \text{eq. 5.7}$$

$$2CH_2O + SO_4^{2-+} + H^+ \Rightarrow 2CO_2 + HS^- + 2H_2O \qquad \text{eq. 5.8}$$

$$2CH_2O \Rightarrow CH_4 + CO_2 \qquad \text{eq. 5.9}$$

The microorganisms that effect these electron-accepting processes compete with each other for available organic carbon sources. Because oxygen is the most efficient electron-accepting process, oxygen-reducing microorganisms outcompete other electron-accepting processes if dissolved oxygen is present in ground water. Once oxygen is depleted, nitrate-reducing microorganisms will predominate if nitrate is available. Similarly, Fe(III)-reduction follows nitrate reduction, sulfate reduction follows Fe(III) reduction, and methanogenesis follows sulfate reduction. This process of competitive exclusion leads to the formation of discrete redox zones in ground-water systems. Furthermore, this zonation can be deduced based on the presence/absence of electron acceptors, and the formation of specific end products (equations 5.5 through 5.9).

For example, if dissolved oxygen is present in ground-water at concentrations greater than 0.5 mg/L, then oxygen reduction (equation 5.5) will be the predominant microbial process. If dissolved oxygen concentrations are less than 0.5 mg/L, but nitrate is present at concentrations greater than 0.5 mg/L, nitrate reduction (equation 5.6) will be the predominant microbial process. Because nitrite (NO_2) is an unstable intermediate product of nitrate reduction (equation 5.6), the presence of measurable NO_2 concentrations is indicative of nitrate reduction. If ground water lacks dissolved oxygen or nitrate, and concentrations of Fe(II) increase along the flow path, Fe(III) reduction (equation 5.7) is the most likely predominant process. If ground water contains concentrations of sulfate greater than 0.5 mg/L and hydrogen sulfide greater than 0.05 mg/L, then sulfate reduction (equation 5.8) is the most likely predominant process. Finally, if the water

lacks dissolved oxygen, nitrate, Fe^{2+}, sulfate, and hydrogen sulfide, but contains concentrations of methane greater than 0.2 mg/L, then methanogenesis (equation 5.9) is the most likely predominant process. This logic is summarized in Figure 5.3 (Chapelle *et al*., 1995).

In practice, uncertainty is inherent in this method. Many products of microbial metabolism, such as Fe(II), hydrogen sulfide, and methane can be transported by ground-water flow. In cases where such transport is significant, it is difficult to determine the exact redox zonation with this water-chemistry information. In these cases, direct measurement of dissolved hydrogen gas (H_2) concentrations can be used to evaluate ambient redox processes (Figure 5.3). Fermentative microorganisms in ground-water systems continuously produce H_2 during anoxic decomposition of organic matter. This H_2 is then consumed by respiratory microorganisms that may use Fe(III), sulfate, or carbon dioxide as terminal electron acceptors. In microbial ecology, this process is referred to as interspecies hydrogen transfer. Significantly, Fe(III)-, sulfate-, and carbon-dioxide-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing H_2. Fe(III) reducers are relatively efficient in utilizing H_2, and thus they maintain lower steady-state H_2 concentrations (0.2 to 0.8 nM) than either sulfate reducers (1-4 nM H_2) or methanogens (> 5 nM H_2).   Because each TEAP has a characteristic hydrogen concentration associated with it, H_2 concentrations can be an indicator of predominant redox processes in ground-water systems.

5.4 ORGANIC CARBON SUBSTRATES THAT SUPPORT REDUCTIVE DECHLORINATION

Reductive dechlorination, a process in which chlorinated solvents serve as an electron acceptor, requires an organic carbon substrate in order to proceed.   These organic carbon substrates initially are degraded by fermentative bacteria that produce molecular hydrogen (H_2) and other organic compounds. This H_2 then reacts directly with the chlorinated solvent, resulting in reductive dechlorination (Figure 5.2). Many different kinds of organic carbon, including BTEX compounds, aliphatic petroleum hydrocarbons, naturally occurring particulate organic carbon (POC) in aquifer sediments, and natural dissolved organic carbon (DOC) can be fermented to H_2 to support reductive dechlorination. However, organic carbon compounds differ substantially in how efficiently they are fermented, and thus in how efficiently they can support reductive dechlorination. In particular, it is difficult to assess how efficiently natural DOC and POC are fermented. For these reasons, it is not currently technically feasible to quantitatively measure the mass of fermentable total organic carbon (TOC), which is the sum of DOC and POC, available in a ground-water system. TOC, some portion of which may be fermentable, can be measured (Table 3.1), and such measurements are appropriate for assessment of the reductive dechlorination capacity of a given system.

While it is difficult to quantify the available mass of fermentable organic carbon supporting reductive dechlorination, it is feasible to assess the geochemical conditions resulting from organic carbon metabolism in an aquifer.   For these reasons, it is more appropriate for assessments of natural attenuation to focus on ambient geochemical conditions (Section 5.3) than on measuring available organic carbon.
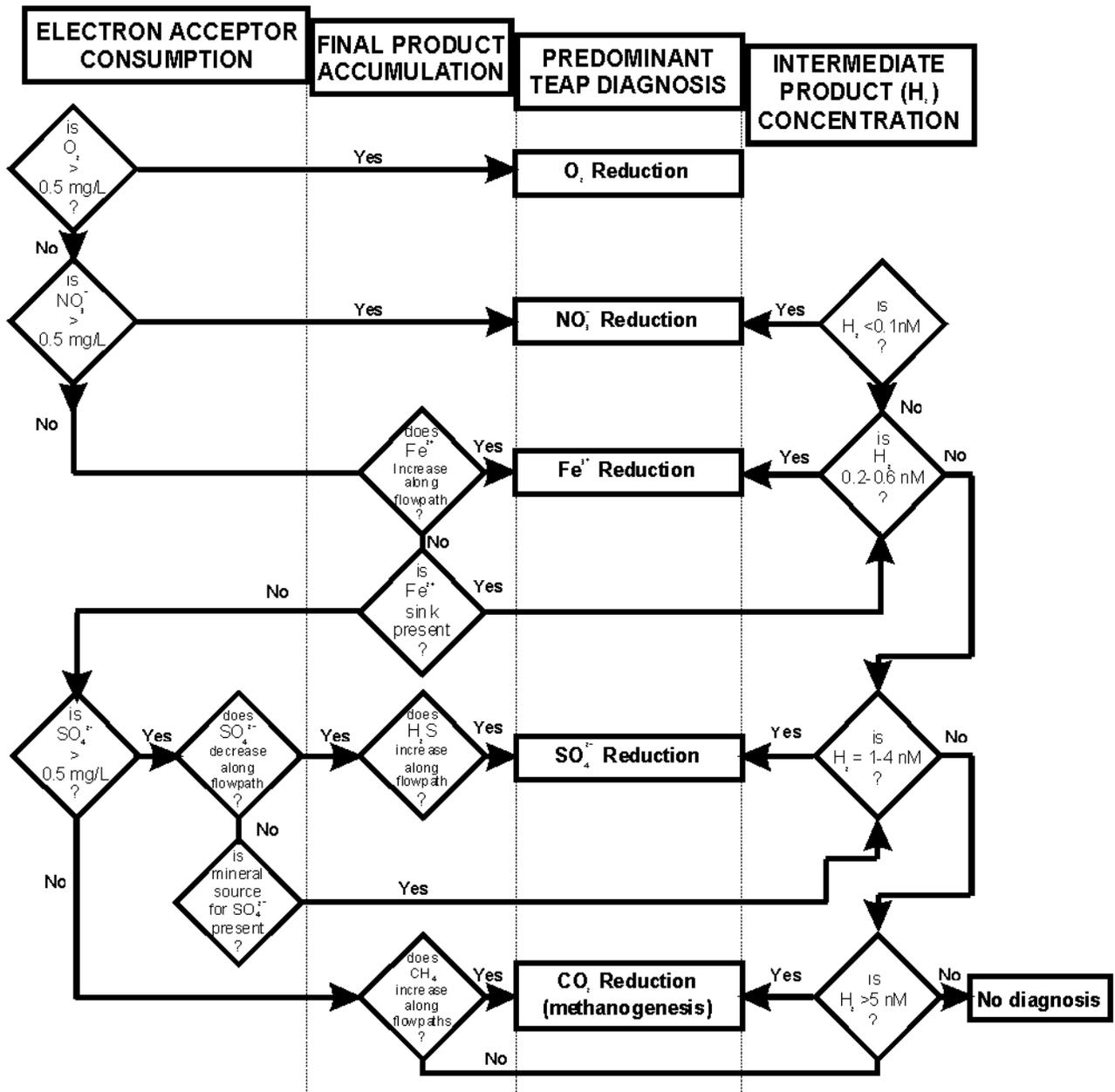
Figure 5.3

Logic for Deducing the Distribution of Terminal Electron-Accepting
Processes in Ground-Water Systems

5.5 Daughter Products as indicators of Reductive Dechlorination

Concentrations of chlorinated solvents and their degradation products give a direct indication of the presence or absence of microbial degradation (both reductive and oxidative) processes. In many cases, the production of *cis*-1,2-DCE, VC, and chloride ions along aquifer flowpaths is direct evidence of intrinsic bioremediation. It is possible that VC and some DCE isomers can be primary contaminants in some ground-water systems. However, VC is not normally present as a primary contaminant in solvent spills associated with military activities, because VC was not used as a solvent. Thus, the presence of VC in ground water associated with a chlorinated ethene spill is strong evidence of reductive dechlorination. Also, *cis*-1,2-DCE (rather than *trans*-1,2-DCE) is usually produced from the reductive dechlorination of TCE. As a rule of thumb, if *cis*-1,2-DCE comprises more than 80 percent of the total DCE, then the DCE is likely of biogenic origin (Wiedemeier *et al*., 1996a). Based on these concepts, VC and *cis*-1,2-DCE are reliable indicators of microbial reductive dechlorination.

5.6 METHODOLOGY FOR EVALUATING THE EFFICIENCY OF NATURAL ATTENUATION OF CHLORINATED ETHENES

The precise methods for assessing redox processes in ground-water systems will vary from site to site depending on ambient conditions. Nevertheless, the following steps are often appropriate to assess the efficiency of natural attenuation in a given ground-water system:

Step 1-- Install sufficient polyvinyl-chloride (PVC-) cased monitoring wells (if hydrogen measurements are to be taken) at the site to delineate the areal and vertical extent of ground-water contamination and to determine the distribution of hydrostratigraphic units (see Section 6). Data quality objectives (DQOs) such as those presented in USEPA (1994) should be used when designing a sampling plan.

Step 2--Measure water levels in the wells, prepare a potentiometric map, determine hydraulic gradient, and perform slug tests or pumping tests to determine the distribution of hydraulic conductivity. Use measured hydraulic conductivity data, hydraulic gradient data, and estimates of aquifer porosity to determine the direction and velocity of ground-water flow using equation 4.1 (repeated below):

$$v_x = -\frac{K}{n_e}\frac{dH}{dL}$$

where v is the average ground-water seepage velocity (ft/d), dH/dL is the hydraulic gradient (dimensionless), K is the hydraulic conductivity (ft/day), and is n_e is the effective porosity (dimensionless).

Step 3--Measure concentrations of the ground-water chemistry parameters listed in Table 3.1.

Step 4--Using the results of Step 3, apply the logic of Figure 5.3 to deduce the distribution of ambient redox processes at the site. In addition, use these data to document contaminant and chloride concentration changes as ground water flows downgradient.

Step 5--Categorize the site according to the progression of redox processes. The most common, but certainly not the only, progressions observed in the field include:

1. Methanogenic conditions at contaminant source area, grading to Fe(III)-reducing conditions immediately downgradient from the source area, and finally grading to oxic conditions further downgradient.

2. Sulfate-reducing or Fe(III)-reducing conditions at contaminant source area, grading to oxic conditions downgradient.

3. Oxic conditions at contaminant source area grading to reducing (Fe(III)-reducing, sulfate-reducing, or methanogenic) conditions downgradient.

4. Uniformly oxic conditions in contaminant source area and downgradient areas.

Step 6--Deduce the efficiency of natural biodegradation according to the progression of redox conditions, mass loss of solvent concentrations, and the production/destruction of daughter products according to the following general guidelines:

♦ **Progression of methanogenic $\Rightarrow$Fe(III) reduction $\Rightarrow$ oxic conditions**--rapid and efficient reductive dechlorination at the source area, followed by oxidation of DCE and VC downgradient of the source area. Extensive mass loss of solvent along aquifer flowpaths, and production and subsequent mass loss of daughter products along aquifer flowpaths. *Highly efficient natural attenuation is probable.*

♦ **Progression of sulfate- or Fe(III) reduction $\Rightarrow$ oxic conditions**--reductive dechlorination at source area followed by oxidation of DCE and VC downgradient from source area. Partial mass loss of solvents, and production and subsequent loss of daughter products along aquifer flowpaths. Low concentrations of PCE and TCE transported to oxic zone, where biodegradation processes stop, but dilution continues. *Moderately efficient natural attenuation is probable.*

♦ **Progression from oxic to anoxic conditions**--No reductive dechlorination at source area, some dechlorination and mass loss of solvent downgradient. Production and degradation of daughter products. *Moderately efficient natural attenuation is probable.*

♦ **Uniformly oxic conditions--**No reductive dechlorination, no production of oxidizable daughter products. *Inefficient natural attenuation is probable.*

Step 7--Evaluate the viability of monitored natural attenuation as a remedial strategy in the context of contaminant transport to receptors.

♦ **Efficient biodegradation, receptors not impacted**--monitored natural attenuation is a viable sole remedial strategy for ground water.

♦ **Efficient biodegradation, receptors impacted**--monitored natural attenuation is not a viable sole remedial strategy, but may be used in conjunction with other remedial strategies.

♦ **Moderate biodegradation, receptors not impacted--**monitored natural attenuation may be either a viable sole remedial strategy, or may be used in conjunction with other remedial strategies.

♦ **Moderate biodegradation, receptors impacted**--monitored natural attenuation is not a viable sole remedial strategy, but may be used in conjunction with other remedial strategies.

♦ **Inefficient biodegradation, receptors not impacted**—physical processes such as dispersion and dilution natural attenuation sufficient to disperse contaminants, monitored natural attenuation a possible remedial strategy.

♦ **Inefficient biodegradation, receptors impacted**--monitored natural attenuation not an appropriate sole remedial strategy, but may be used as part of a treatment train.

Step 8--<u>Engineer a site-specific remediation system.</u> If biodegradation is highly efficient at a site, and receptors are not impacted, it may be appropriate to use monitored natural attenuation as a sole remedial strategy. Natural attenuation, even when it is highly efficient, does not rapidly remove significant sources of contamination. For this reason, it is considered good engineering practice to combine the use of monitored natural attenuation with source removal if feasible. Conversely, if natural attenuation is inefficient and receptors are impacted, then other engineered options for controlling dissolved contaminant migration should be considered. It should be emphasized that the utilization of monitored natural attenuation, either as a stand-alone remedial strategy or in conjunction with other engineered remedial options, is highly site specific. Its successful utilization, or non-utilization, depends ultimately on sound scientific and engineering decision-making.

SECTION 6

IMPLEMENTING LONG-TERM MONITORING

To document that natural attenuation remains an effective and environmentally protective remedial approach, long-term monitoring must be implemented and a contingency plan developed. A comprehensive long-term monitoring and contingency plan is an integral part of any ground-water remedial action plan, and is necessary to demonstrate a commitment to protecting human health and the environment. These plans should be developed on a site-specific basis using the guidance presented below.

6.1 PLACEMENT OF LONG-TERM MONITORING AND CONTINGENCY WELLS, ANALYTICAL REQUIREMENTS, AND SAMPLING FREQUENCY

A typical long-term monitoring plan consists of siting ground-water monitoring wells and developing a ground-water sampling and analysis strategy. This plan is implemented to monitor the plume 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 and the results of the receptor exposure pathways analysis. Table 6.1 presents guidance that can be used to develop a site-specific monitoring program.

The long-term monitoring plan includes two types of monitoring wells. Long-term monitoring wells are intended to determine if the behavior of the plume is changing. Contingency wells are intended to detect movements of the plume outside the negotiated perimeter of containment, and to trigger an action to manage potential expansion. Figure 6.1 depicts (1) upgradient and crossgradient wells in unimpacted ground water; (2) a well in the source area; (3) a well downgradient from the source area in a zone of anoxic treatment; (4) a well in the zone of aerobic (oxic) 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 unimpacted ground water; and (6) three contingency wells. The locations of long-term monitoring wells should be based on the behavior of the plume interpreted from the initial site characterization and on regulatory considerations. Contingency wells should be placed at least 5-years travel time upgradient from potential receptor exposure points in the flow path of the impacted ground water. To be realistically conservative (i.e., protective of human health and the environment), this distance should be based on the advective velocity of the ground water rather than on the solute transport velocity. The final number and location of long-term monitoring and contingency wells should be developed in collaboration with the appropriate regulatory agencies.

Table 6.1
Progressive Monitoring Steps for a Natural Attenuation Program

Step	Description
I. Establish Data Collection Pointgs	Specify points of compliance and the points at which monitoring must be conducted
II. Define What is to be Monitored	Demonstration that natural attenuation is occurring according to expectations accomplished by including steps to: 1. Identify any potentially toxic transformation products; 2. Determine if plume is expanding (downgradient, laterally, or vertically); 3. Ensure no impact to downgradient receptors; detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy; 4. Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; 5. Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, or microbiological) that may reduce the efficacy of any of the natural attenuation processes; and 6. Verify attainment of cleanup objectives.
III. Establish the Time Period for Monitoring	Monitoring should continue as long as contamination remains above required cleanup levels and for a period after cleanup levels have been achieved that is long enough to ensure that concentration levels are stable and will remain below target levels.
IV. Define How Monitoring is to be Done	Demonstration of the monitoring approach being appropriate and verifiable by including steps to: 1. Specify methods for statistical analysis of data (e.g., established tolerances, seasonal and spatial variability); 2. Establish performance standards; • Collect data useful for monitoring the performance of natural attenuation (e.g. EPA/540/R-97/504, EPA/600/R-94/162) • EPA/600/R-94/123: collection and evaluation of performance monitoring data for pump-and-treat remediation systems 3. Establish a time interval 4. Include in reporting: maps, tabulation of data and statistical analysis, identification of trends, recommendations for changes in approach, evaluationsof whether contaminants behave as predicted, and of whether other remedies are required.
V. Define Action Levels or Process to Observe Monitoring	Valid interpretation of the monitoring system is demonstrated by steps to: 1. Establish background levels; 2. Define criteria that show if a plume is expanding or diminishing; 3. Define criteria that show that the conceptual model is applicable to a site; and 4. Establish how measurement of cleanup objectives and effectiveness will be determined.
VI. Define Contingency Plan	Establishment of contingency plan if monitoring system action criteria are exceeded. Make sure that the following actions are taken before the contingency plan is implemented : 1. Ensure that changes in contaminant concentrations are statistically significant; 2. Identify extent and nature of non-predicted behavior; 3. Reevaluate conceptual model; and 4. Evaluate feasible corrective actions from previous and evolving contingency plan

(Modified from Sandia National Laboratories, 1998)

NAPL Source Area

Extent of Dissolved Contaminant Plume

Direction of Plume Migration

LEGEND

● Contingency Well

○ Long-Term Monitoring Well

Not To Scale

Note: Complex sites may require more wells. The final number and placement should be determined in conjunction with the appropriate regulators.

Figure 6.1
Hypothetical Long-Term Monitoring Strategy -
Non-Discharging Plume

C:\navy protocol\figures\fig-6-1.cdr

The results of a solute fate and transport model can be used to help site the long-term monitoring and contingency wells. In order to provide a valid monitoring system, all monitoring wells must be screened in the hydrogeologic unit(s) affected by the contaminant plume. Geochemical data should be used when possible to confirm that downgradient wells are sampling ground water that was once contaminated with organic compounds. Wells downgradient from and completed in the same stratigraphic horizon as a contaminant plume that do not contain organic compounds but have depleted electron acceptor (e.g., dissolved oxygen, nitrate, sulfate) or elevated metabolic byproduct concentrations (e.g., Fe(II), methane, chloride, alkalinity) relative to background provide conclusive evidence that the ground water being sampled flowed through the contaminant plume and has been treated. Because concentrations of electron acceptors and metabolic byproducts will equilibrate with ambient conditions at some distance downgradient from the contaminant plume, it is important to locate at least one well close to the downgradient edge of the contaminant plume. This also will allow better resolution of the behavior of the leading edge of the plume. Figure 6.2 illustrates how geochemical data can be used to ensure correct placement of downgradient monitoring wells.

A ground-water sampling and analysis plan should be prepared in conjunction with contingency and long-term monitoring well placement. For long-term monitoring wells, ground-water analyses should include organic contaminants of concern. In addition, samples for analysis of dissolved oxygen, nitrate, Fe(II), sulfate, methane, and hydrogen (chlorinated solvent plumes only) analyses should be collected on a periodic basis to ensure that the prevailing ground-water geochemistry has not changed to the extent that intrinsic bioremediation ceases. This is particularly important for sites contaminated with chlorinated solvents.

If monitored natural attenuation is selected as part of site remediation, a long-term monitoring program is necessary to verify its effectiveness. The long-term monitoring strategy should consider the possibility that the behavior of a plume may change over time and monitor for the continued availability of a carbon source to support reductive dechlorination.

For contingency wells, ground-water analyses should be limited to contaminants of concern. 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 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 establish baseline conditions. Based on the results of the first year's sampling, the sampling frequency may be reduced to annual sampling (or less). Sampling frequency is dependent on the final placement of the contingency wells and on ground-water flow velocity. The final sampling frequency should be determined after consideration of well spacing and solute transport velocity.

West   East

Extent of Dissolved
Contaminant Plume

$O_2 = 6.5$ mg/L
$NO_3^- = 13$ mg/L
$SO_4^{2-} = 96$ mg/L
$CH_4 < 0.001$ mg/L

I

$O_2 = 8.5$ mg/L
$NO_3^- = 13$ mg/L
$SO_4^{2-} = 89$ mg/L
$CH_4 < 0.001$ mg/L

J

Extent of NAPL

A   B   C D   E F G   H

$O_2 = 8$ mg/L
$NO_3^- = 10$ mg/L
$SO_4^{2-} = 100$ mg/L
$CH_4 < 0.001$ mg/L

$O_2 = 0.1$ mg/L, $NO_3^- = 0.2$ mg/L
$SO_4^{2-} = 3$ mg/L, $CH_4 = 10$ mg/L

$O_2 = 0.3$ mg/L
$NO_3^- = 0.5$ mg/L
$SO_4^{2-} = 8$ mg/L
$CH_4 = 7$ mg/L

L

Ground-Water
Flow Direction

K

West   East

A   B   C D   E F G   H

Extent of Dissolved
Contaminant Plume
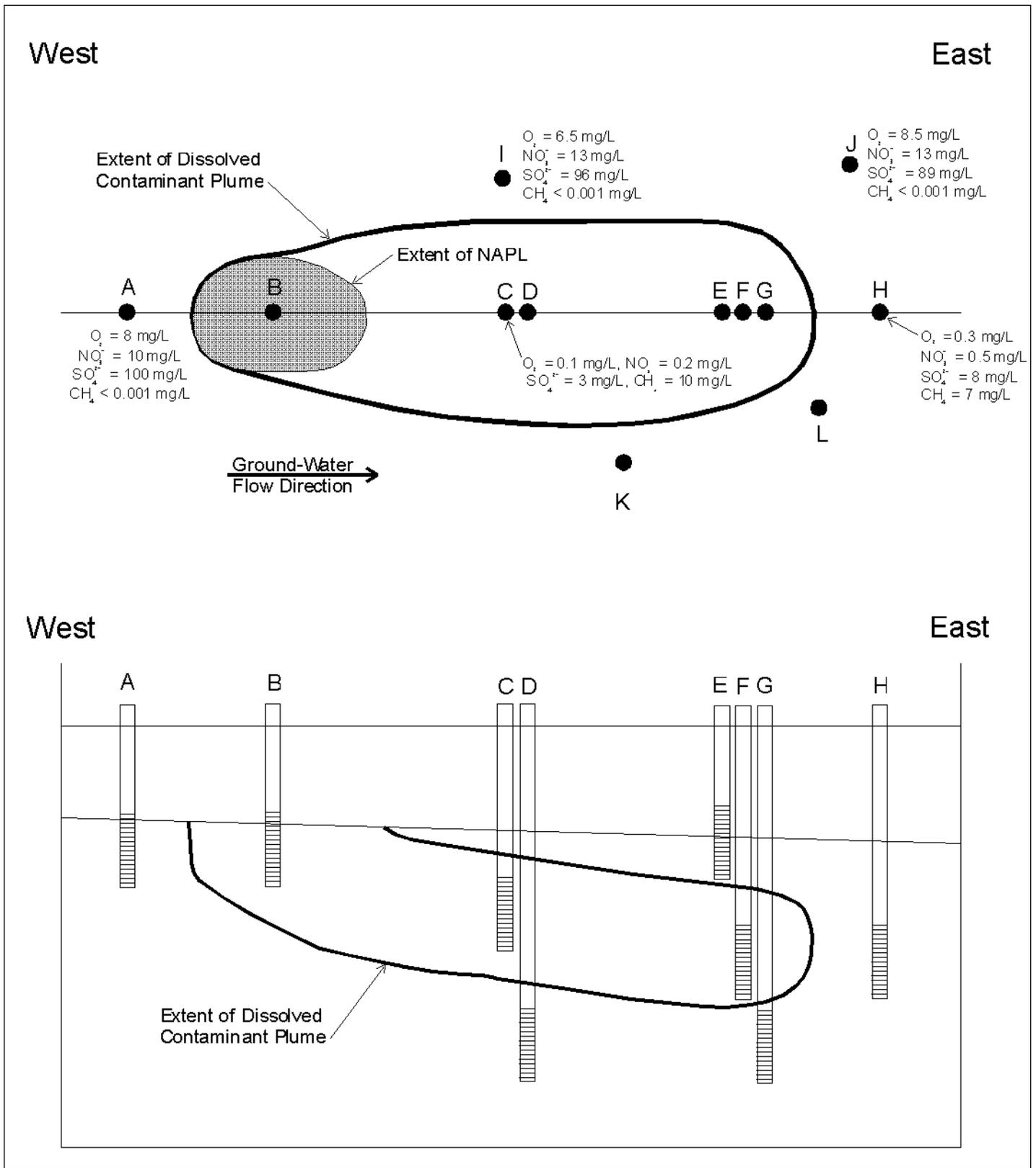
Figure 6.2

Use of Geochemical Data for
Monitoring Well Placement

6.2 Interactions Between Natural Attenuation and Engineered Remediation Systems

The guidance issued by the USEPA (1997) Office of Solid Waste and Emergency Response recommends that source reduction should be considered for all sites where monitored natural attenuation is used for site remediation. Although engineered remediation systems may be effective in removing contaminant mass from ground water, some systems may have an adverse impact on intrinsic bioremediation (Table 6.2). For example, the introduction of oxygen via air sparging into a system contaminated with chlorinated solvents will inhibit reductive dechlorination, thus decreasing the effectiveness of natural attenuation. Similarly, a ground-water pump-and-treat system can affect the natural treatment system by delivering oxygen-rich ground water to the contaminant plume. In light of this, it is very important to consider the interactions between a proposed engineered remediation system and naturally occurring processes. In addition, these interactions can be expected to affect the efficiency and total cost of the remediation effort. The impact of such costs, which are not included in Table 6.2, may be considerable.

6.3 CONTINGENCY PLANS

Because changing site conditions (e.g., redox conditions, ground-water recharge rates, the availability of organic carbon, etc.) can result in variable plume behavior over time, especially with chlorinated solvent plumes, contingency plans should be developed. These plans will ensure protection of human health and the environment should a contaminant plume begin migrating, and typically will involve some kind of engineered remediation. A properly designed contingency monitoring system will allow plume expansion to be detected so that the contingency plan can be implemented before receptors are exposed.

The placement of contingency wells should be made based on the ground-water seepage velocity and the distance to potential receptors. It is important when placing contingency wells and determining sampling frequencies that the guidelines discussed in Section 6.1 be followed. The "trigger" that initiates contingency plan implementation should be based on statistically significant contaminant detections in contingency monitoring wells. For example, one detection of TCE at 3 micrograms per liter in the seventh of 10 sampling events may be due to random error in the data. Thus, depending on the placement of contingency wells relative to potential receptor locations, one detection of contaminants in a contingency well typically is not sufficient to trigger implementation of the contingency plan. Additional time-series data should be collected to determine if the plume is actually migrating. Guidance on statistical significance is given in Gilbert (1987) and USEPA (1989).

Careful thought must be given to the remedial action to be implemented should natural attenuation prove not to be effective. The contingency remedial option should be selected so that it will (1) prevent further plume migration, and (2) minimize the detrimental impacts on the natural treatment system. The most common remediation technologies and their relationship with natural attenuation are listed in Table 6.2.

Table 6.2

Interactions Between Active Remediation Technologies and Natural Attenuation

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	**Chlorinated Solvents**	**Petroleum Hydrocarbons**	**Chlorinated Solvents**
Bioslurping	Volatilization, enhanced oxygen delivery/aerobic biodegradation	Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Pump and Treat	Plume containment, enhanced oxygen delivery/aerobic biodegradation	Plume containment, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Air Sparging	Volatilization, enhanced oxygen delivery/aerobic biodegradation	Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
In-Well Circulation/Stripping	Volatilization, enhanced oxygen delivery/aerobic biodegradation	Volatilization, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Landfill Caps	Source containment/ isolation	Source containment/isolation, reduced oxygen delivery through elimination of recharge/stimulation of reductive dechlorination	Reduced oxygen delivery/aerobic biodegradation	Decreased oxidation of DCE and VC, decreased aerobic cometabolism

Table 6.2

Interactions Between Active Remediation Technologies and Natural Attenuation (Con't)

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	**Chlorinated Solvents**	**Petroleum Hydrocarbons**	**Chlorinated Solvents**
Phytoremediation	Plant-specific transpiration/enzymatically-mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment	Plant-specific transpiration/enzymatically-mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment	None	Unknown
Excavation/Backfilling	Source Removal, enhanced oxygen delivery/aerobic biodegradation	Source Removal, enhanced oxidation of DCE and VC, possible enhanced aerobic cometabolism	None	Enhanced oxygen delivery/decreased reductive dechlorination
Chemical Oxidation (e.g, Fenton's Reagent, potassium permanganate, etc.)	Enhanced oxidation	Enhanced oxidation	None	Enhanced oxygen delivery/decreased reductive dechlorination through oxidation and removal of fermentable carbon substrates. Lowered pH possibly inhibits microbial activity

Table 6.2

Interactions Between Active Remediation Technologies and Natural Attenuation (Concluded)

Technology	Possible Benefits		Possible Detriments	
	Petroleum Hydrocarbons	**Chlorinated Solvents**	**Petroleum Hydrocarbons**	**Chlorinated Solvents**
Chemical Reduction (e.g., sodium dithionate)	Unknown	Scavenges inorganic electron acceptors/enhanced reductive dechlorination	Scavenges inorganic electron acceptors/decreased oxidation	Decreased oxidation of DCE and VC, decreased aerobic cometabolism
Oxygen-Releasing Materials	Enhanced oxygen delivery/aerobic biodegradation	Enhanced oxidation of DCE and VC	None	Decreased reductive dechlorination through oxidation and removal of fermentable carbon substrates.
Carbon Substrate Addition	None	Stimulation of reductive dechlorination	Competing carbon source	Decreased oxidation of DCE and VC, decreased aerobic cometabolism at injection point
Zero-Valent-Iron Barrier Walls	Unknown	Enhanced reductive dechlorination	Unknown	None
Biological Barrier Walls	Unknown	Enhanced reductive dechlorination	Unknown	None

6.4 EXIT STRATEGY

The long-term monitoring plan should include an exit strategy that will allow closure of the site after a reasonable amount of data based on site conditions has been collected to show that natural attenuation will remain protective of human health and the environment. For example, an exit strategy may state that long-term monitoring will cease after remediation goals are achieved. These remediation goals are site-specific and depend on ground-water use, future land development and use, and potential receptor considerations. The exit strategy should be clearly stated in the remedial action plan.

SECTION 7

REFERENCES

Beakins, B.A., E. Warren, and E.M. Godsy, 1998, A comparison of zero order, first order, and Monod biotransformation models: *Ground Water*, v36, 261-268.

Borden, R.C., R.A. Daniel, L.E. LeGrun, and C.W. Davis, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer: *Water Resources Research*, v33, p. 1105-1115.

Bouwer, E.J., and McCarty, P.L., 1984, Modeling of trace organics biotransformation in the subsurface: *Ground Water*, vol. 22, no. 4, p. 433-440.

Bradley, P.M. and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe(III) reducing aquifer sediments. *Environmental Science & Technology* 40: 2084-2086.

Buscheck, T.E., and O'Reilly, K.O., 1995, *Protocol for Monitoring Intrinsic Bioremediation in Groundwater*: Chevron Research and Development Company.

Buscheck, T.E. and Alcantar, C.M., 1995, "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In, Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioreclamation, April 1995

Chapelle, F.H., 1993, Ground-Water Microbiology and Geochemistry: John Wily & Sons, Inc., New York, 424 p.

Chapelle, F.H., 1996, Identifying redox conditions that favor the natural attenuation of chlorinated ethenes in contaminated ground-water systems. Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, EPA/540/R-96/509, p. 17-20.

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resources Research* 31:359-371.

Chapelle, F.H., Bradley, P.M., Lovley, D.R., and Vroblesky, D.A., 1996a, Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods: *Ground Water*, v. 34, no. 4, p. 691-698.

Chapelle, F.H., Landmeyer, J.E., and Bradley, P.M., 1996b, Assessment of intrinsic bioremediation of jet fuel contamination in a shallow aquifer, Beaufort, South Carolina: USGS Water-Resources Investigations Report 95-4262, 30p.

Chapelle, F.H., Vroblesky, D.A., Woodward, J.C., and Lovley, D.R., 1997, Practical considerations for measuring hydrogen concentrations in groundwater: *Environmental Science and Technology*, v. 31:2873-2877.

Davis, J.W., and Carpenter, C.L., 1990, Aerobic biodegradation of vinyl chloride in groundwater samples: *Applied and Environmental Microbiology*, 56:3878-3880.

DeBrunin, W.P., M.J.J. Kotterman, M.A. Posthumus, G. Schraa, and A.J.B. Zehnder. 1992. Complete biological reductive transformation of tetrachloroethene to ethane. *Applied and Environmental Microbiology* 58:1996-2000.

DiStefano, T.D., J.M. Gossett, and S.H. Zinder.1991. Reductive dechlorination of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture in the absence of methanogenesis. *Applied and Environmental Microbiology* 57:2287-2292.

Friedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. *Applied and Environmental Microbiology* 55:2144-2151.

Gilbert, R.O., 1987, Statistical Methods for Environmental Pollution Monitoring: Van Nostrand Reinhold, 320 p.

Kampbell, D.H., Wilson, J.T., and Vandegrift, S.A., 1989, Dissolved oxygen and methane in water by a GC headspace equilibrium technique: *International Journal of Environmental Analytical Chemistry*, v. 36, p. 249-257.

Landmeyer, J.E., Chapelle, F.H., and Bradley, P.M., 1996, Assessment of intrinsic bioremediation of gasoline contamination in the shallow aquifer, Laurel Bay Exchange, Marine Corps Air Station, Beaufort, South Carolina: USGS Water-Resources Investigations Report 96-4026, 50p.

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley, J.F. Pankow, C.D. Church, and P.G. Tratnyek, 1998, Fate of MTBE relative to benzene in a gasoline contaminated aquifer (1993-98): *Ground Water Monitoring and Remediation,* Fall 1998.

Mace, R.E., Fisher, R.S., Welch, D.M., and Parra, S.P., 1997, Extent, mass, and duration of hydrocarbon plumes from leaking petroleum storage tank sites in Texas: Bureau of Economic Geology Geological Circular 97-1.

MacIntyre, W.G., Boggs, M., Antworth, C.P., and Stauffer, T.B., 1993, Degradation kinetics of aromatic organic solutes introduced into a heterogeneous aquifer: *Water Resources Research*, v. 29, no. 12, p. 4045-4051.

McCallister, P.M., and Chiang, C.Y., 1994, A practical approach to evaluating natural attenuation of contaminants in ground water: *Ground Water Monitoring Review*, Spring, 1994, p. 161-173.

McCarty, P.L., and Semprini, L., 1994, Ground-water treatment for chlorinated solvents, In Norris, R.D., Hinchee, R.E., Brown, R., McCarty, P.L, Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bouwer, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and Ward, C.H., editors, *Handbook of Bioremediation*: Lewis Publishers, p. 87-116.

Newell, C.J., McLeod, R.K., and Gonzales, J.R., 1996, BIOSCREEN Natural Attenuation Decision Support System, Version 1.3, U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, San Antonio, Texas (http://www.epa.gov/ada/kerrlab.html).

Rice, D.W., R.D. Grose, J.C. Michaelsen, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.G. Everett, and M.A. Marino, 1995, *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*: California State Water Resources Control Board.

Sandia National Laboratories, 1998, *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites*, Draft, June 29, 1998.

Stauffer, T.B., T.B. Antworth, J.M. Boggs, and W.G. MacIntyre. 1994. "A Natural Gradient Tracer Experiment in a Heterogeneous Aquifer with Measured In Situ Biodegradation Rates: A Case for Natural Attenuation." In *Proceedings of the Symposium on Intrinsic Bioremediation of Groundwate*r, August 30 - September 1, 1994. US Environmental Protection Agency, p. 73 - 84.

USEPA, 1989, *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities – Interim Final Guidance*, EPA/530-SM-09-026, Interim Final, April 1989.

USEPA, 1994, *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, Final, Sept 1994

USEPA, 1997, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, Draft Interim Final :U.S. EPA Office of Solid Waste and Emergency Response Directive 9200.4-17 (http://www.epa.gov/OUST/directiv/9200417z.htm)

Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. *Environmental Science and Technology* 21:721-736.

Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1995a, *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*: US Air Force Center for Environmental Excellence, San Antonio, Texas.

Wiedemeier, T.H., Wilson, J.T., and Miller, R.N., 1995b, Significance of Anaerobic Processes for the Intrinsic Bioremediation of Fuel Hydrocarbons: In *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference*: NWWA/API.

Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Wilson, J.T., Wilson, B.H., Kampbell, D.H., Hansen, J.E., Haas, P., and Chapelle, F.H., 1996a, Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater, Draft - Revision 1:, Air Force Center for Environmental Excellence, San Antonio, Texas.

Wiedemeier, T.H., Swanson, M.A., Wilson, J.T., Kampbell, D.H., Miller, R.N., and Hansen, J.E., 1996b, Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water: *Ground Water Monitoring and Remediation,* v. 16, no. 3, Summer 1996, p. 186-194.

Wiedemeier, T.H., Rifai, H.S., Newell, C.J., and Wilson, J.T., 1998, *Natural Attenuation of Fuels and Solvents in the Subsurface*: John Wiley and Sons, New York, In Press.

APPENDIX A

NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS – A CASE STUDY

ASSESSMENT OF INTRINSIC BIOREMEDIATION OF JET FUEL CONTAMINATION IN A SHALLOW AQUIFER, BEAUFORT, SOUTH CAROLINA
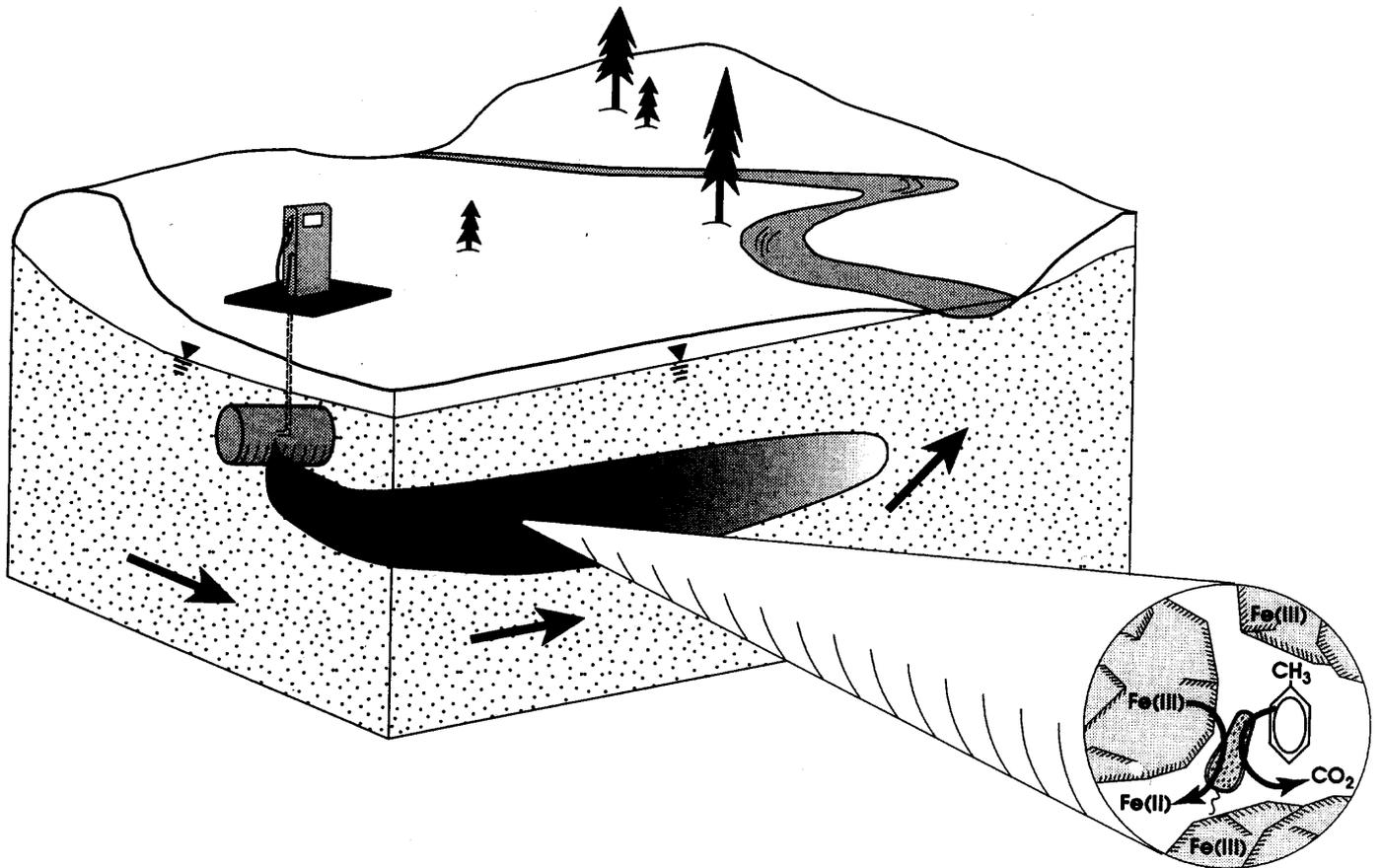
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BRUCE BABBITT, *Secretary*

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ASSESSMENT OF INTRINSIC BIOREMEDIATION OF JET FUEL CONTAMINATION IN A SHALLOW AQUIFER, BEAUFORT, SOUTH CAROLINA

By Francis H. Chapelle, James E. Landmeyer, and Paul M. Bradley

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
foot per foot (ft/ft)	0.3048	meter per meter
square foot (ft^2)	6.09294	square meter
	Flow	
foot per day (ft/d)	0.3048	meter per day
foot per year (ft/yr)	0.3048	meter per year
square foot per day (ft^2/d)	0.09290	square meter per day
	Volume	
gallon (gal)	3.785	liter
ounce	28.35	gram

Temperature: In this report, temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = (1.8 \times °C) + 32$$

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration: In this report, chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Radiochemical activity: In this report, radioactivity units are given in microcuries (µCi)

Biodegradation rate constant: In this report, first-order kinetics are used to model biodegradation rates of petroleum hydrocarbons. First-order rate constants (K_{bio}) are expressed in units of percent of compound degraded per day (%/d). Because percent is dimensionless, this reduces to units of inverse days (d^{-1}).

Adsorption coefficient: In this report, the adsorption coefficient (K_{ad}) is expressed as centimeters cubed per gram (cm^3/g), which are equivalent to units of liters per kilogram (L/kg).

ASSESSMENT OF INTRINSIC BIOREMEDIATION OF JET FUEL CONTAMINATION IN A SHALLOW AQUIFER, BEAUFORT, SOUTH CAROLINA

By Francis H. Chapelle, James E. Landmeyer, and Paul M. Bradley

ABSTRACT

Field and laboratory studies show that microorganisms indigenous to the ground-water system underlying Tank Farm C, Marine Corps Air Station Beaufort, S.C., degrade petroleum hydrocarbons under aerobic and anaerobic conditions. Under aerobic conditions, sediments from the shallow aquifer underlying the site mineralized radiolabeled (^{14}C) toluene to $^{14}CO_2$ with first-order rate constants of about -0.29 per day. Sediments incubated under anaerobic conditions mineralized radiolabeled toluene more slowly, with first-order rate constants of -0.001 per day. Although anaerobic rates of biodegradation are low, they are significant in the hydrologic and geochemical context of the site. Because of low hydraulic conductivities (1.9-9.1 feet per day) and low hydraulic gradients (about 0.004 feet per feet), ground water flows slowly (approximately 20 feet per year) at this site. Furthermore, aquifer sediments contain organic-rich peat that has a high sorptive capacity. Under these conditions, hydrocarbon contaminants have moved no further than 10 feet downgradient of the jet fuel free product. Digital solute-transport simulations, using the range of model parameters measured at the site, show that dissolved contaminants will be completely degraded before they are discharged from the aquifer into adjacent surface-water bodies. These results show that natural attenuation processes are containing the migration of soluble hydrocarbons, and that intrinsic bioremediation is a potentially effective remedial strategy at this site.

INTRODUCTION

In June 1990, a leak occurred from a corroded section of pipe during a jet fuel (JP-5) transfer operation at Tank Farm C, Marine Corps Air Station (MCAS) Beaufort, South Carolina. The leaking pipe was about 3 ft below land surface, and the loss of fuel totaled approximately 10,600 gal. The leak was reported to the South Carolina Department of Health and Environmental Control (SCDHEC), and a site assessment was completed (U.S. Navy Department, 1993). This assessment showed the presence of JP-5 as free product at the point of the original spill, the presence of dissolved hydrocarbons in ground water, and that site remediation would be needed to remove the contaminants.

The U.S. Geological Survey, in cooperation with the Southern Division Naval Facilities Engineering Command, U.S. Navy, and MCAS Beaufort quantified hydrologic, geochemical, and microbial parameters in sediments from the Tank Farm C site to facilitate simulation of intrinsic bioremediation. The objective of the study was to establish a framework for assessing the efficiency of intrinsic bioremediation at the site.

Purpose and Scope

The purpose of this report is to present an evaluation of the feasibility of intrinsic bioremediation to remove soluble hydrocarbons from contaminated ground water, and to assess the degree that contaminants are isolated from points of contact with human or wildlife populations at Tank Farm C. This evaluation included field studies documenting the present location and distribution of soluble benzene, toluene, ethylbenzene, and xylene (BTEX) and the polynuclear aromatic hydrocarbon (PAH) compound naphthalene. Also, hydrologic conditions in the shallow water-table aquifer underlying the site were assessed and discharge areas where contaminants could come into contact with human or wildlife populations were identified. Experimental studies designed to assess biodegradation rates and the adsorption characteristics of hydrocarbons in sediments cored from the site were conducted in the laboratory. Finally, a solute-transport analysis designed to estimate rates of contaminant transport, determine the likely maximum extent of the plume, and quantitatively assess the possibility of contaminant transport to potential points of contact with humans was conducted.

Description of Study Area

Tank Farm C is located at the MCAS Beaufort (fig. 1) and covers an area of about 500,000 ft^2. The site is underlain by alluvial sediments of Pleistocene age. The lithology of these sediments (fig. 2) consists predominantly of woody organic debris (BFT-401-4) in a matrix of fine sand that was deposited in a swampy environment of deposition. Overlying the organic-rich sediments is a layer of medium-grained sand (BFT-TF-12) that was spread over the site as fill material during construction of the tank farm.

Framework for Assessing Intrinsic Bioremediation

The efficiency of intrinsic bioremediation (naturally occurring attenuation processes) to contain contaminant migration in ground-water systems can be assessed by quantitatively comparing rates of contaminant transport to rates of biodegradation. If transport rates are fast relative to rates of biodegradation, contaminants can migrate freely with ground-water flow and possibly reach points of contact with human or wildlife populations. Conversely, if transport rates are slow relative to biodegradation rates, contaminant migration is more confined and less likely to reach points of contact. In either case, the efficiency of intrinsic bioremediation can be assessed by evaluating the presence/absence of contaminant transport to predetermined points of contact. Thus, this assessment includes hydrologic (rates of ground-water flow), microbiologic (rates of biodegradation), geochemical (adsorption properties), and demographic (points of contact) considerations.
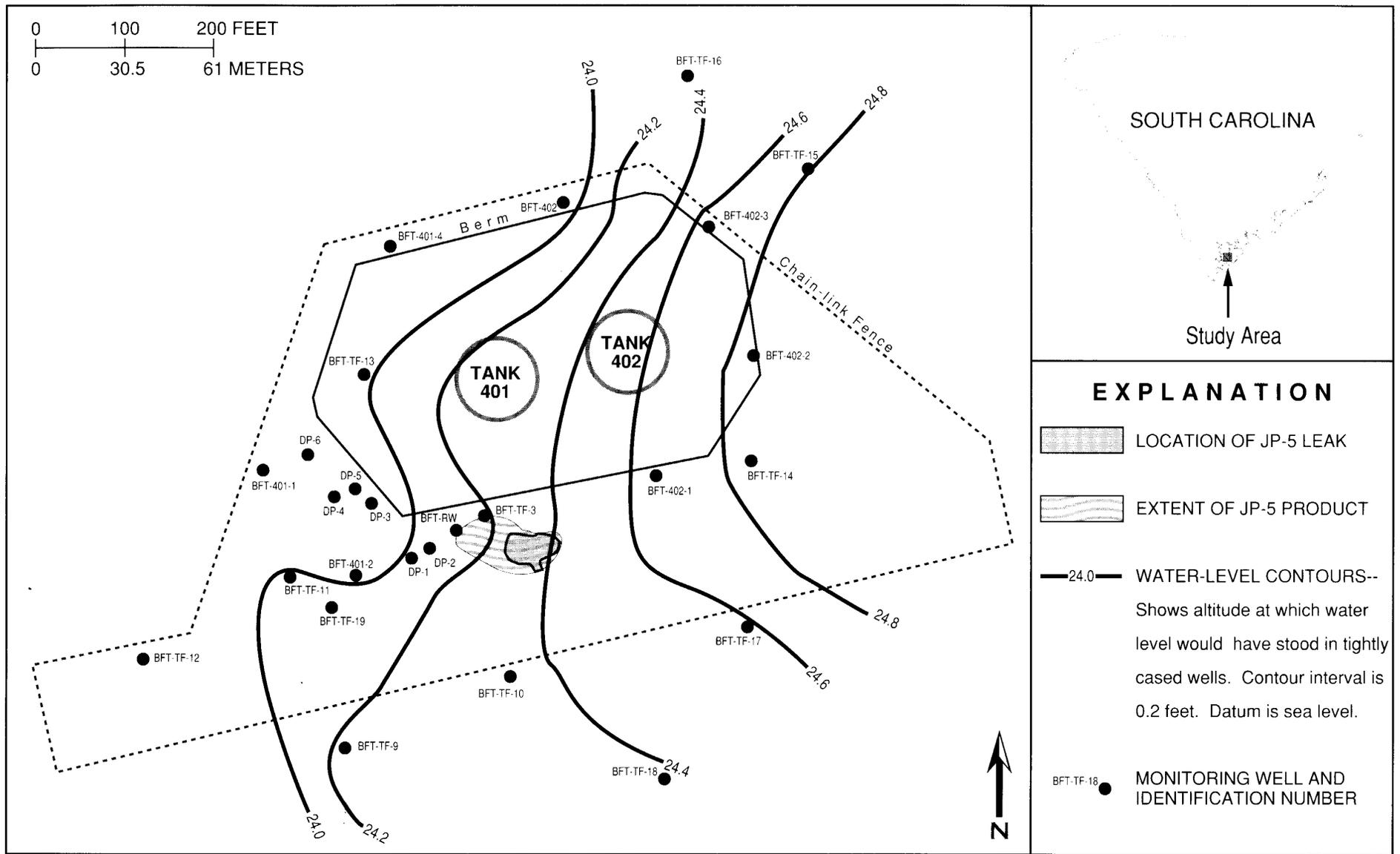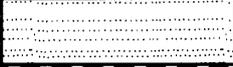
Figure 1. Location of Tank Farm C, Marine Corps Air Station Beaufort, S.C., the location of monitoring wells, and water levels in the shallow water-table aquifer, March 9, 1994.

BFT-401-4

DEPTH, IN FEET	LITHOLOGY	DESCRIPTION
1		Sandy soil
2		Organic-rich sandy sediment. Chips of woody material abundant.
3		Clayey silt, organic rich, stained red with ferric iron.
4		
5		Peat. Organic matter comprises 90% of sediment and consists of decomposed pine-bark material.
6		
7		
8		END HOLE
9		

BFT-TF-12
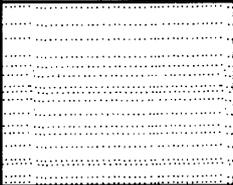
DEPTH, IN FEET	LITHOLOGY	DESCRIPTION
1		Light-brown sandy fill material. -
2		- Gray to white sandy fill material, Qtz ~ 95%
3		
4		Organic-rich peat. Poorly decomposed pine bark material comprises 60-80% of sediment.
5		
6		
7		END HOLE
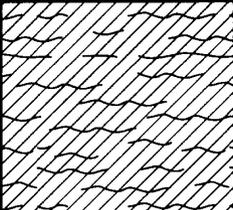
Figure 2. Lithologic description of sediments cored near wells BFT-401-4 and BFT-TF-12.

The U.S. Geological Survey, in cooperation with the Southern Division Naval Facilities Engineering Command, U.S. Navy, and MCAS Beaufort has developed a framework for assessing the efficiency of intrinsic bioremediation. In this framework (fig. 3), hydrologic, geochemical, and microbiologic information are integrated using digital solute-transport techniques in order to assess contaminant transport to pre-defined points of contact (adjacent water-supply wells or surface-water bodies). Because determining model parameters is subject to many uncertainties, it is not usually feasible to define a unique set of parameters that will accurately simulate contaminant transport for a particular site. Because of this, parameter uncertainty is explicitly treated as part of the modeling process, and a range of solutions is used to encompass minimum and maximum rates of solute transport. If, within this range, there is no combination of model parameters that results in contaminant transport to a point of contact, then intrinsic bioremediation may be considered a viable remedial option. Conversely, if certain combinations of model parameters indicate that contaminant transport to points of contact is possible, then intrinsic bioremediation can be ruled out as a remedial option. This framework is consistent with recent regulatory guidance documents (South Carolina Department of Health and Environmental Control, 1994) and are followed in this report.

FIELD AND LABORATORY DATA-COLLECTION METHODS

A site visit was made March 9-11, 1994, for the purpose of collecting water-chemistry data, water samples for BTEX analysis, and sediment samples for laboratory studies on hydrocarbon biodegradation and adsorption. Prior to ground-water sampling, water levels were recorded, and the wells purged (3 well-casing volumes). Measurements of water temperature, pH, and concentrations of dissolved oxygen, dissolved ferrous iron, and dissolved sulfide were made in the field using techniques described by Wood (1976) and Skougstad and others (1978). Samples were collected for BTEX and naphthalene and transported to the laboratory for analysis. Because the existing well network was inadequate for delineating the distribution of contaminants on a fine scale, five temporary well points were installed (wells with the prefix DP, standing for drive point) (fig. 1), and analyzed for contaminants and water-chemistry parameters as described above. Sediment samples were recovered from hydrocarbon-contaminated and uncontaminated sites using a hand auger. Sediments were placed in presterilized wide-mouth glass mason jars, chilled to 4 °C, and transported to the laboratory for analysis.

Laboratory studies were used to evaluate rates of hydrocarbon biodegradation and to evaluate the adsorption characteristics of hydrocarbons on the aquifer material present at the site. In both cases, toluene was used as a model BTEX compound and naphthalene was used as a model PAH compound.
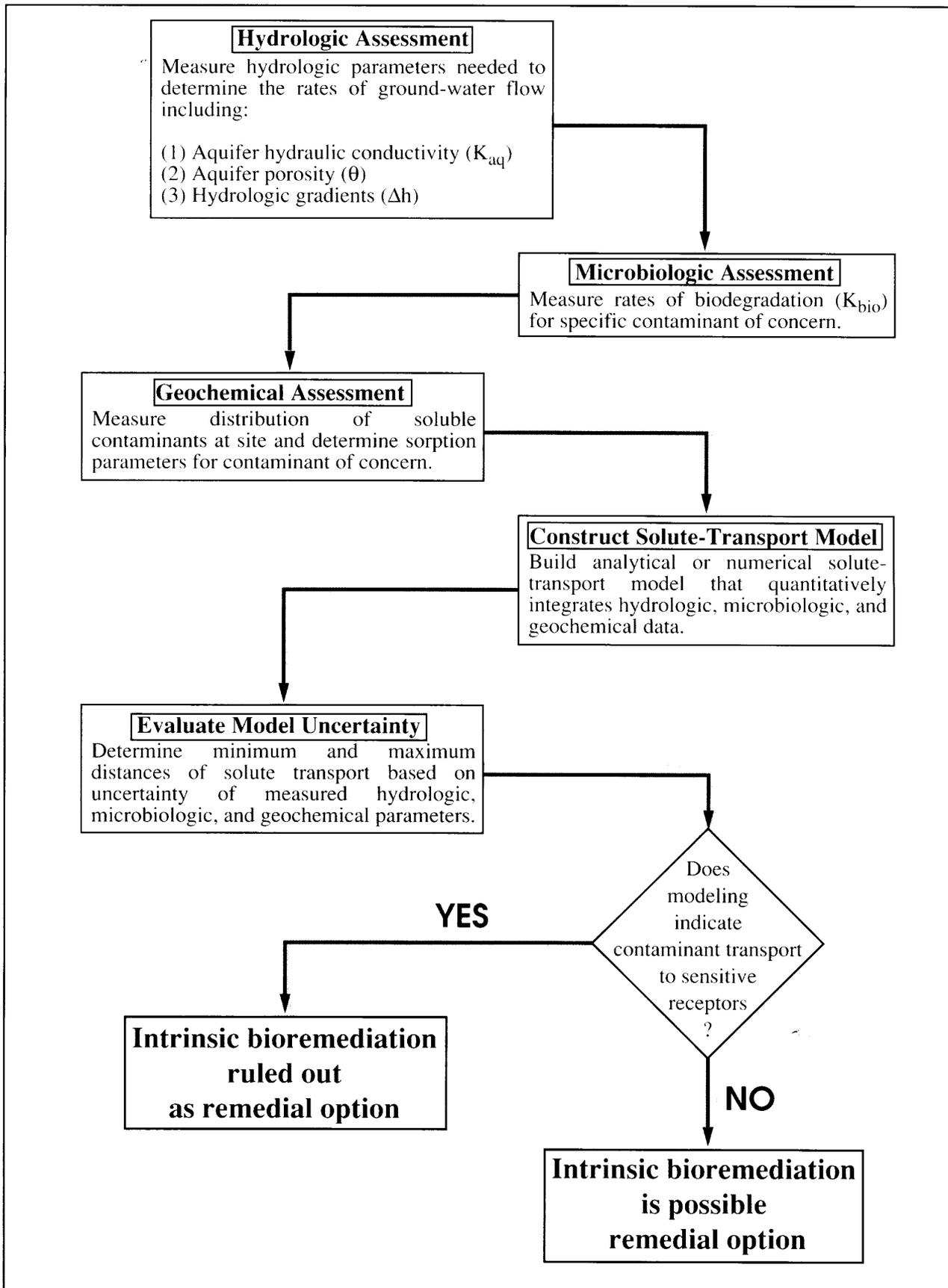
Hydrologic Assessment

Measure hydrologic parameters needed to determine the rates of ground-water flow including:

(1) Aquifer hydraulic conductivity (K_{aq})
(2) Aquifer porosity (θ)
(3) Hydrologic gradients (Δh)

Microbiologic Assessment

Measure rates of biodegradation (K_{bio}) for specific contaminant of concern.

Geochemical Assessment

Measure distribution of soluble contaminants at site and determine sorption parameters for contaminant of concern.

Construct Solute-Transport Model

Build analytical or numerical solute-transport model that quantitatively integrates hydrologic, microbiologic, and geochemical data.

Evaluate Model Uncertainty

Determine minimum and maximum distances of solute transport based on uncertainty of measured hydrologic, microbiologic, and geochemical parameters.

Does modeling indicate contaminant transport to sensitive receptors ?

YES

Intrinsic bioremediation ruled out as remedial option

NO

Intrinsic bioremediation is possible remedial option

Figure 3. Framework for assessing the efficiency of intrinsic bioremediation.

The biodegradation-rate experiments tracked production of $^{14}CO_2$ end products from radiolabeled toluene or naphthalene as an indicator of microbial degradation. Because production of $^{14}CO_2$ from hydrocarbons is unequivocal evidence of microbial transformation, and because this is extremely sensitive, this method is preferable to simply tracking the disappearance of unlabeled hydrocarbons with time. Approximately 0.5 μCi of radiolabeled compound was added to 1.0 gm of sediment in each vial. Heat and mercuric chloride-killed controls were prepared in the same way. At specified times, triplicate vials were acidified with phosphoric acid (H_3PO_4, 2 M), the evolved $^{14}CO_2$ collected in potassium hydroxide (KOH, 3 M) base traps, and ^{14}C measured with scintillation counting. Reported ^{14}C values were corrected for activity in traps at time zero, and for activity in killed controls. The results are given as the mean of triplicate measurements plus or minus one standard deviation.

Adsorption experiments were performed with heat-sterilized sediments, to avoid possible microbial degradation effects, using methods described by Schwarzenbach and Westall (1981). Five grams of sediment were placed in septated serum vials and amended with either 0, 5, 10, or 50 μg of toluene or benzene. The vials were allowed to equilibrate for 1 hour, and the liquid fraction then analyzed for concentrations of toluene or benzene. For each treatment, the amount of adsorbed hydrocarbon was taken as the difference between the amount added and the amount present in solution at the end of the equilibration time.

QUANTIFICATION OF HYDROLOGIC, GEOCHEMICAL, AND MICROBIAL PARAMETERS

The results of hydrologic, geochemical, and microbial investigations are presented in this section. This includes description of site hydrology, ground-water chemistry, aquifer material adsorption characteristics, and microbial degradation rates determined in both field and laboratory studies.

The measured hydraulic conductivities and the water-level data allow rates of ground-water flow to be estimated based on Darcy's equation:

$$v=(K\Delta h)/\theta \qquad (1)$$

where

v is the average velocity of ground water in feet per day;
K is the average hydraulic conductivity in feet per day;
Δh is the hydraulic gradient (dimensionless); and
θ is the effective porosity (dimensionless).

The hydraulic gradient is fairly uniform over the site with an maximum head drop of about 0.8 ft per 200 ft, indicating values on the order of 0.004 ft/ft. This very shallow gradient combined with the low- to medium-hydraulic conductivities (1.9 - 9.1 ft/d) indicates that ground-water flow is slow at this site. Assuming a porosity of 0.4 (reasonable for the poorly compacted organic-rich sediments), rates of ground-water flow are on the order of 0.06 ft/d, or about 20 ft/yr. Thus, in the 4 years between the JP-5 spill and sampling ground-water chemistry for this project, the maximum distance that soluble contaminants would be expected to migrate is about 80 ft.

Hydrologic and Hydrogeologic Framework

The organic-rich aquifer sediments at Tank Farm C are characterized by low- to medium-hydraulic conductivities. The results of slug tests (U.S. Navy Department, 1993) showed hydraulic conductivities ranging from 1.9 to 9.1 ft/d with a mean value of 4.5 ft/d. The water-table surface at the site (measured on March 9, 1994) indicates that ground water flows from east to west toward low-lying areas east of the site (fig. 1). A small drainage ditch located near well BFT-401-1 appears to be a discharge area for the water-table aquifer and is the nearest potential point of contact for contaminants moving from the site of the JP-5 leak.

Hydrologic conditions at this site change rapidly with climatic changes. This is because the water-table aquifer is closely connected with the surface. For example, the measured water level in well BFT-401-3 on April 4, 1993, was 27.11 ft above sea level during a wet spring (U.S. Navy Department., 1993). The water level measured about one year later on March 9, 1994, was 24.17 (fig. 1), after a fairly dry spring. These data indicate that water levels at the Tank Farm C site rise and fall several feet depending on recent precipitation events. Significantly, however, the hydrologic gradients were similar for the 1993 and 1994 water-level measurements, both of which indicate values of about 0.004 ft/ft. This suggests that even though water levels rise and fall, the hydrologic gradient stays fairly constant. This, in turn, suggests that rates of ground-water flow are less variable than water levels in the aquifer.

Ground-Water Chemistry

Concentrations of BTEX and naphthalene ranged from less than 5 to 572 mg/L in ground water from the Tank Farm C site (table 1). Two distinct plumes of contaminated ground water were observed. The first and largest (fig. 1) was associated with the original spill site and was characterized by the highest concentrations of contaminants. A smaller zone of contamination, located in the drainage ditch west of the original spill, was delineated by the drive-point wells DP-4 and DP-5 (table 1). Significantly, even wells associated with measurable JP-5 free-product contamination (well BFT-401-3) showed only modest concentrations (<1,000 µg/L) of petroleum hydrocarbons.

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Table 1.--*Concentrations of benzene, toluene, ethylbenzene, total xylenes, and naphthalene in ground water from monitoring wells at Tank Farm C, Marine Corps Air Station Beaufort, South Carolina, March 9, 1994*

[Units in micrograms per liter (μg/L); NA, not analyzed; <, less than]

Monitoring well number (fig. 1)	Benzene	Toluene	Ethylbenzene	Xylene (total)	Naphthalene
BFT-TF-9	<5.0	<5.0	<5.0	<10.0	<5.0
BFT-TF-11	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-TF-12	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-TF-13	<5.0	<5.0	<5.0	19	NA
BFT-TF-15	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-TF-16	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-TF-19	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-401-1	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-401-2	19.4	<5.0	13.4	51.4	34
BFT-401-3	107	31	141	372	212
BFT-401-3 (replicate)	141	35	184	572	NA
BFT-402-1	<5.0	<5.0	<5.0	<10.0	<10.0
BFT-402-3	<5.0	<5.0	<5.0	<16.0	<10.0
BFT-RW	37.6	29.7	108	340	161
BFT-RW (replicate)	41	28	105	328	159
DP-1	<5.0	<5.0	<5.0	<10.0	<10.0
DP-2	<5.0	<5.0	<5.0	<10.0	<10.0
DP-3	<5.0	<5.0	<5.0	<10.0	<10.0
DP-4	<5.0	<5.0	19.2	30.8	<10.0
DP-5	<5.0	<5.0	16.2	31.3	46
DP-6	<5.0	<5.0	<5.0	<10.0	<10.0

Concentrations of dissolved oxygen, ferrous iron, hydrogen, and sulfide in ground water from the site are given in table 2. Ground water at this site not associated with petroleum hydrocarbon contamination is aerobic, despite the organic-rich nature of the aquifer sediments. In contrast, water from contaminated zones was generally anaerobic and contained relatively high concentrations of dissolved iron. Hydrogen concentrations in anaerobic ground water were in the 0.1 to 1.5 nM range, which is characteristic of Fe(III) reduction and sulfate reduction as the predominant terminal electron-accepting processes.

Table 2.--Field-measured water-chemistry parameters of ground water from monitoring wells at Tank Farm C, Marine Corps Air Station Beaufort, South Carolina, March 9, 1994

[mg/L, milligrams per liter; nM, nanomoles per liter; °C, degrees Celsius; NA, not analyzed; <, less than]

Monitoring well number (fig. 1)	Dissolved oxygen (mg/L)	Ferrous iron [Fe(II)] (mg/L)	Sulfide [S⁻] (mg/L)	pH [units]	Dissolved hydrogen (nM)	Temperature (°C)
BFT-TF-9	4.1	0.6	<0.01	4.03	NA	16.9
BFT-TF-11	4.1	1	.05	6.83	NA	17.3
BFT-TF-12	3.85	<.1	<.01	5.35	NA	17.9
BFT-TF-13	<.1	.8	.35	4.93	.6	18.3
BFT-TF-15	NA	NA	NA	4.65	NA	NA
BFT-TF-16	1.26	3.8	<.01	3.86	NA	NA
BFT-TF-19	<.1	2	.45	5.6	.5	21.8
BFT-401-1	.18	1.1	.01	4.91	.04	17.4
BFT-401-2	<.1	.8	.75	5.31	1.5	21.1
BFT-401-3	<.1	1.8	.01	5.46	NA	17.1
BFT-402-1	.18	1.4	<.01	3.58	NA	17.7
BFT-402-3	<.1	6.5	.95	4.01	NA	17.7
BFT-RW	<.1	4.0	.15	4.21	.38	18.8

Concentrations of nitrate (table 3) were generally low, except for high values in water from wells BFT-TF-11, BFT-TF -15, and BFT-402-1. These high values of nitrate may be related to the use of nitrogen fertilizers on the grass, and subsequent nitrate transport to the saturated zone. Sulfate concentrations ranged from 0.8 to 150 mg/L. The highest values (150 mg/L) were associated with the recovery well (BFT-RW) and suggest an anthropogenic source of sulfate. Sulfate concentrations of 1 to 30 mg/L can be attributed to sulfate delivered to the system from atmospheric recharge. The lowest concentrations of sulfate were in water from the most contaminated well (BFT-401-3) and may indicate the removal of sulfate due to microbial sulfate reduction. Phosphate concentrations were below 0.01 mg/L in all samples.

Table 3.--*Concentrations of anions and gases in ground water from monitoring wells at Tank Farm C, Marine Corps Air Station Beaufort, South Carolina, March 9, 1994*

[Units in milligrams per liter; <, less than]

Monitoring well number (fig. 1)	Chloride	Bromide	Nitrate	Phos-phate	Sulfate	Dissolved inorganic carbon	Dissolved methane
BFT-TF-9	9.8	<0.05	<0.05	<0.01	19.3	20.1	<0.1
BFT-TF-11	2.1	<.05	2.8	<.01	9.9	13.4	<.1
BFT-TF-12	1.7	<.05	.35	<.01	9.1	18.6	<.1
BFT-TF-13	2.6	.03	.12	<.01	3.2	123.6	<.1
BFT-TF-15	5.1	<.05	3.3	<.01	55.1	66.8	<.1
BFT-TF-19	4.4	<.05	<.05	<.01	36.7	95.5	<.1
BFT-401-1	2.5	<.05	.72	<.01	9.4	54.2	<.1
BFT-401-2	3.7	.06	<.05	<.01	12.2	132.4	3.9
BFT-401-3	2.8	.07	.05	<.01	.82	212.4	2.1
BFT-401-3 (replicate)	2.8	.08	.05	<.01	.83	213.5	2.1
BFT-402-1	2.3	<.05	5.3	<.01	36.6	48.1	<.1
BFT-402-3	10.3	.12	<.05	<.01	18.7	197.6	<.1
BFT-RW	2.7	.09	<.05	<.01	142	214	1.0
BFT-RWR (replicate)	2.7	.09	<.05	<.01	150	213.9	2.0

Concentrations of cations such as sodium, potassium, magnesium, and calcium (table 4) were in the range typical of shallow aquifers in the Coastal Plain of South Carolina. There were measurable concentrations of ammonium present (table 4), and comparison with nitrate concentrations (table 3) indicates that most of the dissolved organic nitrogen in this system is present as reduced ammonium. These data indicate the presence of reducing conditions in the aquifer even though the ground water generally contains measurable concentrations of dissolved oxygen.

Table 4.--*Concentrations of cations in ground water from monitoring wells at Tank Farm C, Marine Corps Air Station Beaufort, South Carolina, March 9, 1994*

[Units in milligrams per liter; <, less than]

Monitoring well number (fig. 1)	Sodium	Ammonium	Potassium	Magnesium	Calcium
BFT-TF-9	8.1	<0.05	0.41	0.83	4.0
BFT-TF-11	5.3	<.05	.94	.32	4.0
BFT-TF-12	1.7	<.05	.53	.71	4.8
BFT-TF-13	3.1	1.1	1.24	.82	4.2
BFT-TF-15	34.3	<.05	1.33	2.17	6.1
BFT-TF-19	14.2	.31	41.37	1.10	10.8
BFT-401-1	3.1	.29	2.89	.51	2.57
BFT-401-2	4.2	.67	1.89	.83	9.66
BFT-401-3	2.1	3.32	1.83	.51	8.99
BFT-401-3 (replicate)	2.1	3.26	1.85	.49	8.96
BFT-402-1	2.4	.06	2.98	1.02	6.19
BFT-402-3	6.1	1.34	.80	1.82	2.86
BFT-RW	6.2	1.50	1.16	.29	3.23
BFT-TF-RW (replicate)	6.2	1.84	1.14	.27	3.19

Microbial Degradation

Biodegradation of toluene and naphthalene was rapid under aerobic conditions, with about 10 percent of the total radiolabel mineralized in 10 hours (figs. 4 and 5). Biodegradation was much slower under anaerobic conditions with about 3 percent of the radiolabeled compounds mineralized in about 30 days. Oxygen carried into the aquifer by vertically percolating recharge would be available to support aerobic metabolism, but once the oxygen is consumed, anaerobic metabolism would prevail. Given the mosaic of aerobic and anaerobic conditions at this site, overall rates of hydrocarbon biodegradation are probably intermediate between the aerobic and anaerobic extremes shown on figures 4 and 5.

Adsorption Coefficient

Laboratory studies were conducted to determine adsorption coefficients for benzene and toluene in sediments from Tank Farm C. Toluene is more strongly adsorbed ($K_{ad} \sim 31.6$ cm^3/mg) than benzene ($K_{ad} \sim 3.08$ cm^3/mg) by the organic-rich sediments at the site (fig. 6). The adsorption isotherms were linear over the wide concentration range evaluated experimentally. Similar experiments conducted with organic-poor sediments characteristic of the Laurel Bay site, MCAS Beaufort (James E. Landmeyer, U.S. Geological Survey, written commun., 1994), showed substantially lower K_{ad} values that ranged from 0.08 to 0.15 cm^3/mg. The high K_{ad} values characteristic of the Tank Farm C site can be attributed to the organic-rich nature of the aquifer materials. Furthermore, these relatively high K_{ad} values indicate that the movement of dissolved petroleum hydrocarbons will be significantly retarded relative to ground-water flow at this site.

ASSESSMENT OF INTRINSIC BIOREMEDIATION

The distribution of contaminated ground water at the site, as well as records of the contamination event, indicates two plumes of contaminated ground water. The larger plume is associated with the spill site, and reflects hydrocarbons leaching into the ground water from free product floating on the water table. A smaller plume is delineated by drive-point wells (DP-4 and DP5). This smaller plume is not connected to the larger free-product plume as demonstrated by uncontaminated ground water encountered at DP-3, DP-2, and DP-1 (fig. 1). Eyewitness accounts of the spill event indicate that some free product reached land surface and flowed overland to the drainage ditch where it formed a pool. The smaller plume probably represents fuel transported to the drainage ditch that subsequently percolated into the ground and reached the water table.
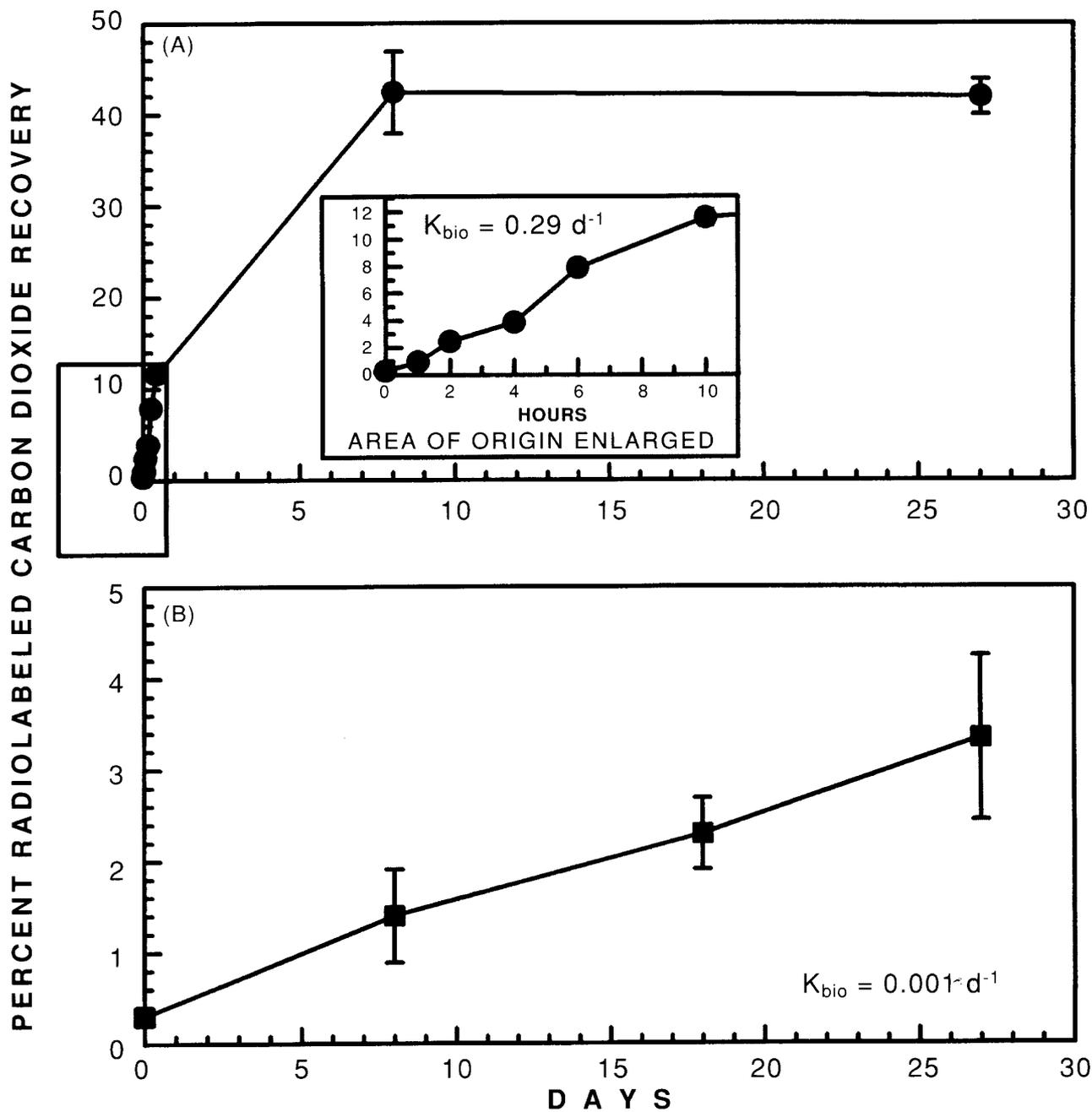
Figure 4. Mineralization of ^{14}C-toluene to $^{14}CO_2$ under (A) aerobic and (B) anaerobic conditions in sediments from Tank Farm C.
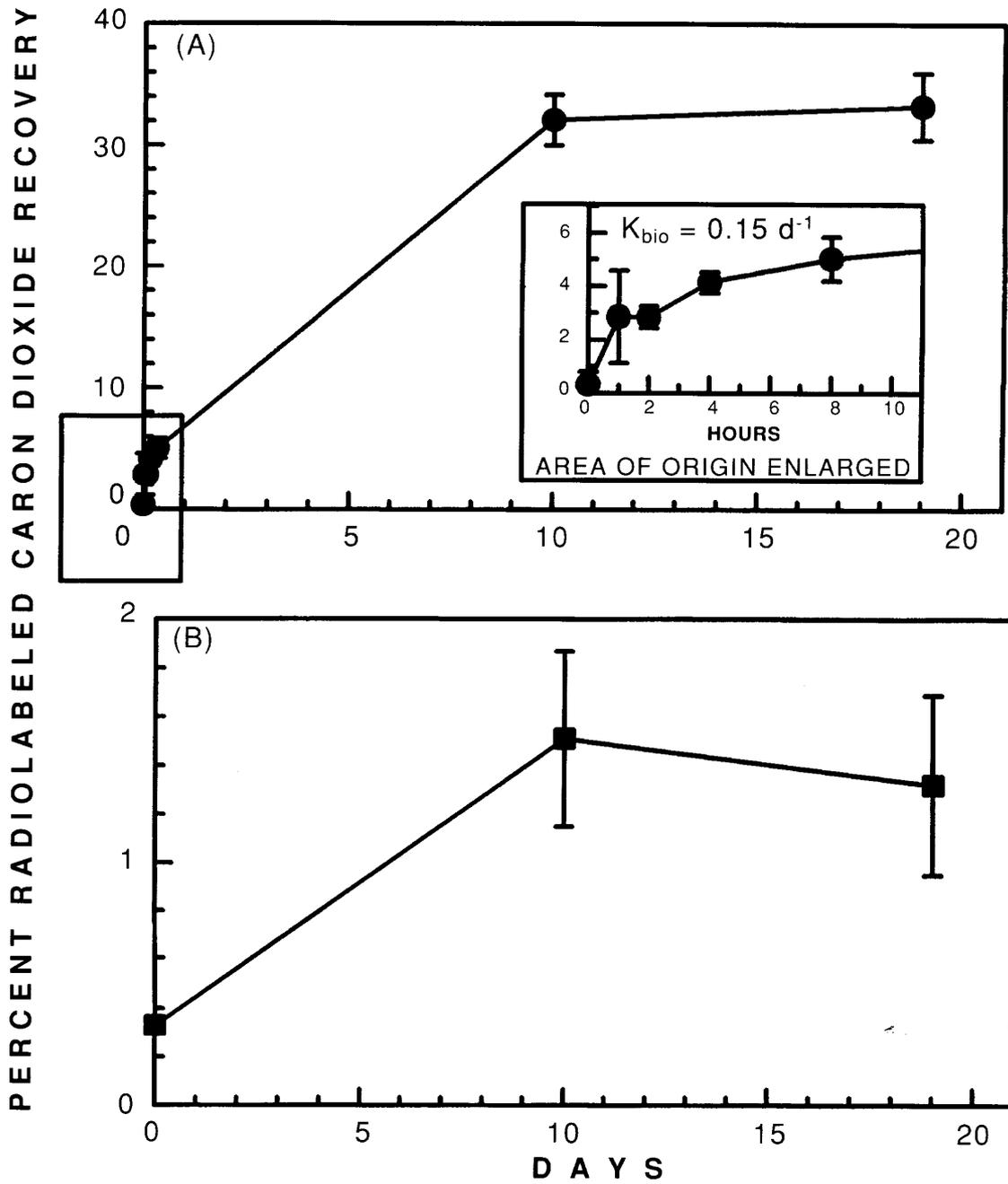
Figure 5. Mineralization of ^{14}C-naphthalene to $^{14}CO_2$ under (A) aerobic and (B) anaerobic conditions in sediments from Tank Farm C.
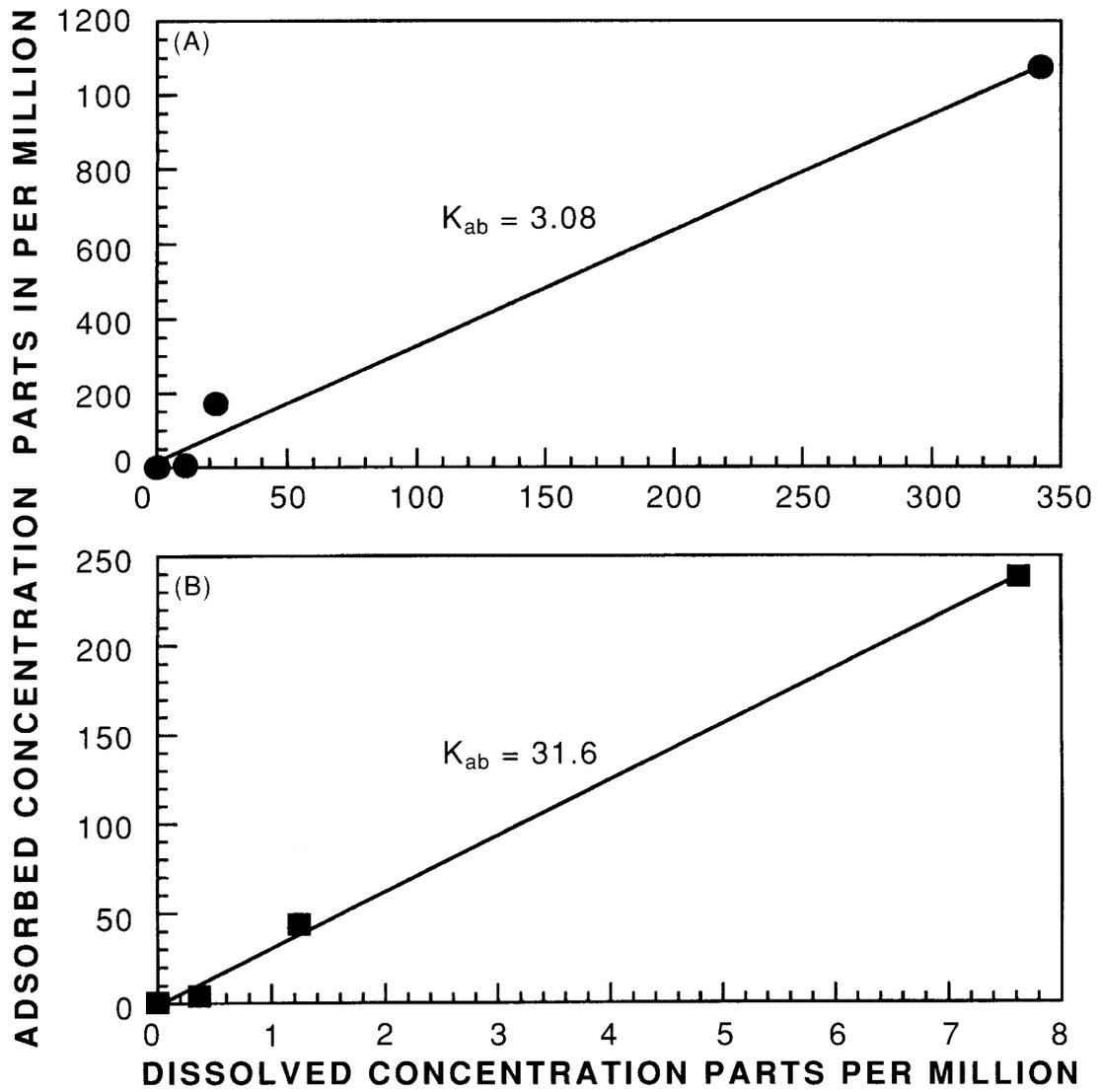
Figure 6. Adsorption isotherms for (A) benzene and (B) toluene on Tank Farm C sediments.

The data indicate that the larger plume has not migrated extensively away from the site of the original spill, and that the plume is characterized by very sharp concentration gradients between contaminated and uncontaminated ground water. For example, concentrations of toluene at BFT-RW and BFT-401-3, which are in the large plume of contaminated ground water, are 28 and 31 mg/L, respectively (fig. 1). Water from well DP-2, which is about 20 ft from TFC-RW, and water from well BFT-401-2, which is about 50 ft from BFT-RW, is uncontaminated. To some extent, the lack of plume migration can be attributed to slow rates of ground-water flow. However, given a ground-water-flow rate of 20 ft/yr, it would be expected that contaminants would have migrated as much as 80 ft from the spill source. Because this is not observed, it is evident that other processes are serving to retard the migration of contaminated ground water.

The migration of soluble contaminants in ground-water systems is affected by hydrologic, geochemical, and microbiologic processes. The principal hydrologic factors are the dispersion of contaminants and advective mixing of contaminated with uncontaminated water. There are a wide variety of geochemical processes that can affect the transport of contaminants including mineral precipitation-dissolution reactions and adsorption-desorption reactions. Petroleum hydrocarbons in ground water are not, in general, subject to significant mineral precipitation reactions so that the most important geochemical process affecting transport are sorption reactions. Finally, the microbial degradation of hydrocarbons is an important factor affecting contaminant transport.

The effects of these different hydrologic, geochemical, and microbiologic processes on contaminant transport can be quantified by writing a mass balance equation that includes terms for each individual process. Where dispersion, advection, sorption, and microbial degradation are the principal processes affecting transport in one dimension, this equation may be written

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - SC^n - kC, \qquad (2)$$

where

  C is concentration of solute in micrograms per liter;
  t is time in days;
  D is the coefficient of hydrodynamic dispersion in square feet per day;
  x is distance in feet;
  v is the velocity of ground-water flow in feet per day;
  S and n are adsorption isotherm parameters; and

  k is a first-order microbial degradation rate constant in day^{-1}.

Equation 2 is most readily solved by numerical methods. In this study, the solute-transport code SUTRA (Saturated-Unsaturated TRAnsport) as described by Voss (1984) was used to obtain solutions in two dimensions subject to hydrologic, geochemical, and microbial conditions at Tank Farm C.

The hydrologic conditions at Tank Farm C were simulated by assigning hydraulic conductivities at the site (U.S. Navy Department, 1993) and by reconstructing the observed potentiometric surface of the aquifer. Hydrologic data show that water levels at the site are highly dynamic, rising or falling as much as 3 ft depending on the amount of precipitation. However, the data also show that hydrologic gradients remain fairly constant with time. Thus, rather than attempting to simulate the complex rise and fall of water levels, the observed gradients were imposed on the model area by holding water levels on the boundary constant. This is a significant simplification of the actual hydrologic system. The geochemical and microbiologic conditions at the site were estimated experimentally as has been previously discussed.

Approach to Solute-Transport Simulation

There are two distinct approaches to modeling complex hydrologic systems. The first, often called consolidative modeling, seeks to simulate every possible feature of a hydrologic system in order to arrive at a unique solution to the solute-transport problem at hand. While conceptually appealing, consolidative modeling assumes that all relevant parameters can be measured, and that the spatial and temporal variability of these parameters can be defined. This approach inevitably comes into conflict with the uncertainties inherent in all hydrologic systems. It is not possible, for example, to precisely measure the distribution of hydraulic conductivity at a site, so that uncertainty in model results is inevitable. When the uncertainties inherent in measuring all of the relevant hydrologic, geochemical, and microbiologic parameters are taken into account, it is clear that to arrive at the single unique solution envisioned by consolidative modeling is generally not technically feasible.

A second approach to modeling hydrologic systems, often called exploratory modeling, explicitly recognizes these inherent uncertainties. Rather than attempting to arrive at a single unique solution, exploratory modeling shows the range of possible solutions given the uncertainty of the measured parameters. For example, if the hydraulic conductivity of a system is uncertain, with measurements ranging from a minimum of 1.9 ft/d to a maximum of 9.1 ft/d, an exploratory model can evaluate solute transport for both of these possible extremes. Then, even though the exact solute-transport behavior of the system is not precisely known, there is a high likelihood that this behavior falls between the two extremes.

For purposes of assessing the efficiency of intrinsic bioremediation to contain contaminant migration, the exploratory modeling approach is most appropriate. In such an assessment, the most relevant question is the likelihood that contaminants will reach a point of contact under any possible conditions. If it can be shown that for the possible range of parameters there is no combination that results in solute transport to a point of contact, then it can be concluded with reasonable confidence that intrinsic bioremediation is a feasible remedial alternative. On the other hand, if the given range of parameters suggests that solute transport to a point of contact is possible, then it can be concluded with similar confidence that intrinsic bioremediation is not a feasible alternative to contain contaminants.

Solute-Transport Simulations of Hydrocarbon Migration

Data gathered at the Tank Farm C site define the range of hydraulic gradients (fig. 1), hydraulic conductivities (U.S. Navy Department, 1993; tables 3-4), adsorption isotherm parameters (fig. 6), and microbial degradation rates (figs. 4 and 5) determined at the site. Of these parameters, the most uncertainty resides in the hydraulic conductivity data and microbial degradation rates. The mean value of four hydraulic conductivity measurements (U.S. Navy Department, 1993) was 4.5 ft/d, but the observed range from 1.9 to 9.1 ft/d indicates significant variability. Similarly, measured microbial degradation rates varied between 0.2 d^{-1} for aerobic conditions to 0.001 d^{-1} for anaerobic conditions. Given this variability, the modeling approach was to calculate the distribution of hydrocarbons for the possible extremes in order to evaluate the possibility of solute transport to the nearest point of contact at the site. To do this, a set of most probable values was selected, based on measurements made at the site, and used to construct a Standard Model. This model assumes that the water-table gradients remain constant over time (that is, the water-level distribution is the same as of March 9, 1994), that microbial degradation proceeds under aerobic and anaerobic conditions ($K_{bio} \sim 0.01$ d^{-1}), that the solute being transported is toluene (in other words, toluene is representative of the behavior of other BTEX compounds), and that the aquifer exhibits strong adsorption properties ($K_{ad} = 31.6$ cm^3/mg) for toluene. The Standard Model is not intended to represent "best" estimates of parameters, but rather to have a point of comparison for different model runs in which parameters were varied within measured ranges.

The area modeled is 120 by 150 ft and is oriented so that the free product is located on the upgradient side (fig. 7), and the nearest point of contact (the drainage ditch) is located on the downgradient edge. Thus, solute transport to the downgradient edge of the model would indicate contaminants reaching a point of contact. In addition, the modeled area is oriented so that water-chemistry data are available at the free-product zone where the plume begins (BFT-RW, BFT-401-3), immediately downgradient (30 ft) of the free-product zone (DP-2), and at the downgradient edge of the model (DP-3).

The development of the contamination plume from a constant source (JP-5 derived from the 1990 spill) through 1994 was simulated assuming conservative solute transport (no biodegradation and no adsorption), and reactive solute transport assuming the parameters of the Standard Model (fig. 8). As expected, the simulated plume of a conservative solute gradually expands at a rate of about 20 ft/yr, finally extending 80 ft downgradient, but not reaching the downgradient edge of the model (fig. 8A). However, this simulation indicates that a conservative solute would reach well DP-2. In contrast, the plume simulated by the Standard Model (fig. 8B) is much more confined, with contaminants extending less than 20 ft downgradient and not reaching well DP-2. In the case of conservative transport, the plume enlarges continuously with time. The results of the Standard Model, however, indicate that the plume will grow much more slowly.
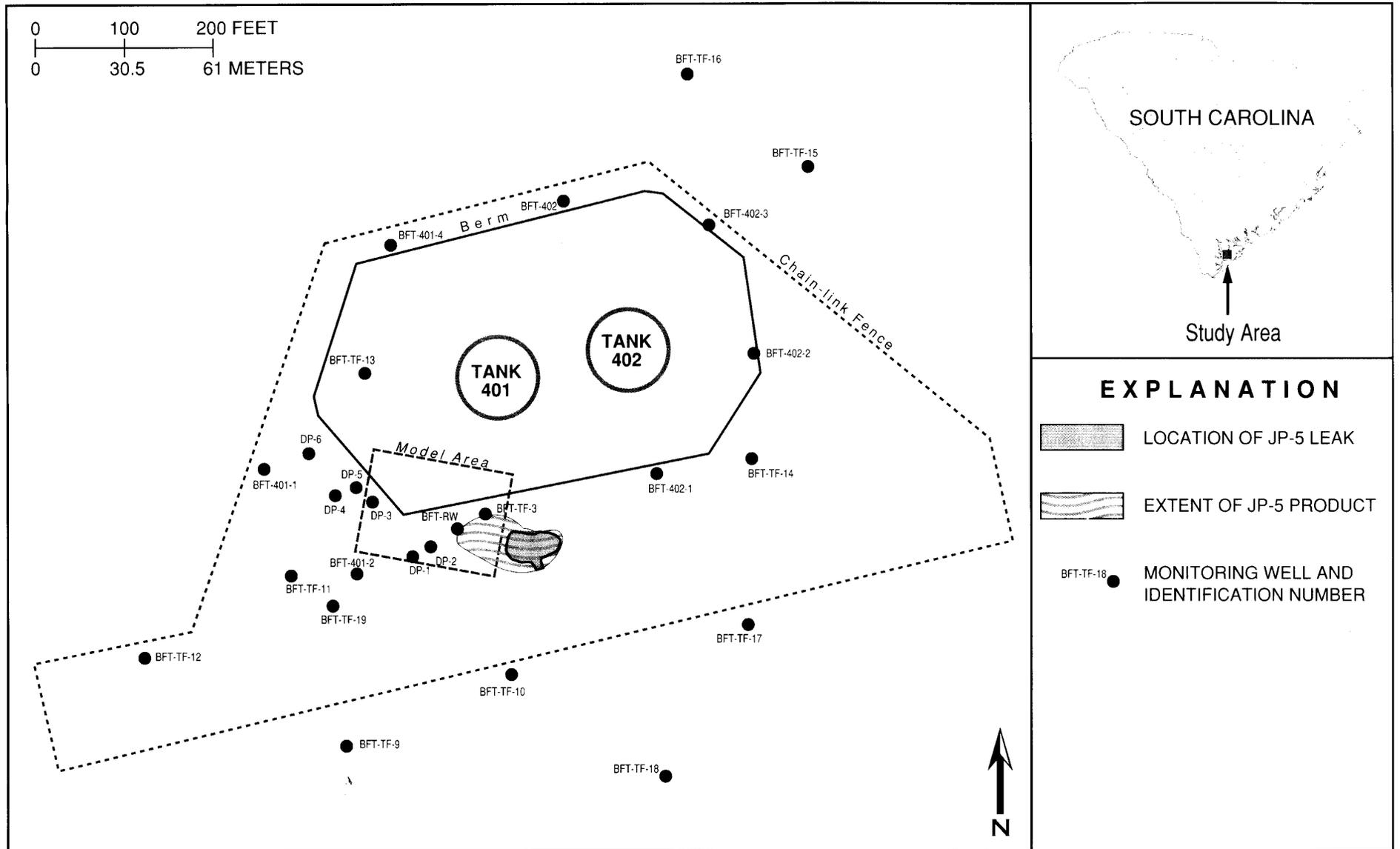
Figure 7. Location and orientation of the modeled area.
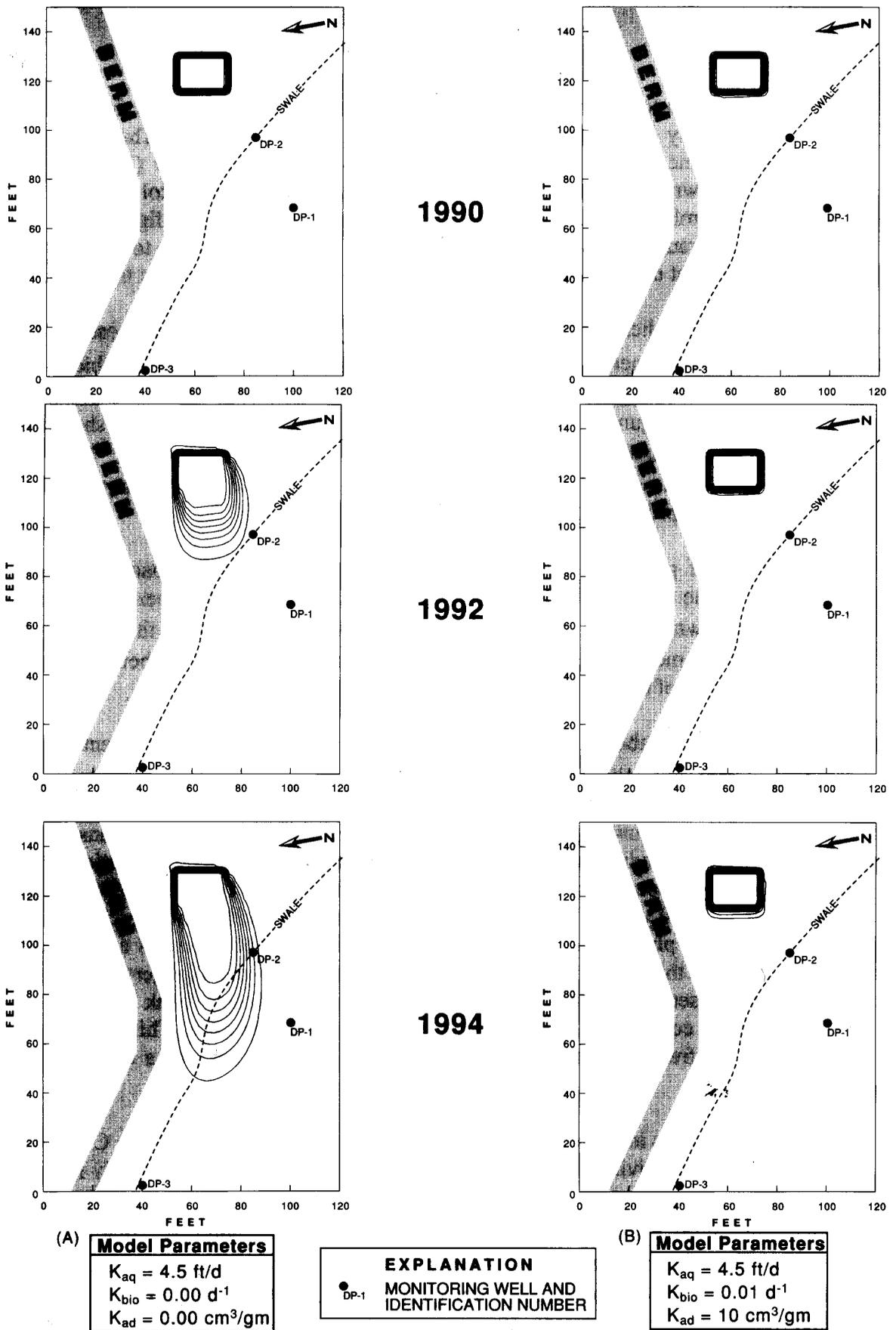
Figure 8. Simulated solute transport of toluene at Tank Farm C for (A) conservative solute transport and, (B) reactive solute transport, given the parameters of the Standard Model.

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The first question to be addressed by exploratory modeling is the effects that uncertainty in hydraulic conductivity at the site can have on contaminant transport. The simulated 1994 distribution of toluene, assuming the aquifer system has a uniformly low (1.9 ft/d) hydraulic conductivity, is shown in figure 9A. The simulated 1994 distribution of toluene, assuming the aquifer has a uniformly high (9.1 ft/d) hydraulic conductivity, is shown in figure 9B. As can be seen, the higher hydraulic conductivity results in a larger plume. This is due to the higher rates of ground-water flow that develop, and consequently higher rates of contaminant transport.

The laboratory studies indicated that rates of biodegradation (K_{bio}) could possibly be as low as 0.001 d^{-1} (uniformly anaerobic conditions), or as high as 0.2 d^{-1} (uniformly aerobic conditions). The results of a simulation designed to explore how such a range in K_{bio} can affect solute transport are shown in figure 10. The effect of assuming the lower K_{bio} value is shown in figure 10A, and the effect of assuming the higher K_{bio} value is shown in figure 10B. The maximum extent of the plume is less given the higher rate of degradation, and contaminants are contained within 2 ft of the free-product source.

Degradation of petroleum hydrocarbons at this site occurs under anaerobic and aerobic conditions. Thus, the effective value of K_{bio} is probably intermediate between the values used in the simulations shown in figure 10. The intermediate K_{bio} value used in the Standard Model (fig. 8) is probably more representative of *in situ* conditions given the better match to the measured distribution of toluene (table 1.)

The results of the laboratory experiments to determine adsorption coefficient (K_{ad}) values indicated significant variability ranging from 4.1 to 31.6 cm^3/g. The effects of this variability on model results are shown in figure 11 for a 30-year simulation of solute transport. When the adsorption coefficient is low (fig. 11A), the plume reaches steady-state conditions (that is, the plume is no longer expanding with time) within the first 10 years of the simulation. However, when the adsorption coefficient is high (fig. 11B), the plume does not reach steady-state conditions even after 30 years. The net effect of the adsorption coefficient, therefore, is to affect the rate at which the plume reaches steady-state conditions. When there is a high adsorption coefficient, such as is the case at Tank Farm C, the plume will take much longer to achieve steady-state conditions. Based on this analysis, it seems likely that the plume at Tank Farm C has not yet reached steady-state conditions and may continue to migrate in the future. This, in turn, indicates that removal of the free product source of dissolved contaminants may be a desirable remedial option at this site.

The model analysis indicates that the extent of contamination at Tank Farm C is sensitive to aquifer hydraulic conductivity (K_{aq}) and biodegradation rates (K_{bio}), and relatively insensitive to adsorption (K_{ad}). Because high values of K_{aq} and low values of K_{bio} lead to more extensive contaminant migration, a simulation was performed that used the highest K_{aq} reported at the site and the lowest K_{bio}. The results of this simulation (fig. 12A) show an extensive plume developing that is similar to that of the conservative transport simulation (fig. 8A). The results of this simulation represent the worst-case scenario of solute transport at the site. Furthermore, measured water-chemistry data from DP-1 and DP-2 (table 1) show that this scenario
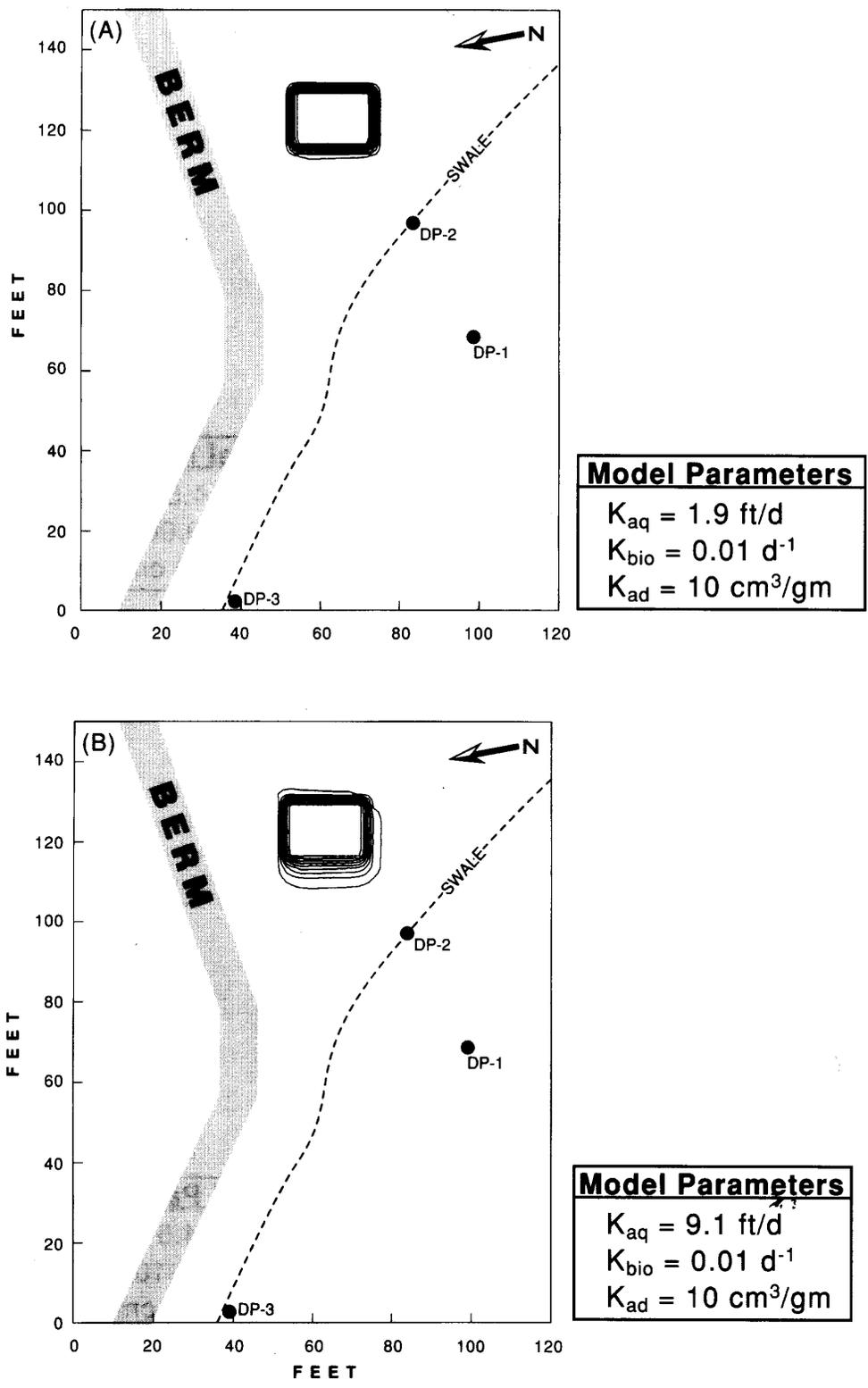
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Figure 9. Simulated 1994 distribution of toluene at Tank Farm C for (A) minimum and, (B) maximum values of hydraulic conductivity (K_{aq}).
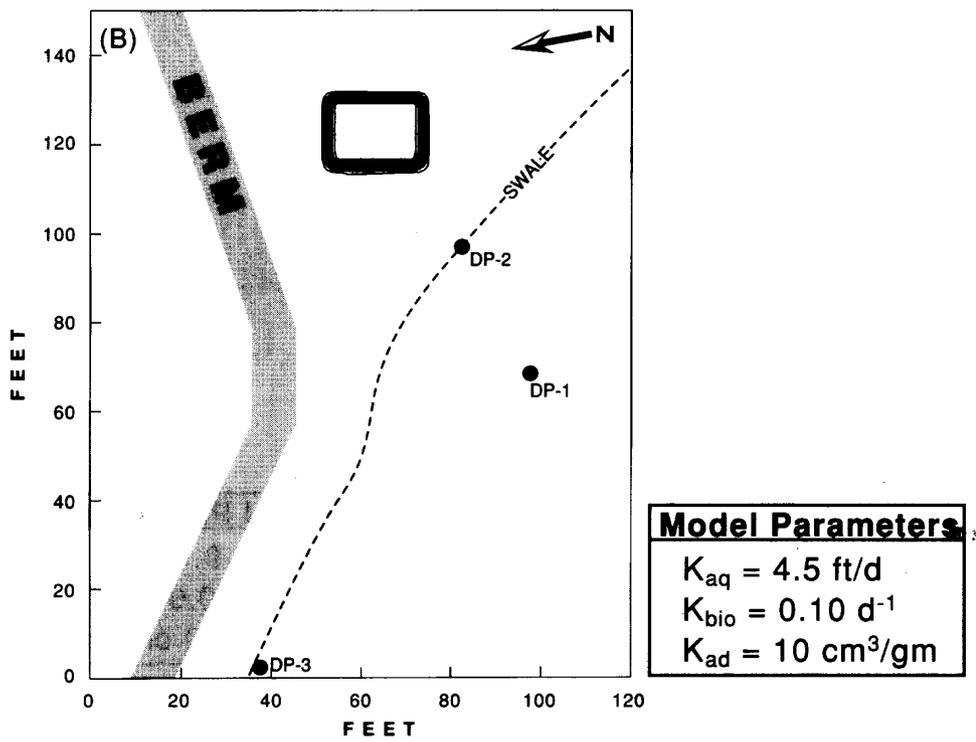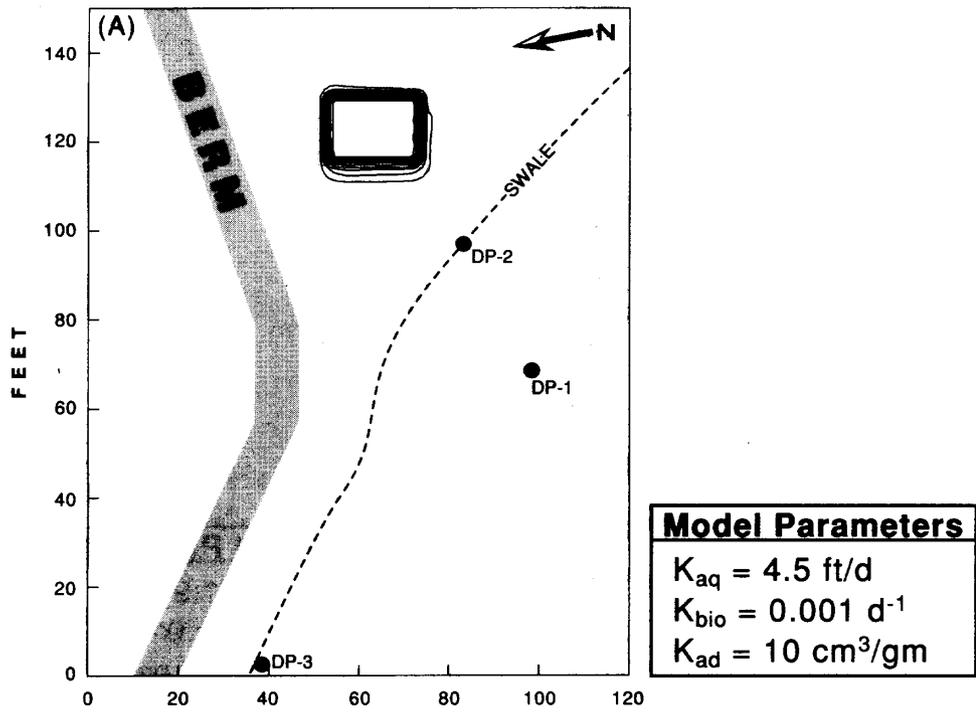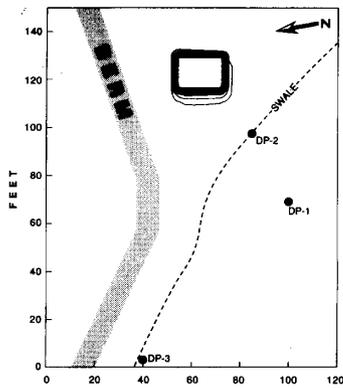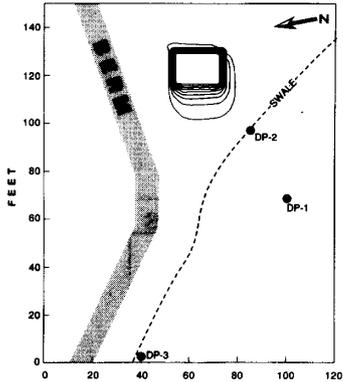
The figure panel (A) contains a box labeled "Model Parameters" with:
$K_{aq} = 1.9$ ft/d
$K_{bio} = 0.01$ d^{-1}
$K_{ad} = 10$ cm^3/gm

The figure panel (B) contains a box labeled "Model Parameters" with:
$K_{aq} = 9.1$ ft/d
$K_{bio} = 0.01$ d^{-1}
$K_{ad} = 10$ cm^3/gm

Figure 10. Simulated 1994 distribution of toluene at Tank Farm C for (A) minimum and (B) maximum values of microbial degradation rate constant (K_{bio}).
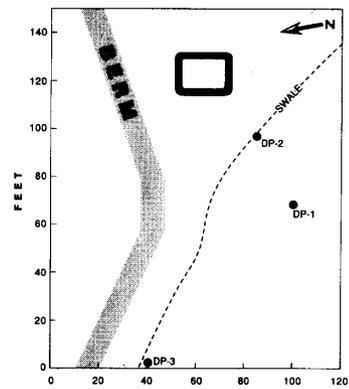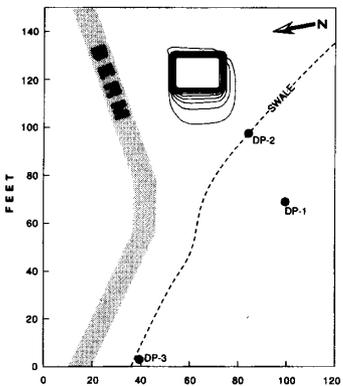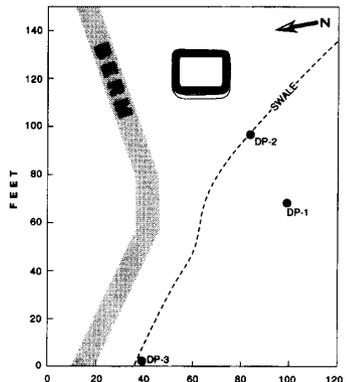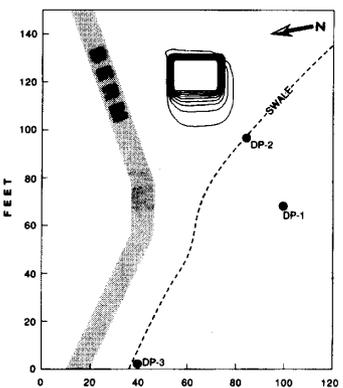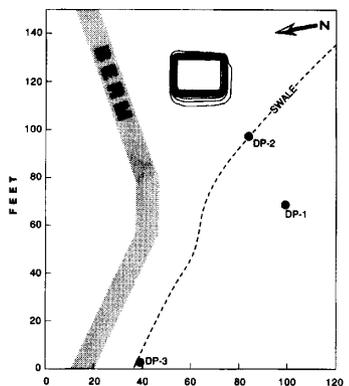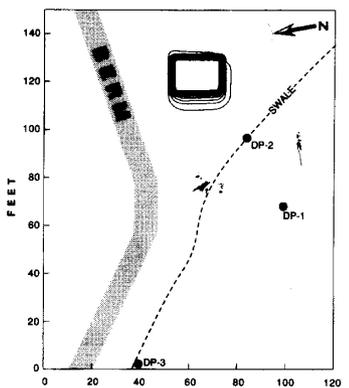
Figure 11. Simulated concentration changes of toluene over a 30-year period for (A) minimum and (B) maximum values of the adsorption coefficient (K_{ad}).
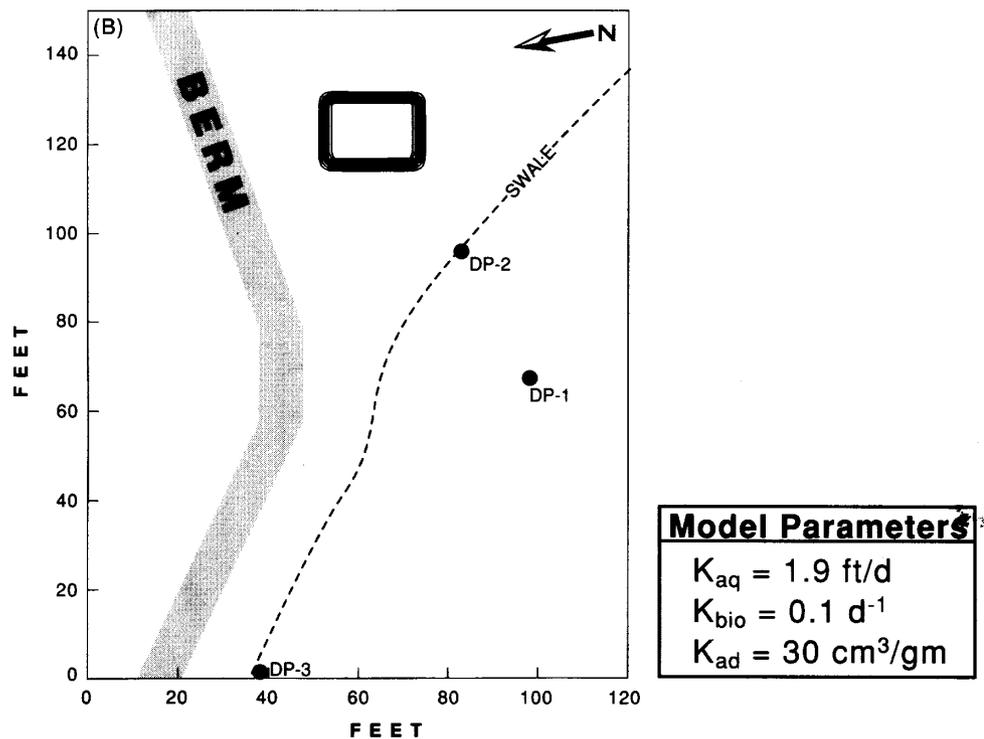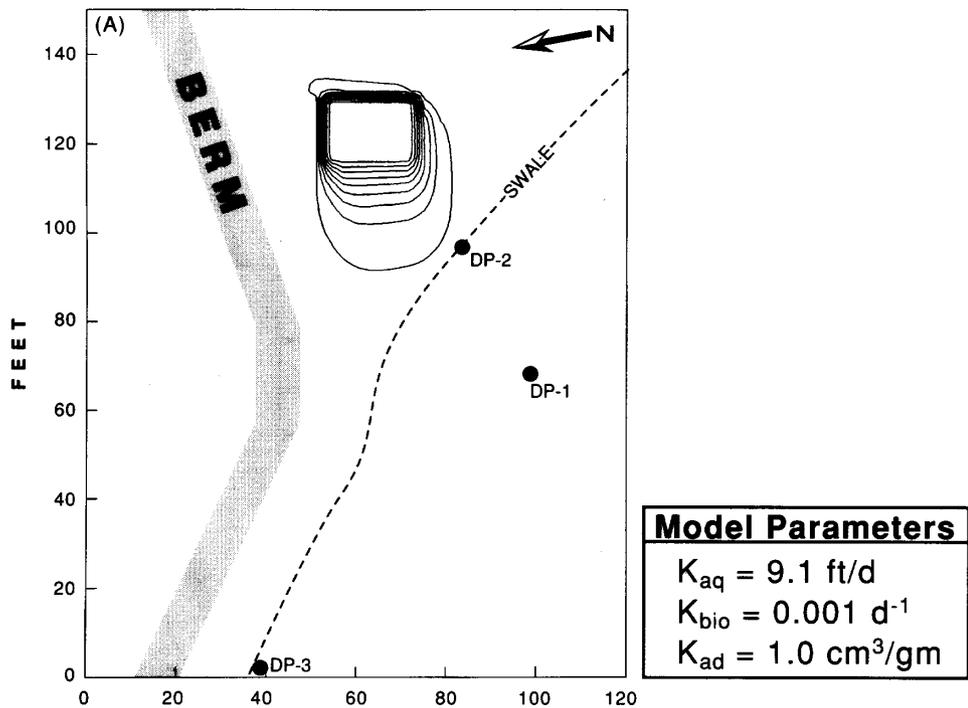
Figure 12. Simulated 1994 distribution of toluene at Tank Farm C for (A) maximum and (B) minimum solute-transport parameters.

overestimates contaminant transport. The important feature of this simulation, however, is that even given the overestimate of solute transport, contamination is not predicted to reach the nearest point of contact (the discharge point in the drainage ditch), which is located at the downgradient edge of the model grid. Thus, it can be concluded with reasonable confidence that no combination of transport parameters at this site will lead to contaminants reaching the nearest point of contact in this hydrologic system.

The converse of this simulation, where the lowest possible K_{aq} value and highest K_{bio} value is shown in figure 12B. In this best-case scenario, contaminants are totally immobilized and do not migrate at all from the free-product source

As a practical matter, parameter values intermediate between those used in figures 12A and 12B are probably better estimates of *in situ* conditions, and these are incorporated into the Standard Model simulations shown in figure 8B. Due to the inherent uncertainties of measuring the hydrologic, geochemical, and microbiologic parameters, the lack of contaminant transport given the maximum transport parameters (fig. 12A) is strong evidence that contaminants are effectively contained by natural attenuation processes at this site.

The simulated remedial effects of removing the free-product source of contaminants is shown in figure 13. The parameters used in this simulation are those of the Standard Model. As can be seen, contaminants are not predicted to degrade quickly with time, with concentrations of toluene of 100 mg/L remaining after 20 years. This behavior is a direct result of the high sorptive capacity of the organic-rich sediments present at this site. Because of this sorptive capacity, a large pool of sorbed BTEX compounds will remain trapped in the sediments even after free-product removal. Furthermore, continual desorption will result in relatively high BTEX concentrations in ground water. However, the combination of sorption and biodegradation still serve to contain soluble contaminants.

These simulations illustrate the dual role of sorption in affecting contaminant transport at this site. On one hand, the high sorption capacity serves to greatly restrict contaminant migration from the free-product source area. On the other hand, this high sorption capacity provides a large pool of sorbed contaminants that will continue to contaminate ground water for a long time into the future.

These simulations also suggest a remedial strategy to deal with this feature of the hydrologic system. It is possible to excavate JP-5-contaminated sediments to remove the main source of soluble contaminants. It is also possible, however, to excavate the sorption-contaminated sediments as well. Because the simulations indicate that sorption-contaminated sediments will be restricted to within a few feet of the free product, those sediments can be excavated along with the JP-5 contaminated sediments as part of the remedial strategy.
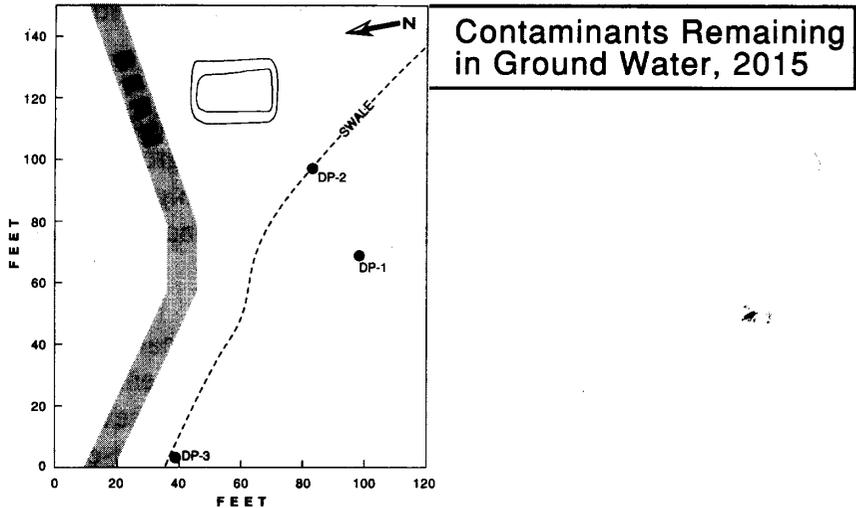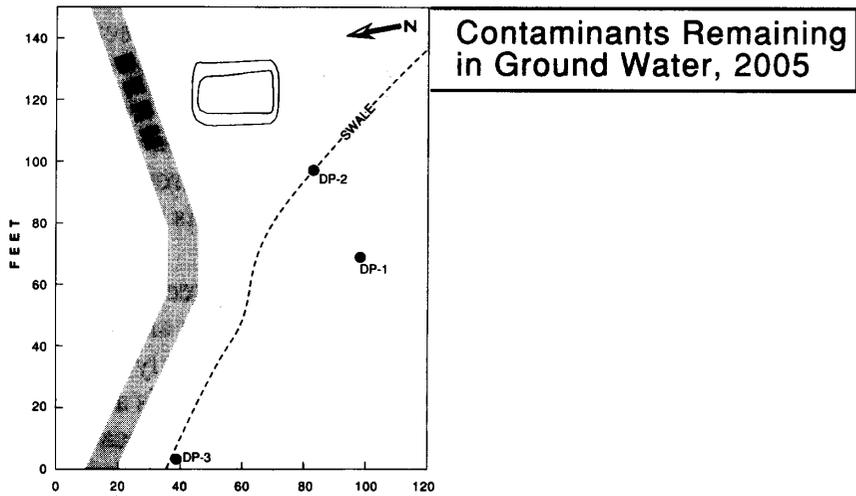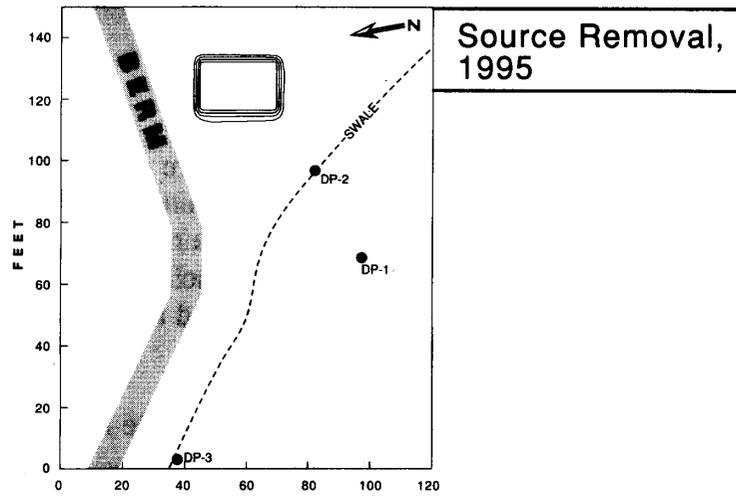
Model Parameters

K_{aq} = 4.5 ft/d
K_{bio} = 0.01 d^{-1}
K_{ad} = 4.0 cm^3/gm

Figure 13. Simulated changes in toluene concentrations at Tank Farm C following removal of the free-product source in 1995.

CONCLUSIONS

The results of this evaluation indicate that no combination of reasonable hydrologic, microbiologic, and geochemical conditions are present that could result in contaminant transport to a point of contact with humans or wildlife at Tank Farm C. This indicates that contaminants are effectively isolated under current site conditions, that they are not affecting adjacent surface-water bodies, nor are they likely to in the future. This, in turn, indicates that intrinsic bioremediation is a possible remedial option for containing contaminated ground water at Tank Farm C. Available evidence indicates that removal of free product- and sorption-contaminated sediments can accelerate the intrinsic bioremediation of contaminated ground water at this site.

APPENDIX B

NATURAL ATTENUATION OF CHLORINATED SOLVENTS – A CASE STUDY

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.
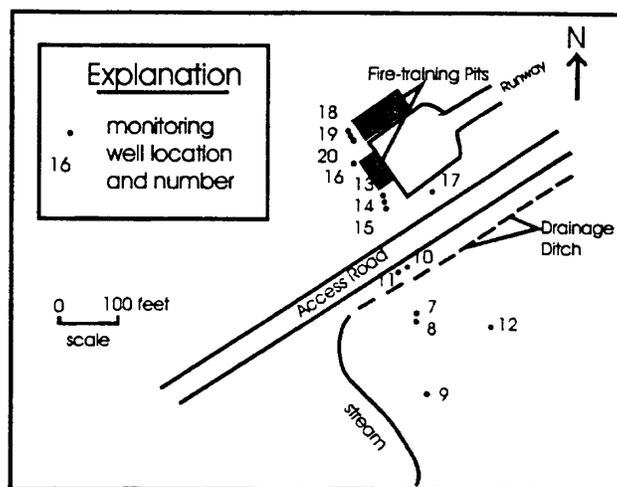

Figure 1. Map showing location of fire-training pits and monitoring wells, Site 8, NAS Cecil Field, Florida.

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-
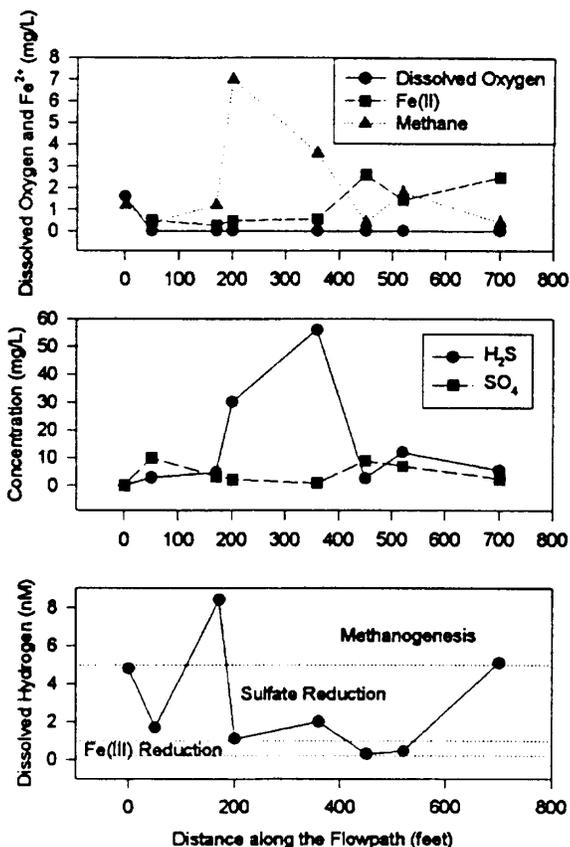
18

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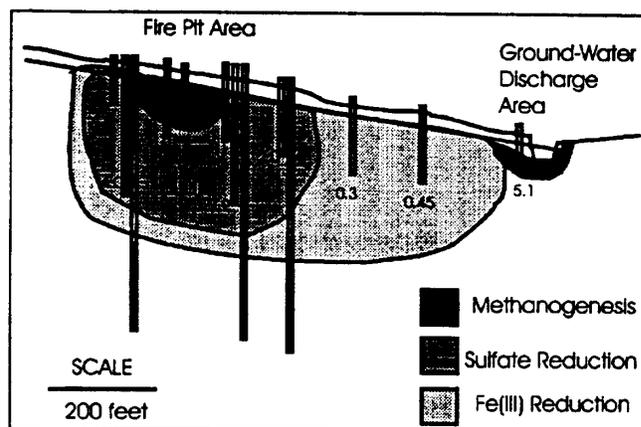

Figure 3. Concentrations of dissolved hydrogen (nM) and the zonation of predominant redox processes, Site 8, NAS Cecil Field, Florida.
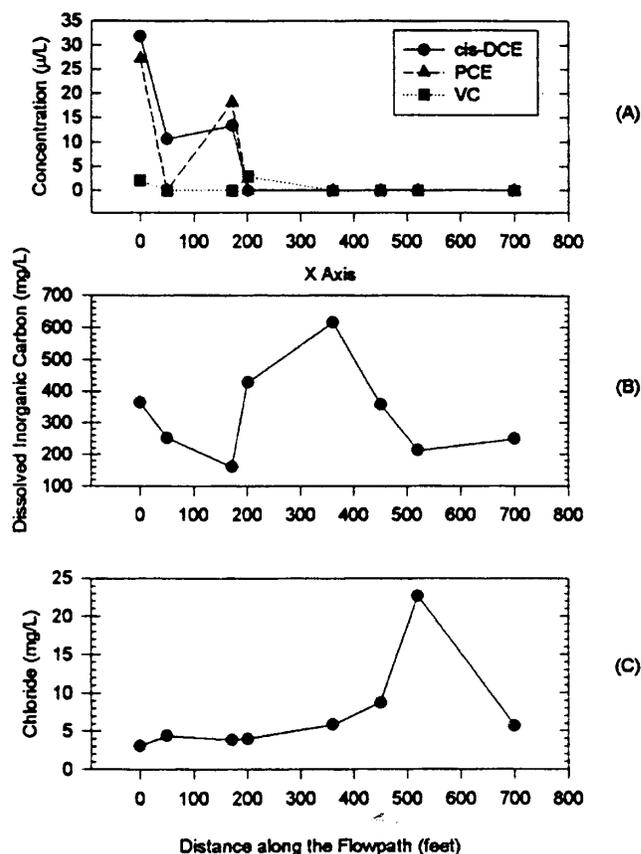

Figure 4. Concentration changes of chloride, dissolved inorganic carbon, and chlorinated ethenes along ground-water flowpaths.

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 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.

References

1. Hinchee, R.E., J.A. Kittel, and H.J. Reisinger, eds. 1995. Applied bioremediation of petroleum hydrocarbons. Columbus, OH: Batelle Press.

2. Weidemeyer, T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical protocol for implementing the intrinsic remediation with long-term monitoring option for natural attenuation of dissolved-phase fuel contamination in ground water. U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, San Antonio, TX. p. 129.

3. Chapelle, F.H., J.M. Landmeyer, and P.M. Bradley. 1996. Assessment of intrinsic bioremediation of jet fuel contamination in a shallow aquifer, Beaufort, South Carolina. U.S. Geological Survey Water Resources Investigations Report 95-4262.

4. Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21:721-736.

5. Friedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55:2144-2151.

6. DeBrunin, W.P., M.J.J. Kotterman, M.A. Posthumus, G. Schraa, and A.J.B. Zehnder. 1992. Complete biological reductive transformation of tetrachloroethene to ethene. Appl. Environ. Microbiol. 58:1996-2000.

7. DiStefano, T.D., J.M. Gossett, and S.H. Zinder. 1991. Reductive dechlorination of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture in the absence of methanogenesis. Appl. Environ. Microbiol. 57:2287-2292.

8. Davis, J.W., and C.L. Carpenter. 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. Appl. Environ. Microbiol. 56:3878-3880.

9. Bradley, P.M., and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe(III) reducing aquifer sediments. Environ. Sci. Technol. 40:2084-2086.

10. McCarty, P.L., and L. Semprini. 1994. Groundwater treatment for chlorinated solvents. In: Handbook of bioremediation. Boca Raton, FL: Lewis Publishers. pp. 87-116.

11. Stumm, W. and J.J. Morgan. 1981. Aquatic chemistry. New York, NY: John Wiley & Sons. p. 780.

12. Lovley, D.R., and S. Goodwin. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reaction in aquatic sediments. Geochim. Cosmochim. Acta 52:2993-3003.

13. Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resour. Res. 31:359-371.

14. Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. Environ. Sci. Technol. 28:1255-1210.